Key enabling technologies according to feedstock type introduction

CA 20127

Waste biorefinery technologies for accelerating sustainable energy processes (WIRE)

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INTRODUCTION

Waste biomass represents a significant untapped resource with immense potential for energy generation, chemical production, and environmental sustainability. Efficient utilization of this resource requires the application of various conversion technologies designed to transform waste biomass into valuable products such as biofuels, chemicals, and bioenergy.

Conversion technologies for waste biomass can be broadly categorized into four main types: biochemical, thermochemical, physicochemical, and emerging technologies. Each category provides distinct pathways and processes for transforming various waste biomass feedstocks into energy carriers and bio-based products. This diverse array of technologies enables optimization tailored to the specific characteristics and composition of the biomass, enhancing overall efficiency and effectiveness.

Biochemical conversion technologies utilize microbial and enzymatic processes to break down waste biomass, resulting in the production of bioethanol, biogas, and biohydrogen. These processes harness the natural capabilities of microorganisms and enzymes to efficiently convert organic materials into energy-rich products, which are essential for sustainable energy generation.

Thermochemical processes encompass a range of techniques, including direct combustion, torrefaction, pyrolysis, gasification, hydrothermal processes, and plasma technologies. These methods rely on high-temperature chemical reactions to transform biomass into valuable outputs such as bio-oil, syngas, bio-crude oil, hydro-char, and solid biofuels like torrefied biomass and bio-char. By applying heat and pressure, these processes break down biomass at the molecular level, facilitating the extraction of energy and other valuable compounds.

Physicochemical methods, such as transesterification and emulsification, play a critical role in converting biomass into biofuels like biodiesel. These processes are essential in the pre-, post-, and conversion operations of biorefineries. While the principles are well defined, some physicochemical operations are still in the developing stage and may eventually replace certain existing processes. These techniques involve physical and chemical changes that alter the structure of biomass, enabling the production of fuel that can be used in existing engines and machinery. The versatility of these methods makes them important for integrating biofuels into current energy systems.

Emerging technologies focus on innovative approaches to biomass conversion, including advanced catalysts, hybrid processes, and bioelectrochemical systems. These technologies aim to enhance efficiency and effectiveness in converting biomass into biofuels and other valuable products, often by leveraging novel materials and processes that improve reaction rates and product yields. By exploring these cutting-edge methods, researchers are paving the way for more sustainable and efficient biomass utilization in the future.

The diverse array of conversion technologies for waste biomass utilization highlights the potential of these processes to contribute to sustainable energy and chemical production. Ongoing research and technological advancements aim to improve the efficiency, cost-effectiveness, and scalability of these technologies, ensuring a more sustainable and resource-efficient future.

This report, developed within the framework of **WG2 (Waste Biorefinery Technologies for Accelerating Sustainable Energy Processes) of the WIRE COST Action**, provides an in-depth analysis of each technology, exploring their principles, advantages, and challenges. It highlights the immense potential of waste biomass to drive the bioeconomy while reducing environmental impacts. For this purpose, the *Report on Key Enabling Technologies According to Feedstock Type* is divided into four sections, each focusing on different conversion technologies.

WG2 Leader Note of Appreciation:

I would like to extend sincere gratitude to all authors, editors, and reviewers for their hard work and dedication in contributing to the *Report on Key Enabling Technologies According to Feedstock Type.* Your efforts have been invaluable in ensuring the quality, depth, and relevance of this important work.

This report reflects the fruitful collaboration fostered through the **WIRE COST Action (CA 20127)**, which has successfully connected remarkable researchers in this field. I am grateful for your commitment, collaboration, and valuable insights throughout the process.

Thank you for your contributions!

Dr Marta Trninić,

Senior Lecturer and Senior Research Associate

KEY ENABLING TECHNOLOGIES ACCORDING TO FEEDSTOCK TYPE

Part I

Biochemical Conversion Technologies

CA 20127

Waste biorefinery technologies for accelerating sustainable energy processes (WIRE)

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Thank you for your commitment and collaboration!

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Table of contents

List of acronyms

ABE	Acetone, Butanol, and Ethanol fermentation
AD	Anaerobic digestion
AF	Alcoholic fermentation
CBP	Consolidated bioprocessing
CSTR	Continuous stirred-tank reactors
DIC	Instant controlled pressure drop
GHG	Greenhouse gas
HRT	Hydraulic retention time
ILs	Ionic liquids
LCB	Lignocellulosic biomass
LEA	Lipid-extracted algae
MECs	Microbial electrolysis cells
MSW	Municipal solid waste
OFMSW	Organic fraction of municipal solid waste
SE	Steam-Explosion
SHF	Separate hydrolysis and fermentation
SSCF	Simultaneous saccharification and co-fermentation
SSF	Simultaneous saccharification and fermentation
TRL	Technology readiness level
VFAs	Volatile fatty acids
1G	First-generation bioethanol
2G	Second-generation bioethanol
3G	Third generation of bioethanol
4G	Fourth generation of bioethanol

List of figures

List of tables

Executive summary

Biochemical conversion technologies harness biological processes, such as anaerobic digestion, fermentation, and composting, to transform biomass into valuable biofuels and chemicals. Biochemical conversion technologies are performed at lower temperatures and conversion rates than chemical and thermochemical conversion processes. These technologies are particularly effective for processing agricultural, forest/wood, agro-industrial and other biodegradable waste biomass.

Anaerobic digestion is a biological process that breaks down organic material in the absence of oxygen, resulting in the production of biogas, which primarily consists of methane and carbon dioxide, along with digestate—a nutrient-rich byproduct. This process has a variety of applications: biogas serves as a renewable energy source for generating electricity and heat, while also significantly reducing the volume and environmental impact of organic waste. The digestate, being rich in nutrients, can be effectively used as a sustainable fertilizer, contributing to soil health and enhancing agricultural productivity. Overall, anaerobic digestion not only provides a viable solution for waste management but also supports the transition to renewable energy and sustainable agriculture. Different types of biomasses wastes that can be effectively utilized by anaerobic digestion include agricultural residues, animal manure, the organic fraction of municipal solid waste, agro-industrial wastes, and sewage sludge. Each of these biomass sources offers unique characteristics and benefits for the anaerobic digestion process, contributing to the production of biogas and nutrient-rich digestate. Agricultural residues, such as crop leftovers, provide a significant feedstock, while animal manure offers both organic material and valuable nutrients. The organic fraction of municipal solid waste contains a variety of biodegradable materials, making it an excellent candidate for biogas production. Agro-industrial wastes, generated from food processing and other agricultural activities, can also be efficiently processed, while sewage sludge presents an opportunity to manage wastewater and recover energy. Collectively, these biomass wastes contribute to sustainable waste management and renewable energy generation through anaerobic digestion.

Fermentation is extensively utilized for producing biofuels, particularly bioethanol, which can serve as a standalone fuel or as a fuel additive to enhance energy efficiency. In addition to bioethanol, this process generates valuable biochemicals such as lactic acid and acetone, which are employed in a wide range of industrial applications. This versatility not only supports the development of sustainable energy solutions but also contributes to the production of essential chemicals used in various sectors, underscoring fermentation's significant role in both renewable energy and the biochemical industry. Fermentation can process a diverse range of biomass wastes, including agricultural residues, fruit and vegetable waste, byproducts from food processing. Additionally, it can effectively utilize the organic fraction of municipal solid waste, including kitchen scraps and garden waste. This versatility makes fermentation a valuable method for converting various biomass wastes into renewable energy and valuable bioproducts, contributing to sustainable waste management and resource recovery.

Composting is an aerobic process that decomposes organic matter, such as food scraps and yard waste, in the presence of oxygen, resulting in the production of nutrient-rich compost. This compost serves multiple applications, including enhancing soil health and fertility as a soil amendment, reducing landfill waste by recycling organic materials, and promoting plant growth in urban gardening and agricultural settings. By transforming organic waste into a valuable resource, composting not only supports sustainable waste management practices but also contributes to improved agricultural productivity and environmental sustainability.

These applications highlight the versatility and importance of biochemical conversion technologies in various sectors.

1. General introduction of biochemical conversion technologies

Carbohydrates, proteins, and lipids containing carbon, hydrogen, and oxygen are an integral part of biomass, making it an adequate raw material in biotechnological processes. Conversely, for the transport and processing of different types of biomasses, their characteristics, such as high moisture content and low energy content, represent a limitation. Biocatalysts break down and convert organic compounds from biomass into various products such as biofuels, food/feed, chemicals, etc. Bioprocesses are performed at lower temperatures and conversion rates than chemical and thermochemical conversion processes. Biochemical processes are natural processes that require low energy and few other chemicals but require control and regulation systems to maximize the desired product and minimize side reactions (Demirel, 2018). Biomass residues and waste are generated as by-products when the desired raw products are planted, processed and consumed, in contrast to biomass specifically cultivated for energy purposes (Lee et al., 2019). In this report, waste biomass is classified into four groups: agricultural, forest/wood, agro-industrial and other biodegradable biomass, based on a comprehensive literature review (Jha et al., 2022, Cuadrado-Osorio et al., 2022, Zihare et al., 2018, , Azelee et al., 2020, Sadh et al., 2018, Vučurović et al., 2024, Lee et al., 2019, Titus et al., 2021), and is presented in Figure 1.

Agricultural biomass is divided into agricultural field residues that remain in the field after crop harvesting (stalks and straw of different crops), agricultural process residues that are obtained after processing of crops (corncobs, chaff and husks), and different types of animal wastes and excrements.

The second group includes forest or wood biomass, which in addition to forest and wood processing industry residues also includes wood waste as well as discarded wood products.

Agro-industrial biomass includes two large groups, industrial residues that are generated after primary processing of different raw materials (fruit and vegetable peels, pomace, frying oil, food processing industry wastewaters, etc.) and industrial by-products obtained at the end of processing (molasses, bagasse, oil cakes, etc.).

The fourth group includes other biodegradable biomass, such as kitchen and food waste, as well as organic fraction of municipal solid waste, industrial and municipal wastewaters and sludge.

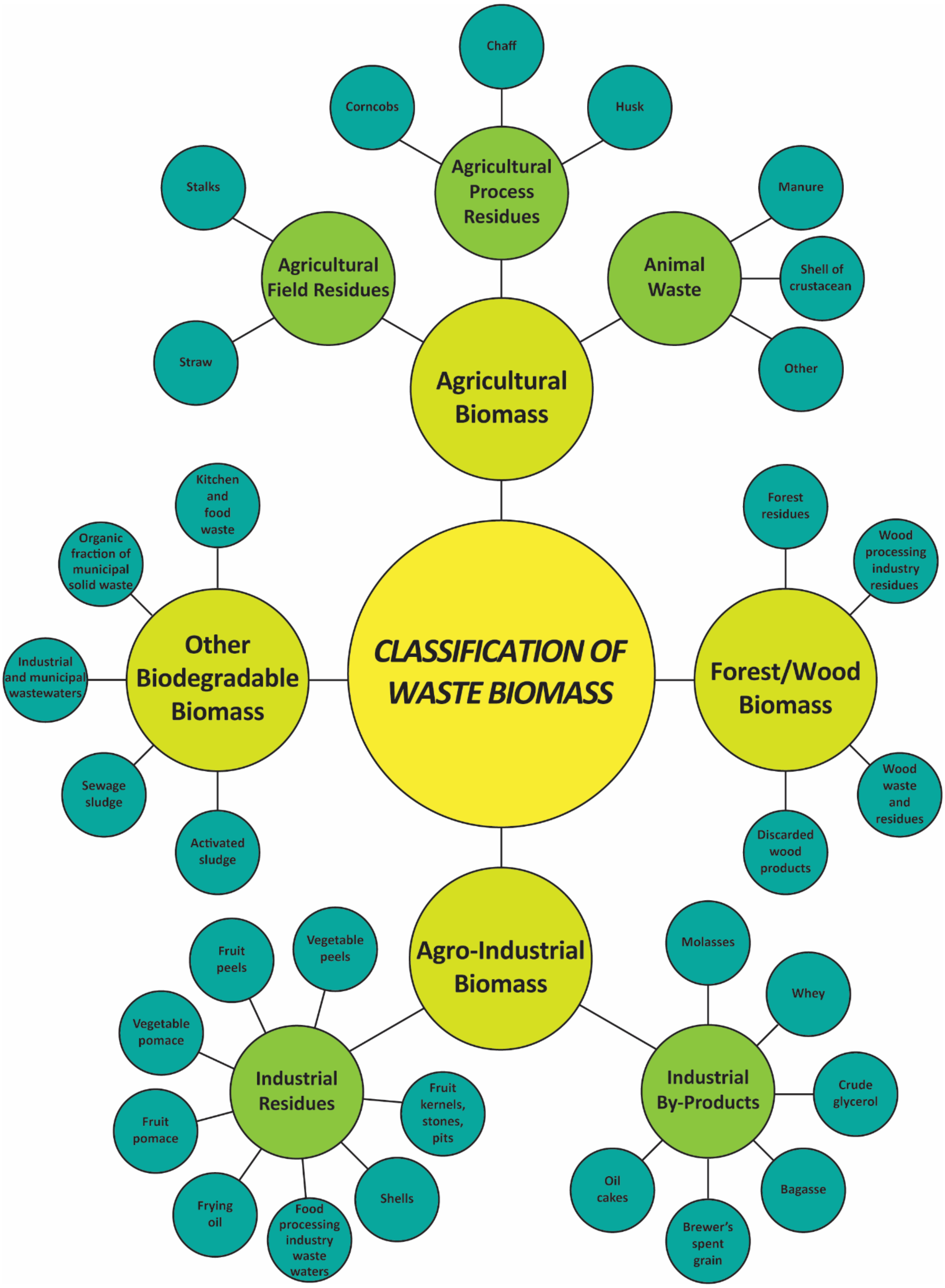

Figure 1. Classification of waste biomass.

When selecting suitable raw materials for large-scale biotechnological production, it is necessary first to identify the main components of the raw material, determine their concentration, the biological availability of these components, and consider factors such as the consistency and prevalence of the raw material, its seasonal availability, alternative uses, and the local technological potential. Carbon sources should ideally be readily convertible into consumable substances using cost-effective and ecologically acceptable techniques. However, most waste biomass types primarily consist of complex carbon sources, such as cellulose, hemicellulose, and lignin, which have limited or low biological availability. Depending on the carbon source concentration, the raw material can be a solid, oily, syrupy (concentrated liquid), or diluted liquid. Raw materials may be accessible year-round or limited to specific seasons or campaigns. The duration of their seasonal availability varies depending on their consistency. Additionally, the continual supply of raw materials with consistent quality can be interrupted because waste biomass quantity and composition are not consistently regular (Smith, 2004, Vučurović et al., 2024).

Bioenergy refers to energy obtained from different waste biomass raw materials. Waste biomass may be transformed into many valuable energy sources through several processes. The conversion of waste biomass to energy is accomplished using three primary process technologies: biochemical, thermochemical, and physiochemical and Figure 2. illustrates various waste biomass-to-bioenergy conversion technologies (Adams et al., 2018).

The selection of a waste biomass conversion technology is influenced by several aspects, including the type, quantity, and characteristics of the waste biomass, the required energy form, environmental regulations, policy considerations, economic conditions, and project-specific variables. Adams et al. (2018) assert that the required energy form and available waste biomass determine the suitable processing technology.

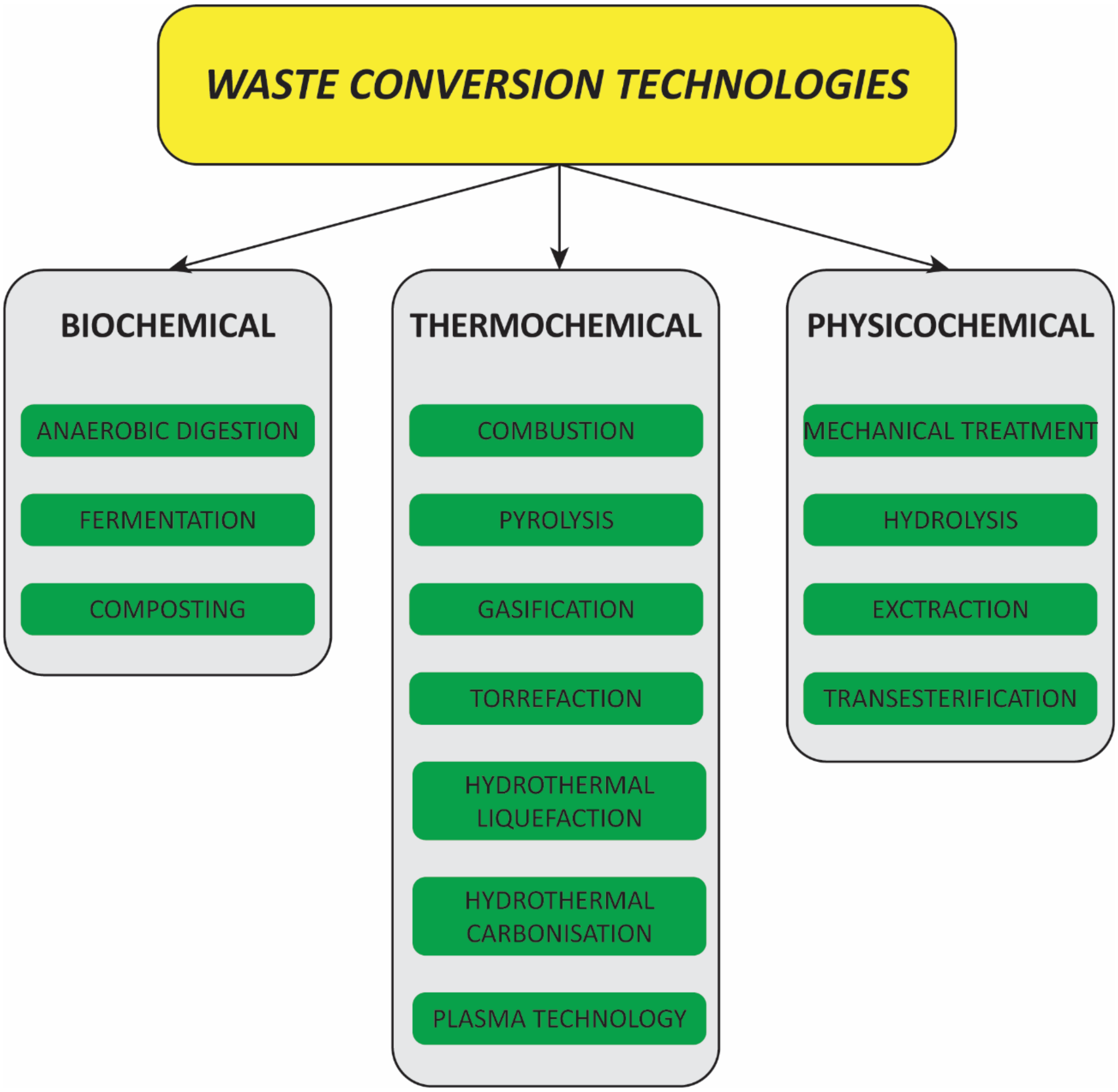

Figure 2. Biomass waste conversion technologies.

1.1. Pretreatment of waste biomass used in conversion technologies

The term pretreatment refers to the processes applied to the biomass materials to make them more suitable for subsequent conversion into biofuels, chemicals, or other valuable products. So raw biomass is usually submitted to several operations, including chopping, mechanical comminution or size reduction, drying, densification, or others, with the general objective of having these materials ready to enter the conversion process. This stage is crucial in breaking down the complex structure of biomass, making its components more accessible for further processing, such as enzymatic hydrolysis, fermentation, or thermochemical conversion.

Especially in the case of the biochemical route for utilizing biomass, pretreatment aims to reduce cellulose crystallinity, increase the cellulose accessibility to enzymes, partially dissolve lignin, and hydrolyze hemicelluloses (Alvira et al., 2010).

Pretreatments are usually classified according to their nature: mechanical, physicochemical, biological, or a combination of these. Mechanical pretreatments include particle size reduction by grinding or action in an extruder. Among physicochemical pretreatments, hydrothermal pretreatments, such as steam explosion or hot pressurized water, are widely applied to residual biomasses; the fundamental characteristic is that no chemical agents other than water are used, although variants with diluted acids or ammonia explosion are also employed. In the case of biological pretreatments, microorganisms (usually fungi) are used to achieve the desired effect.

1.1.1. Physical pretreatment

A. Milling

Is a frequently used pretreatment technique for reducing the biomass particle size. Some of the major advantages offered by this process are (1) decrease in cellulose crystallinity, (2) improvement in the available surface for enzymatic hydrolysis, (3) decrease in the degree of cellulose polymerization, and (4) improvement in the mass transfer due to particle size lowering (Zakaria et al., 2014).

B. Freezing/thawing pretreatment

Is a very promising pretreatment method for converting raw feedstock to a substrate susceptible to hydrolytic enzymes. This method can damage cells' membrane due to the severe dehydration appearing after freezing. Multiple forms of membrane damage can occur due to freeze-induced cellular dehydration. The advantages of freezing/thawing pretreatment include the absence of chemicals and dangerous reagents and mild environmental conditions (no toxic products and no wastes are released). However, it requires further equipment and a longer processing time (Messaoudi et al., 2023a; Smichi et al., 2016, Su et al., 2023).

C. The use of radiations (microwaves or ultrasound)

The use of radiations, such as microwaves or ultrasound is also possible and will increase the porosity of the lignocellulosic biomass (LCB), and therefore its contact surface. Microwaves work by breaking bonds and heating the biomass from within through molecular agitation, which is far more effective than external heating (Puligundla et al., 2016). Ultrasound, on the other hand, causes cavitations within the LCB, resulting in very high localized pressures and temperatures, and thus degrading the sugars (Velmurugan and Incharoensakdi, 2016). The advantages of these techniques lie in the speed and precise control of pretreatment, but the radiation is not uniform and imposes high energy costs.

1.1.2. Physicochemical pretreatment

A. Steam-Explosion (SE) pretreatment

Is one of the most commonly used pretreatment options, as it uses both chemical and physical techniques in order to break the structure of the LCB. This hydrothermal pretreatment method subjects the material to high pressures and temperatures for a short duration of time after which it rapidly depressurizes the system, disrupting the structure of the fibrils. The disruption of the fibrils increases the accessibility of the cellulose to the enzymes during hydrolysis. Compared with other pretreatment methods, SE process has the advantages of including a significantly lower environmental impact, it requires lower capital investment, and implies less hazardous chemicals. However, because of such high temperature (up to 260 °C) and high pressure (up to 5000 kPa), SE is a high-energy/consuming process. Moreover, it leads to an important thermal degradation of sugars into numerous fermentation inhibitors, such as formic acid, acetic acid, furfural, 5-HMF, etc (Smichi et al., 2020, Pielhop et al., 2016, Auxenfans et al., 2017).

B. Instant controlled pressure drop (DIC) technology

Is compared to SE as being a thermomechanical/texturing treatment, it implies using much lower steam pressure and temperature (up to 600 kPa and 160 °C) than SE. DIC, as getting much lower severity than SE can get, implies producing much higher ethanol yield thanks to producing a much lower amount of compounds issued from the thermal degradation of sugars and acting as inhibitors to enzymatic and fermentation reactions. Also, since DIC implies lower treatment temperature and much lower treatment pressure level, energy consumption was proved to be much lower, although the presence of vacuum at an absolute pressure of 5 kPa (Messaoudi et al., 2023b; Smichi et al., 2020; Smichi et al., 2018).

1.1.3. Chemical pretreatment (acid, alkaline, organosolv, ionic liquids, etc.)

A. Acid pretreatment of LCB

Acid pretreatment of LCB is mainly used to remove hemicelluloses, which results in improved accessibility of enzymes towards cellulose. Its severity depends on acid content, temperature and process time; it is efficient on mostly all LCBs. The most commonly used acids are sulphuric acid, acetic acid and phosphoric acid. A key advantage of acid pretreatment is that a subsequent enzymatic hydrolysis step is sometimes not required, as the acid, itself hydrolyses the biomass to yield fermentable sugars. Hemicelluloses and lignin are solubilized with minimal degradation, and the hemicelluloses are converted into sugars. However, extensive washing and/or a detoxification step is required to remove the acid before a fermentation step. Another drawback is the production of fermentation inhibitors like furfural and 5-HMF (hydroxymethyl furfural) that decrease the effectiveness of the pretreatment method and further processes (Du Pasquier et al., 2023).

B. Alkaline pretreatment

Alkaline pretreatment causes extensive changes in the structure and accessibility of carbohydrates in the cell wall, leading to sugar release in the solution. Alkaline pretreatment breaks the bonds between lignin and carbohydrates and disrupts the lignin structure. It is indicated that the structure of lignin plays a significant role in determining the magnitude of inhibition involved in cellulose hydrolysis. Even low and below-0°C temperatures can be used, thus limiting cellulose degradation (Zhao et al., 2008) The major disadvantages of the alkaline pretreatment process include high post pretreatment cost involved for the neutralization of slurry, longer residence time, and its inability to pretreat the biomass feedstocks with high lignin content (e. g., wood) (Saravanan et al., 2022).

C. Organosolv pretreatment

Organosolv pretreatment method involves the use of organic solvents like methanol, ethanol, tetrahydrofurfuryl alcohol, ethylene glycol or acetone diluted in water for the pretreatment of biomass. Sometimes organic acids or bases are also used as catalysts. During this process, lignin and hemicellulose linkages are cleaved via solubilization, which results in improving the overall surface area of cellulose for enzymatic hydrolysis. Although organosolv is used as an effective pretreatment process for several years, it is associated with some disadvantages like high solvent cost, volatility, flammability, and difficulty in the recovery thus making the overall process energy-intensive and costly (Saravanan et al., 2022, Zhao et al., 2009).

D. Ionic liquids (ILs)

Ionic liquids (ILs) are salts with very high chemical and thermal stability, thanks to a multitude of possible combinations between an organic cation and an inorganic anion. They will mainly cause delignification and the loss of the crystalline structure of cellulose (Galbe et al., 2019). But despite an increase in the available surface area of the cellulose, enzymes degrade rapidly in ILs, so a biomass regeneration step must therefore be taken into account to eliminate them before enzymatic hydrolysis. Advantageously, ILs can be reused for LCB pre-treatment, thus limiting the amount of waste produced. The main obstacle, however, remains the very high cost of ILs (Hou et al., 2017). New chemicals, known as deep eutectic solvents, have physical and chemical properties comparable to IL, while being less expensive and safer for the environment. The sugar yields of pretreatments obtained with these solvents are similar to those of IL (Sharma et al., 2022).

1.1.4. Biological pretreatment

Biological pretreatments use the characteristics of micro-organisms and their enzymes to degrade the structure and components of the biomass. The advantage is the use of gentle pretreatment conditions, with low temperatures and no need to add chemicals. The main limitations of this type of pretreatment lie in its nature: the living process takes time, up to several tens of days, and the results are sometimes variable (Galbe et al., 2019). The main class of micro-organisms to act on LCB recalcitrance are fungi, themselves classified into three categories according to their action: white, brown or soft rot. White rot is of particular interest in the context of biorefineries, as it mainly degrades the lignin of LCB with the help of peroxidases and laccases, providing direct access to polysaccharides (Singh, 2021). Brown rot will preferentially attack the latter, producing enzymes that hydrolyze glycosidic bonds, leading to the degradation of cellulose and hemicellulose fractions. Although not its ideal substrate, brown rot also degrades a fraction of the lignin, unlike soft rot, which only deals with the polysaccharides of LCB. These last two types of rot are of limited interest in the context of cellulose recovery, as they will consume part of the lignin for their growth, and thus alter yields. Despite much less stringent cultivation conditions than for other pretreatments, the low yields obtained, the long processing times for LCB and the need to keep the procedure sterile make the use of fungi 4 to 15 times more expensive than more conventional processes (Singh, 2021).

1.2. Anaerobic Digestion

Anaerobic digestion is a promising waste conversion technology widely acknowledged for its environmental and economic benefits. This process, which involves the microbial breakdown of organic material in the absence of oxygen, offers a range of advantages that make it a viable option for waste management. However, like any technology, it has its limitations. The following sections outline both the advantages and disadvantages associated with anaerobic digestion, highlighting its effectiveness in reducing waste volume, controlling greenhouse gas emissions, and producing valuable by-products such as fertilizers. When considering anaerobic digestion as waste conversion technology the following advantages and disadvantages should be considered (Kumar and Samadder, 2020; Foster et al., 2021; Kumar and Samadder, 2017; Munir et al., 2021; Dhanya et al., 2020; Massaro et al., 2015; Katinas et al., 2019).

Anaerobic digestion presents several advantages as a waste management technology. It is both economically and environmentally sustainable, contributing to the reduction of organic municipal solid waste (MSW) volume by up to 60%. The process effectively controls greenhouse gas emissions and does not produce odors, making it a cleaner alternative to traditional waste treatment methods. Its compact design requires less land area and allows for small-scale operations. Additionally, the digestate produced can be repurposed as a nutrient-rich fertilizer, adding value to the process. Anaerobic digestion also has several disadvantages that should be considered when evaluating it as a waste management solution. It is suitable only for organic waste, and its effectiveness can be influenced by a variety of process parameters and substrate composition, making it complex to manage. Effective waste segregation is required to improve digestion efficiency, and the biogas produced must be treated before it can be used. Moreover, the investment and operating costs can be high, and local subsidies are often necessary to make the technology economically viable.When considering whether a certain type of waste biomass is suitable for use as a substrate in anaerobic digestion, the following should be taken into account (Deublein and Steinhauser, 2008):

- the organic matter content should be appropriate,
- the potential for biogas formation should be as high as possible,
- the substrate should not contain pathogenic microorganisms (or substrate should be sterilized),
- the content of hazardous materials should be as low as possible,
- the composition of the gas should be suitable for further use,
- the composition of the digestate should be such that it can be used as fertilizer.

Vats et al. (2019a) examined the possibility of biogas production by mixing thermal-acid pretreated sugar cane waste and kitchen waste in different ratios. The experiments were performed in six batch bioreactors at ambient conditions, with 450 mL working volume, and in each bioreactor, a different ratio of the two applied substrates was used. The maximum biogas production of 7338 mL was obtained in a mixture in which the ratio of sugarcane waste and kitchen waste was 35:65. The same group of authors (Vats et al., 2019b) also examined the influence of the ratio of sugarcane waste and fruit and vegetable waste, on the yield of biogas in anaerobic co-digestion. The maximum biogas yield of 2600 mL per day was achieved in a bioreactor that had a 70:30 ratio of fruit and vegetable waste and sugarcane waste, respectively.

Khayum et al. (2018) investigated the possibility of spent tea waste for biogas production. The spent tea waste was mixed with cow manure, in different proportions and the highest biogas yield of 1669.25 mL was produced in a bioreactor in which the ratio of cow manure and spent tea waste was 70:30.

Fish processing waste was used as a substrate in biogas production examined by Choe et al. (2019). Research included experiments that examined the effect of temperature of hydrothermal carbonization and the addition of bamboo hydrochar on an anaerobic digester of fish processing waste. The results show that the maximum biogas yield 292 L/kgVS, was produced in the bioreactor that contained bamboo hydrohydrate processed at a temperature of 200°C, mixed with waste from fish processing in a ratio of 1:2.

Dasgupta and Chandel (2019) research results showed that hydrothermal pretreatment is of great importance in improving biodegradability of complex organic matter, which affected the cumulative increase in methane production and the reduction of the time of anaerobic digestion. The highest biogas yield of 200 mL/gVS with 68.6% of methane content after 18 days was achieved with the pretreatment of the organic fraction of municipal waste at 140°C for 30 minutes, while untreated waste had a biogas yield of 152 mL/gVS with 50.3% methane content after 28 days.

Onthong and Juntarachat (2017) investigated the potential of biogas production from five raw and processed agricultural wastes, which are soybean residues, papaya peels, sugarcane bagasses, rice straws and greater galangals. The average production of biogas in a continuous bioreactor, during 60 days, of soybean residue, papaya peel, bagasse, straw and greater galangal was 63.01, 54.63, 16.28, 13.94 and 0.68 L/days, respectively.

The potential methane yield is used to assess the possibility of using different types of waste biomass as raw material in anaerobic digestion (Figure 3. Al Seadi et al., 2008).

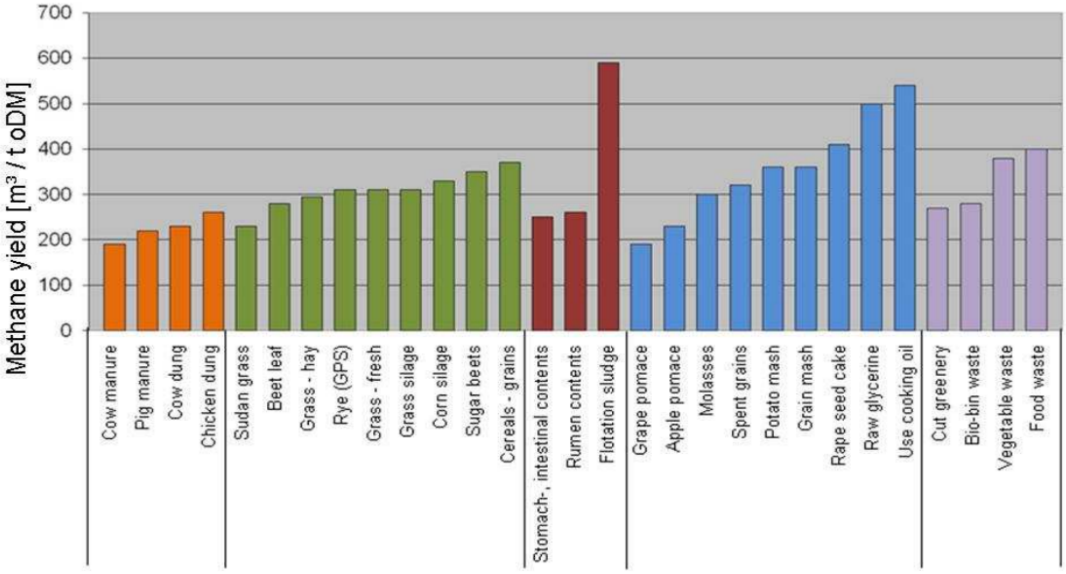

Figure 3.The potential methane yield of different waste biomass types.

Anaerobic digestion (AD) is an intricate biological process where organic biomass is transformed into biogas, which consists of methane (50–75%), carbon dioxide (30–40%), and small amounts of other components, such as hydrogen, hydrogen sulfide, siloxane, etc., by an anaerobic microorganism consortium (Borja and Rincón, 2017). It is a complex process which includes four different steps - hydrolysis, acidogenesis, acetogenesis and methanogenesis (Figure 4., Kumar and Samadder,2020), and in each of them the specific microorganism group is required. These microorganisms are commensal in relation (Mel et al., 2015).

An effectively operating anaerobic digester is characterized by the complete conversion of intermediate products, which are the products of the first three process steps of anaerobic digestion. Consequently, the concentrations of these intermediate products, when continuously measured, are quite low (Kondussamy and Kalamdhad, 2014).

Hydrolysis is the first stage and represents the process of breaking down complex compounds of plant or animal origin. It limits the rate of the overall process because it is relatively slow (Kondussamy and Kalamdhad, 2014). During hydrolysis, lipids, polysaccharides, proteins, and nucleic acids are broken down into fatty acids, monosaccharides, amino acids, and purines and pyrimidines, respectively. Hydrolysis takes place with the help of extracellular enzymes, hydrolases (esterase, glycosidase or peptidase) (Kondussamy i Kalamdhad, 2014).

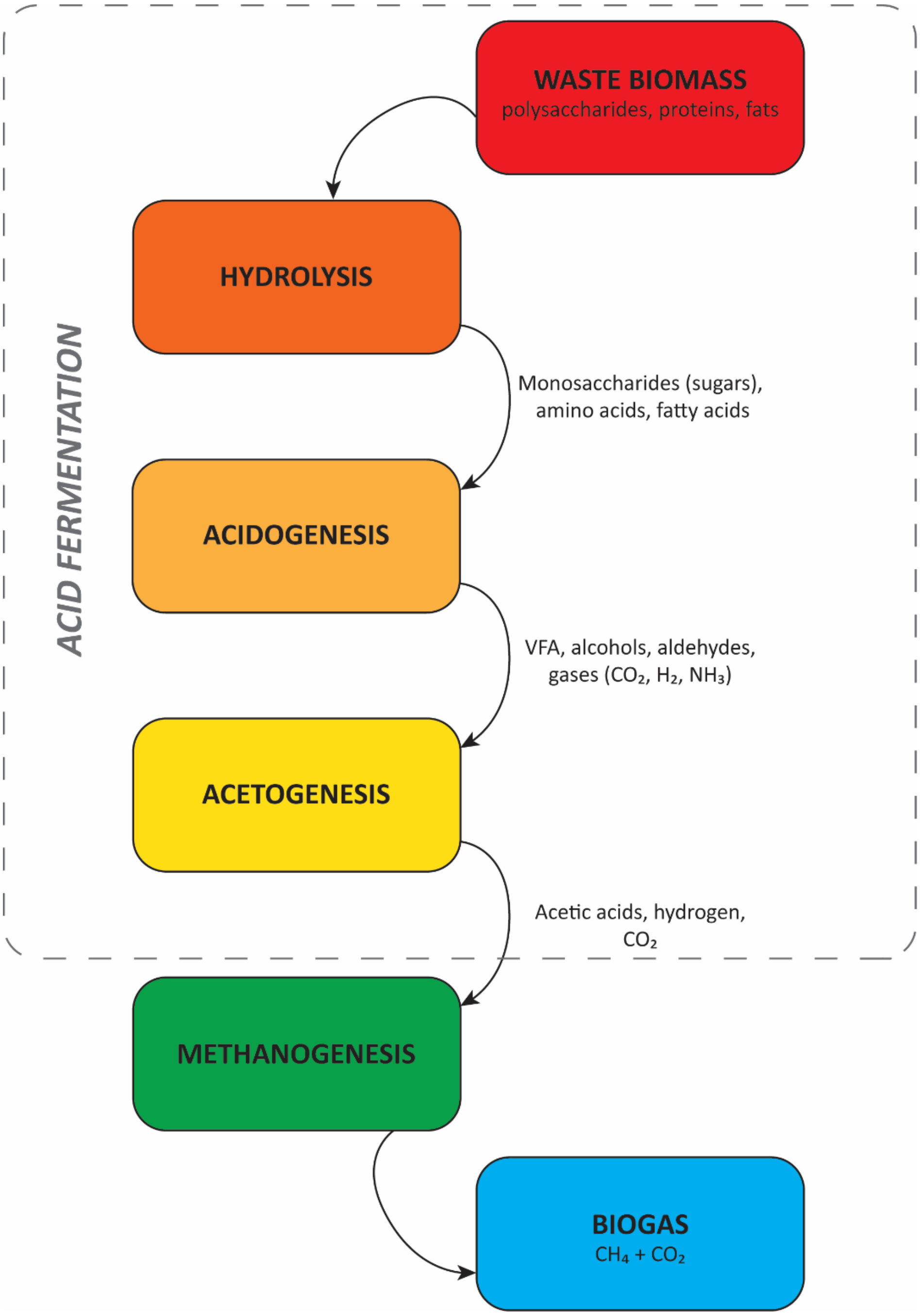

Figure 4. Anaerobic digestion.

The second stage of anaerobic digestion is acidogenesis or acidification and represents the conversion reaction of the hydrolyzed products from the previous step into simple molecules with a low molecular weight, such as volatile fatty acids (VFAs), alcohols, aldehydes and gases (carbon dioxide, hydrogen and ammonia) by acidogenic bacteria (Mel et al., 2015).

In the third stage of anaerobic digestion, the products of the acidogenesis serve as a substrate for bacteria in the acetogenic phase (Deublein and Steinhauser, 2008). Volatile fatty acids and alcohols are oxidized to acetates, hydrogen and carbon dioxide (Mel et al., 2015).

To produce acid, oxygen and carbon are necessary, so these bacteria consume dissolved or bound oxygen, which creates the anaerobic conditions necessary for the next phase to take place. The first three steps of anaerobic digestion are grouped together under the name acid fermentation. During acid fermentation, organic matter is not removed from the liquid phase, but transformed into a form suitable as a substrate for the subsequent methanogenesis process (Kondussamy and Kalamdhad, 2014).

In the last, fourth phase of anaerobic digestion, the products of acid fermentation (mostly acetic acid) are converted into carbon dioxide and methane by methanogenic bacteria. Methane can be produced in two ways: by fermentation of acetic acid to methane and carbon dioxide with acetoclastic methanogens and as a product of the activity of hydrogenotrophic methanogens in the carbon dioxide reduction reaction. The most common methanogenic bacterial species for biogas production are: Methanobacterium, Methanothermobacter, Methanobrevibacter, Methanosarcina, and Methanosaeta (Kondussamy and Kalamdhad, 2014).

In the methanogenic phase, methane formation occurs under strictly anaerobic conditions (Deublein and Steinhauser, 2008). Methanogenic bacteria are obligate anaerobes and are very sensitive to fluctuations in the environment. Temperature, pH, raw material composition is just some of the factors that must be carefully monitored. Organic load, pH and the presence of oxygen can act together to stop methane formation (Mel et al., 2015).

The optimal process conditions for anaerobic digestion are: an organic loading rate of approximately 10.1 g COD/L per day; C/N ratio of 30:1; pH range of 6.8-7.2; temperature ranges mesophilic (30-40 °C) and thermophilic (45-65 °C); about 85 wt % of moisture content and retention time of around 15 days (Munir et al., 2021).

1.2.1. Evaluation of Biomass Types for Anaerobic Digestion

The application of specific biomass for anaerobic digestion offers a promising approach to renewable energy production, organic waste management and environmental impact reduction. Each type of biomass presents unique opportunities and challenges, necessitating tailored strategies for optimal biogas production. Advances in pre-treatment technologies, co-digestion strategies, process and technology optimization continue to enhance the feasibility and efficiency of anaerobic digestion (AD) systems.

The EU has a diverse approach to use biomass for anaerobic digestion, influenced by regional availability, economy and policies. Countries such as Germany, France and Italy, lead AD with extensive use of agricultural waste, energy crops and organic fraction of municipal solid waste (OFMSW), while in European nordic countries (Netherlands, Denmark, Sweden) there is an extensive use of sewage sludge or lignocellulosic biomasses. For these reasons, while each biomass type presents unique advantages and challenges, their integration into AD processes across the EU is driven by regional resource availability, policy frameworks, and technological advancements. In developing countries, biogas/biomethane production and its utilization are still facing different problems, among which is the lack of capital or funds, the lack of adequate knowledge and expertise, and the lack of adequate policymaker or government support, representing barriers to overcome (Aworanti et al. 2023).

Biomass is composed of a range of macromolecules, including carbohydrates (sugars, cellulose, hemicellulose, and lignin), lipids (fats, oils, and glycerols), and proteins. However, not all of these components are equally biodegradable. For instance, lignin is highly resistant to degradation. The breakdown of cellulose requires several weeks, whereas hemicelluloses, fats, and proteins can be degraded in a few days, while volatile fatty acids, sugars and alcohols can be broken down in several hours (Sarker et al. 2019). Hence, the selection of a certain type of biomass waste determines a specific reactor design, feedstock disposal, feeding strategy and process monitoring.

A wide variety of feedstocks can be used for AD. The different types of biomass wastes can be grouped into six broad categories: agricultural residues, animal manure, organic fraction of municipal solid waste, agro-industrial wastes, sewage sludge and aquatic biomass (e.g., micro and macroalgae) (Sarker et al. 2019).

1. Agricultural residues include *crop residues*, such as field residues after crop harvesting or crop processing, and *secondary crops* (i.e. crops grown between two primary crops).
   a. *Crop residues* have a high total solids content and carbon/nitrogen ratio. Their biomethane yield is influenced by harvesting processes and timing, plus site properties. Examples are stalks (i.e. maize, sunflower, soya), straw (i.e. wheat, oat, rye, rice) and corncobs. They are characterized by high lignocellulosic content and have a high energy potential, which make them a valuable feedstock for anaerobic digestion. However, the recalcitrant nature of lignocellulose can make these residues more challenging to digest; for this reason, they often require pretreatment to enhance biogas production efficiency. These crop residues should be harvested at an optimal time and co-digested with nutrient-rich substrates to compensate for their low water and micronutrients content.
   b. *Secondary crops*, also called “sequential” crops or “energy” crops, are grown between two harvested crops as a soil management solution that helps to preserve the fertility of soil, retain carbon in the soil and avoid erosion; these do not compete for agricultural land with crops grown for food or feed production.

2. Animal manure, obtained from cattle, sheep, goats, pigs, chickens, and other less common animals, generally contain high moisture (70-92%), lignocellulose, proteins, and polysaccharides. The pH, total solids, volatile solids, and carbon/nitrogen ratio vary by animal type. Manure from cattle can have lower biogas yields due to its high water and lignin content, this one due to the presence of straw. However, manure can buffer low nitrogen substrates, control volatile fatty acids and contribute with microflora to the microbiology of the anaerobic digestion process, as it naturally contains a diverse range of microorganisms that are beneficial for the breakdown of the substrate. Enhancing biogas production from manure often involves pretreatment and co-digestion with other materials.
3. Organic fraction on municipal solid waste derived from waste sorting and treatment, is characterized by variable levels of carbohydrates, proteins and fats, trace elements, low pH, medium moisture content and volatile solids, indicating a high proportion of organic matter available for decomposition. These properties make it highly suitable for AD due to its significant biogas and methane production potential. However, OFMSW it’s very heterogeneous due to its seasonality, regionality and different sorting processes; moreover, excessive protein content may cause ammonia inhibition, and it may also contain non-biodegradable contaminants such as plastics, metals, and glass, necessitating effective sorting and pre-treatment to reduce contamination.
4. Agro-industrial wastes include wastes, residues, and byproducts that are generated from different agroindustrial activities, such as food industry, dairy, brewery, olive oil and wine industry. They are characterized by variable moisture content, high biodegradability, substantial volatile solids content, and significant biogas potential. However, variations in moisture content and carbon to nitrogen ratio necessitate careful management and often co-digestion with other substrates for optimal performance.
5. Sewage sludge deriving from wastewater treatment can be utilized for biogas production. It is a very well known matrix containing a low content of total and volatile solids, an it is easy to manage in the anaerobic digestion process due to its high homogeneity; it might contain different contaminants, such as trace metals and organic pollutants, which might inhibit the microorganisms in the process (Aworanti et al. 2023).
6. Aquatic biomass, such as macro- and microalgae and seaweeds, offers a high potential for biogas production due to its high polysaccharides, lipids, and protein content and low or no lignin. Aquatic biomass does not compete with arable land and grows rapidly. However, its use in AD is limited by recalcitrant cell walls, toxic substances, poor carbon/nitrogen ratio, long-chain fatty acid inhibition, and ammonia inhibition.

Pretreatment and co-digestion can overcome some of these challenges (Aworanti et al. 2023).

Using waste and residues as feedstock avoids the land-use issues associated with energy crops and can capture methane that could otherwise escape to the atmosphere as they decompose, contributing to greenhouse gas emissions reduction and to the sustainability of the biogas and biomethane production processes. (International Energy Agency (IEA) 2020).

1.2.2. Design of Anaerobic Digestion Technology

Anaerobic digestion takes place in a sealed reactor, commonly referred to as a digester, providing an environment in absence of oxygen. Various AD technologies exist and their employment depends on feedstock characteristics, feeding frequency, type of process, mixing type, temperature, and other factors.

Indeed, the AD process technology can typically be categorized or classified based on the following:

1. the total solids content
2. the feeding mode
3. the operating temperature
4. the number of operational stages
5. the type of digester and reactor configuration

The dry and wet AD process technologies are dependent on the amount of total solid content in the system. In the wet process, feedstock moisture content exceeds 85%. Mechanical stirring inside the tank needs to cover all the volume in order to prevent solid precipitation. Substrates are generally fed continuously and removed after a specific hydraulic retention time (HRT), this last one a parameter identifying how long the feedstock stays inside the digester. Wet digestion is suitable for high-moisture content feedstocks, like sewage sludge and animal manure, whose higher water content produces a better homogenization of the digester’s content, increasing the interaction between bacteria and nutrients, reducing diffusion problems, and diluting any potential inhibitors. However, one of the main disadvantages of the wet process is the larger volume of digester required (Aworanti et al. 2023).

Dry processes are used for feedstocks with higher solid content (>15%). Typically, it allows for treating or handling higher quantities of waste per digester volume (Rocamora et al. 2020); hot water or slurry can be applied to these processes to maintain the required digestion temperature and eventually lower the total solids content in the inlet flow. Substrates such as solid animal manure, organic fraction of municipal solid waste (OFMSW), food waste, yard trimmings, and energy crops are ideal for dry digestion.

In a batch digester, feedstocks are added at the start and remain covered for a set period before the digester is emptied and refilled. While simple to operate and maintain, batch digesters produce biogas periodically. Continuous digesters, on the other hand, allow for constant feeding and simultaneous removal of biogas and digestate, leading to consistent biogas production with minimal downtime. Most digesters operate in a semi-batch or semi-continuous mode, enabling continuous operation with periodic maintenance.

Along the process parameters, reactor temperature is very important to consider when designing the process. Three different temperature intervals might be used:

- Psychrophilic (<25°C)
- Mesophilic (37-40°C)
- Thermophilic (50-55°C)

Mesophilic and thermophilic conditions are the most commonly used in anaerobic digestion. Mesophilic conditions reduce heating demands while maintaining a stable process with stable gas production. Thermophilic conditions have a faster biogas production kinetics, but they can be less stable and more sensitive to inhibition, particularly from ammonia nitrogen, as higher temperatures shift the equilibrium towards ammonia, which might result toxic for the microorganisms. However, thermophilic reactors with an adequate minimum retention time efficiently kill pathogens, lowering overall heating demands compared to a mesophilic plant with pasteurization pre-treatment.

Psychrophilic systems are less or no common for biogas production with energy purposes; they require minimal or no heating, but have significantly lower methane production rates, needing about twice the retention time to match mesophilic gas production. Psychrophilic conditions are mainly suitable for diluted systems, where low hydraulic retention time is beneficial, and for low-cost systems like covered lagoons. They may also be appropriate for feedstocks with high ammonia levels.

Most commonly, anaerobic digestion is conducted in single stage process, meaning that the whole degradation steps happen in just one reactor; however, some configuration divide the process into two stage, having one reactor for the first step of degradation (hydrolysis and acidogenesis) and one for the last ones (acetogenesis and methanogenesis). Each reactor can be optimized individually to fit the needs of the respective microbial groups, which often results in fast and efficient biogas production in the second stage. The first (acidogenic) stage is typically performed at a low hydraulic retention time range of two to five days and a pH range of five to six, while the second stage (methanogenic) is operated at a hydraulic retention time of 20 to 30 days and a pH range of six to eight. Comparing the two stage process to the single stage process, the first allows rapid and efficient biogas/biomethane generation in the second stage (Aworanti et al. 2023), with the first stage acting as a biomass “chemical” pretreatment.

Several standard digester designs exist for AD, each optimal based on feedstock composition, environmental temperature, and microbial needs.

Covered lagoons are the simplest anaerobic digester technology. Feedstocks are stored in an underground lagoon covered with a gas-tight flexible cover. Lagoons act both as storage and reactor. Sometimes, two connected lagoons are used in series; the first (cell 1) for biogas production and the second (cell 2) for further processing of digester effluent. Covered lagoons are best suited for warmer regions where ambient temperature meets the digestion requirements. They work well with low solid content feedstocks (0.5–2%) due to easy handling of large volumes. However, its drawbacks include a low rate of reaction due to the low reaction temperature and coagulation of solids at the bottom of the digester due to no mixing, which results in less contact between the bacteria and feed (Aworanti et al. 2023).

A complete stirred tank reactor (CSTR) is an above-ground tank made of insulated concrete or steel. It uses a rigid or flexible cover, commonly called gasometer, to collect produced biogas via gas collection pipes. Heat exchangers maintain the digestion temperature, and mechanical mixing systems ensure complete mixing of the feedstock. Complete mix digesters can handle non-homogeneous feedstocks with higher solid content (3–10%) and are suitable for any ambient conditions. It is the most common technology achieving good conversions of solids into biogas and it is widely used both in industries and agricultural processes.

Plug flow digesters are horizontal, cylindrical reactors which do not use mechanical mixing. Feedstock enters from one side and digestate exits from the other. The incoming feedstock pushes out an equal amount of digestate while different stages of the digestion occur along the way. Plug flow digesters are usually in-ground and covered with a flexible cover. They require high solid content feedstock (20–25%) to ensure fluid movement through the reactor.

Mixing the AD feedstock is essential to ensure a uniform environment and avoid dead spots, where digestion stops, occupying unnecessary volume and potentially concentrating toxic compounds. Mixing can be achieved through mechanical agitation, biogas recirculation, or by pumping digester content. Although mixing increases design complexity and operating costs, the resulting higher biogas production can offset these costs (Karlsson et al.).

AD technology offers a sustainable solution for converting organic waste into renewable energy and valuable byproducts like digestate, which can be used as a soil conditioner or fertilizer. The advantages of this technology include its economic and environmental sustainability, as it reduces the volume of municipal solid waste by approximately 60% and helps control GHG emissions. Additionally, AD produces minimal odors, has a compact design that requires less land area, and can be implemented on a small scale, making it accessible for diverse applications. One significant benefit of AD is its potential to generate biogas, which can be used as a renewable energy source for heating, electricity, or as a vehicle fuel after purification. This reduces reliance on fossil fuels and contributes to energy security. Moreover, the digestate produced as a byproduct is rich in nutrients and can be used as a natural fertilizer, thereby closing the nutrient loop and promoting sustainable agriculture.

However, the technology has limitations that must be considered. One of the primary drawbacks is that only organic waste is suitable for anaerobic digestion, making the process reliant on effective waste segregation at the source. The process itself is complex and influenced by multiple parameters, including substrate composition, temperature, and retention time, which can affect the efficiency of digestion. Moreover, biogas produced often requires further treatment to remove impurities like hydrogen sulfide and carbon dioxide before it can be utilized, adding to the operational complexity.

From a financial perspective, AD involves substantial initial investment in infrastructure and technology. The costs of building digesters, installing gas treatment facilities, and maintaining equipment are significant. Operating costs, such as energy consumption, feedstock management, and regular maintenance, also add to the overall expenses. Due to these high costs, the economic viability of AD systems often depends on local subsidies or incentives to offset the financial burden and make the technology competitive. (Zulkepli et al. 2017)

In summary, while anaerobic digestion presents numerous environmental and economic advantages, it also involves challenges such as high capital and operating costs, process complexity, and the need for effective waste segregation. A detailed cost-benefit analysis, along with government support, is crucial to ensure the successful implementation and sustainability of this technology in waste management systems.

1.2.3. The technology status of anaerobic digestion

AD technology has evolved significantly, reaching TRLs between 7 and 9, depending on the specific configuration and application (Gómez-Camacho et al. 2021). Commercial-scale systems such as continuous stirred-tank reactors (CSTRs), plug-flow digesters, and advanced two-stage reactors are already in operation globally. (Elsayed te al. 2024) The maturity of the technology is further demonstrated by its ability to treat diverse feedstocks, including agricultural residues, municipal solid waste, and industrial by-products. Despite these advances, the adoption rate varies across regions due to differing policy frameworks, financial incentives, and the availability of suitable feedstocks (Gómez-Camacho et al. 2021). Recent technological enhancements have focused on optimizing digestion processes, reducing costs, and minimizing environmental impacts.

Anaerobic digestion technology faces several key challenges that influence its performance and economic feasibility. One major challenge is feedstock variability and availability, as the heterogeneous nature of organic materials can lead to inconsistent biogas yields and increased pre-treatment costs (Bhatt et al. 2020). Additionally, inhibitory compounds such as ammonia, volatile fatty acids, and heavy metals can disrupt microbial activity, leading to decreased efficiency or process failure (Che net al. 2008). Biogas quality and utilization is another critical issue, as raw biogas often contains impurities that require costly upgrading before use. Lastly, economic and policy constraints present barriers to widespread adoption due to high initial capital and operating costs, necessitating supportive policies, subsidies, or integration with other waste treatment systems to achieve financial viability (Bhatt et al. 2020).

1.2.4. Landfill Gas Dynamics: Methane Generation

The biodegradation of waste within landfills produces a complex mixture known as landfill gas, primarily composed of methane and carbon dioxide, with trace amounts of other gaseous compounds. Due to the heterogeneous nature of landfills, which vary significantly in waste composition and landfill conditions, developing a simple, universally applicable model for estimating landfill gas generation remains challenging.

The transformation of waste can be monitored based on the composition of the released gases and leachate. Based on this, five stages (phases) of the decomposition process can be distinguished (Figure 5.) Methane is produced in landfills through the anaerobic decomposition of organic waste materials over time.

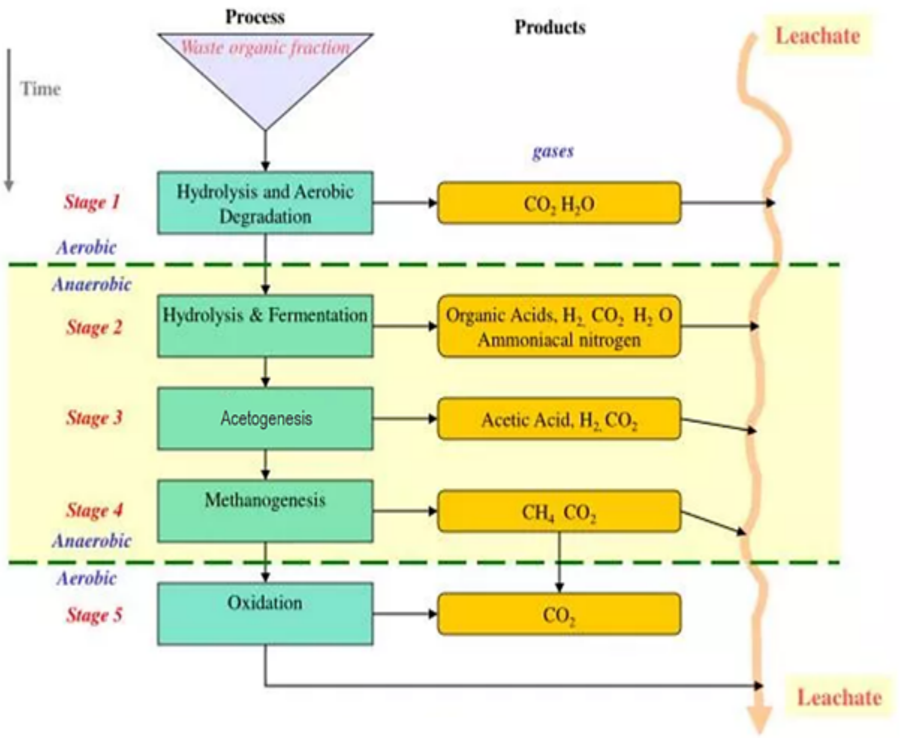

Figure 5. Stages of the waste decomposition process in landfills (HSMO, 1995).

Phase I - Aerobic phase

The first stage in the decomposition of solid waste is the decomposition of easily degradable solid organic matter. During the first stage of decomposition, aerobic bacteria use oxygen, breaking the long molecular chains of complex compounds that make up organic waste: carbohydrates, proteins, and fats. A by-product of this process is carbon dioxide. At the beginning of this phase, the nitrogen concentration is high (about 20 % oxygen and 80 % nitrogen), but this concentration decreases as the "landfill moves" through the stages of waste decomposition. During the initial phase of decomposition, oxygen is depleted, and aerobic microorganisms break down organic components into simpler compounds. This process produces CO_2, water, and nitrates as by-products. For example, the aerobic decomposition of glucose occurs according to the reaction:

$$C_6H_{12}O_6 + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O \qquad (1)$$

The primary source of aerobic and anaerobic microorganisms responsible for the decomposition of waste is the covering material applied as a daily and final covering. Another source is digestion sludge from wastewater treatment plants, which is disposed of in many landfills and recirculated leachate.

Aerobic digestion begins immediately after the waste is disposed of in a landfill. Aerobic processes produce landfill gas containing much CO_2 (up to 30%), low CH_4 content, and high temperatures (54 °C to 71 °C). The duration of the aerobic phase depends on the conditions at the landfill, i.e. primarily on the possibility of air penetration into the interior of the landfill (EPA , 2012) .

The duration of the aerobic phase is usually no more than 3 months, although it can be extended to a period of 6 months.

Phase II - Anaerobic phase, non-methane (transition phase)

With the decrease in the amount of oxygen, while aerobic processes are still underway in the landfill's upper layers, the anaerobic decomposition of organic substances formed in the previous phase begins. Anaerobic digestion begins with the fermentation of organic matter by acid bacteria, converting it into acids and alcohols, making the landfill acidic and inhibiting methane formation. The acids mix with moisture, releasing nutrients for bacteria. Gaseous by-products are carbon dioxide and hydrogen. If oxygen reaches the landfill, aerobic decomposition restarts. Additionally, organic matter is broken down into water-soluble components through an enzymatic process called hydrolysis.

It's important to note that this process is heavily dependent on the presence of moisture and the active role of microorganisms, particularly bacteria, in decomposing the waste. Organic waste decomposes in enzyme-catalysed reactions to the basic components:

Cellulose → *cellulase* → Glucose
Protein → *protease* → Amino acids
Starch → *amylase* → Glucose
Fats → *lipase* → Fatty acids

Gaseous components are not generated during the hydrolysis phase. The formed sugars of monosaccharides and higher organic acids, through various metabolic processes, are transformed by microbes, into simpler organic acids, water, carbon dioxide, ammonia, and hydrogen (H_2).

During this phase, in which the fermentation of acids takes place, CO_2 is generated immediately after the start of the process. Different studies show different gas compositions: 50-70% CO_2 after 11 to 23 days, or even 90% CO_2 after 40 days.

In summary, this phase can be represented by the following reaction mechanisms:

II-a. Hydrolysis: No gas production

II-b. Anaerobic acidic fermentation of glucose (CO_2 and H_2 gases are produced):

$$C_6H_{12}O_6 \rightarrow CH_3COOH + C_2H_5COOH + CO_2 + H_2 \qquad (2)$$

and

$$C_6H_{12}O_6 \rightarrow C_3H_7COOH + CO_2 + 2\,H_2 \qquad (3)$$

Phase III - Anaerobic, initial methanogenic phase, unstable

Stage III degradation begins when certain types of anaerobic bacteria consume the organic acids produced in phase II and start to form acetates. This process causes the acidity of the environment to become closer to a neutral pH value of 7 to 8, which corresponds to methane-producing bacteria (methane bacteria). The high presence of these bacteria is highly toxic to acid bacteria, emphasising the urgency of managing the process. The duration of Phase III can start approximately from the 180th day after the waste is deposited and last up to the 500th day after the deposit.

During the anaerobic decomposition phase, the temperature in the interior of the landfill drops to the range of 35 °C to 54 °C, where the first phase of anaerobic decomposition is the thermophilic phase with temperatures around 55 °C. In comparison, methane formation is followed by further lowering the temperature to 52 °C.

Significant methane production usually begins after six months of waste disposal.

Phase IV - Anaerobic, methane, stable methanogenic phase

Stage IV decommissioning begins when landfill gas composition and production become relatively constant. At this stage, it becomes the dominant group of microorganisms that converts acetic acid and hydrogen into methane and carbon dioxide. The landfill gas then contains about 45-60% methane, 40-60% carbon dioxide and 2-9% other gases. Gas is produced continuously in the fourth stage, usually for 20 years, and the emission of gas can continue even after 50 years of waste disposal. Gas production may take longer, especially if more organic waste is present.

III & IV. Methane enzymatic reaction of glucose (CO_2 and CH_4 gases are produced):

$$C_6H_{12}O_6 \rightarrow 3\ CO_2 + 3\ CH_4 \qquad (4)$$

In a simplified way, the process of anaerobic digestion of solid waste under the action of microorganisms can be represented by the expression (EPA, 2012):

Organic matter (solid waste) + H_2O → biodegraded organic matter + CH_4 + CO_2 + other gases (5)

Phase V - Maturation phase

The fifth phase begins with the penetration of air into the landfill, reducing microbial methanogenic activity. This leads to the extinction of methane bacteria and the restoration of aerobic conditions. Moisture continues to migrate through the waste, enabling the breakdown of previously inaccessible biodegradable material. As a result, air penetration increases, creating aerobic surface layers that allow for the biological oxidation of methane. Depending on closure measures, small amounts of oxygen and nitrogen may be present in the landfill gas. The changes in gas composition during the biodegradation stages of solid waste are shown in Figure 6.

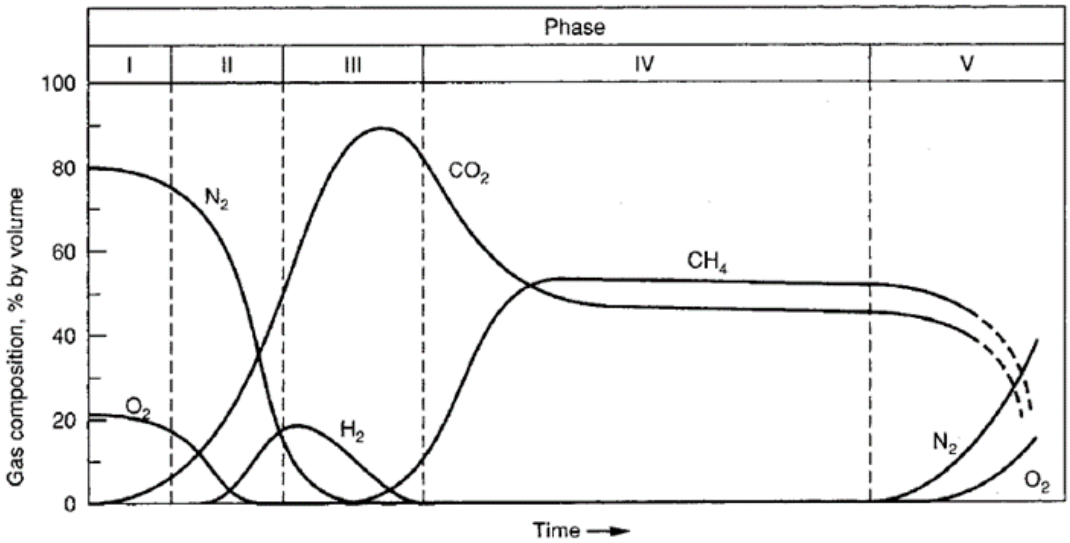

Figure 6. Change in gas composition during the biodegradation stages of solid waste (Tchobanoglous et al. 2002).

The above description of the decomposition process applies to ideal and homogeneous waste. However, in practice, waste composition is rarely ideal and homogeneous, leading to deviations from the described process.

The actual breakdown time is influenced by several factors. The aerobic stage, lasting several weeks or days, is followed by the prolonged anaerobic digestion process, which can span several years. The rough structure of the waste prevents uniform wetting; in some places, there are waterproof layers, and in some places, wide squeezing paths are formed. Biochemical decomposition of organic matter also leads to a change in the structure of the landfill. The soil structure of landfills differs from natural soil and contains significantly more organic matter.

In addition to atmospheric water, the landfill water regime is also affected by the moisture content of waste and water formed as a result of biochemical reactions. The moisture content of compacted waste can be 20-40 % (by weight), but it can contain significantly more moisture. Water is a by-product of aerobic biochemical processes, while anaerobic decomposition is ruled by water-consuming fermentation.

Capturing methane from municipal solid waste can be a practical way to recover energy and reduce greenhouse gas emissions. Numerous factors influence the quantity, generation rate, and composition of landfill gas produced in landfills (as shown in Table 1.). Some factors can be controlled, while others can only be estimated. Additionally, the continuous and progressive disposal of waste in landfills leads to an ongoing overlap of decomposition phases over time. These factors collectively determine biogas production dynamics within the landfill environment and can be categorised into four main groups.

Table 1. Factors that determine dynamics of landfill gas production (Tchobanoglous et al. 2002), (Rodrigo-Ilarri et al. 2020).

1. Waste characteristics:	**3. Landfill design and management:**
- Total mass stored - Organic matter content - Moisture levels - Presence of nutrients and methanogenic inhibitors	- Site topography - Operational procedures - Leachate and biogas management systems - Use of intermediate cover layers
2. Waste treatment methods:	**4. Climatic conditions:**
- Sorting techniques	- Precipitation levels
- Particle size reduction	- Ambient temperature
- Leachate recirculation practices	- Evaporation rates

So, the exact dynamics of the formation of landfill gas in the processes of biodegradation of the organic component from solid waste can only be determined by experimental studies. While there are many studies on landfill gas generation, no single model applies universally to all types of landfill sites (Alivojvodic et al. 2015). The average composition of landfill gas from several MSW landfills is shown in Table 2.

Table 2. Average composition of landfill gas from MSW landfills (Rodrigo-Ilarri et al. 2020).

Component	1	2 (MOV)	3	4	5	6	7
CH_4	63.8	88	40–60	45–60	35–60	60	63.4
CO_2	33.6	89.3	40–60	40–60	35–45	39.62	18
O_2	0.16	20.9	-	-	0–2.5	0.55	4.8
N_2	2.4	87	5	2–5	0–20	-	13.8
H	0.05	21.1	-	0–0.2	-	-	-
H_2O	1.8	4	-	-	1–10	-	-
CO	-	-	0.001	0–0.2	-	49.52*	-
CO	-	-	0.001	0–0.2	-	49.52*	-
NH_3	-	-	30	0–0.2	-	-	-
H_2S	-	0.015	0–1	0–1	0–0.1	34.21*	11

Even so, despite numerous challenges, this energy source, if properly used, can significantly contribute to the portfolio of renewable energy sources while simultaneously reducing greenhouse gas emissions.

1.3. Bioethanol fermentation

Ethanol is a widely used solvent in chemical synthesis, paints, coatings, inks, and adhesives production and in the pharmaceutical and cosmetic industry**.** Bioethanol can be converted into other industrial chemicals such as ethylene, propylene, 1,3-butadiene, iso-butylene, hydrogen, acetaldehyde, ethylene oxide, *n*-butanol, acetic acid, ethyl acetate, acetone, and dimethyl ether by catalytic conversion through e.g., dehydration, dehydrogenation, oxidation, reforming, gasification, decomposition, coupling, etc. (Posada et al, 2013). The major use of bioethanol nowadays is biofuel with its liquid transportation property as a blend. More importantly, it can be further converted into fuels, namely gasoline-range, jet-range, and diesel-range hydrocarbons (Xie et al., 2024).

The technology status of bioethanol production is directly dependent on the used feedstock. According to the used feedstock, bioethanol is classified into four generations. First-generation bioethanol is produced from sugary or starchy crops such as sugar cane, sugar beet, cereals, potatoes, etc. These crops are also food and feed, with enhancing costs due to food scarcity. They provide high ethanol yields, have lower processing costs, and good industrial practices to efficiently use all secondary and by-products. Second-generation bioethanol uses low-cost lignocellulosic feedstocks with the potential to be applied widely. However, despite the significant research and technological development in second-generation bioethanol, it is still not economically and energy efficient, and hence it is uncompetitive with fossil fuels. Third-generation bioethanol is produced from algae, while fourth-generation bioethanol uses genetically modified algae to enhance bioethanol yield. Currently, 99% of global bioethanol production comes from the first-generation route by developed industrial production corresponding to a technology readiness level (TRL) of 9. Second-generation bioethanol is slowly developing and is currently produced in several first-of-the-kind plants (TRL 7-8). Third- and fourth-generation bioethanol production is still in the lab and pilot stages (TRL 1-4). Although 3G bioethanol may be produced on non-arable lands it still does not fulfill energy efficiency and carbon footprint requirements. Key challenges for the development of bioethanol production are using low-cost renewable raw materials by applying efficient processing technology to utilize all feedstock constituents with low energy input and obtain high ethanol yield and productivity, without negative influence on the environment.

Alcoholic fermentation for bioethanol production is conventionally performed on an industrial scale using freely suspended yeast cells as biocatalysts. In recent decades, the development of alcoholic fermentation in contemporary bioreactors implies the application of yeast cells immobilized on different kinds of carriers to obtain high ethanol content and increase fermentation efficiency. Immobilization of yeast cells involves the procedure by which yeast cells are chemically or physically attached to the surface of various solid supports. Immobilized cell systems can be used multiple times as biocatalysts in discontinuous processes and for continuous fermentation processes, maintaining a high catalytic activity for a long time. By using immobilized cells for alcoholic fermentation, it is possible to achieve a high concentration of active yeast biomass in the bioreactor and good contact between the cells and the nutrient medium, and to achieve high ethanol concentration and productivity of the fermenter, improving the stability of the process and obtaining a product of uniform quality.

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1.3.1. Evaluation of Biomass Types for Bioethanol Fermentation

Raw materials for bioethanol production include sugar-rich biomass, starch-rich biomass, and lignocellulosic biomass. If waste biomass contains only simple sugars, physical size reduction is usually sufficient as a pretreatment. However, for starchy biomass or lignocellulosic biomass, more complex pretreatments are necessary to release fermentable sugars and enable efficient bioethanol production. Different biomass types that can be utilized for bioethanol production (Table 3.) offers distinct advantages and processing challenges, contributing to the overall sustainability of bioethanol as a renewable energy source.

Table 3. Waste biomass used for bioethanol production.

WASTE BIOMASS		REFERENCES
Agricultural Biomass	Rice hulls	Dagnino et al., 2013
	Wheat straw	Linde et al., 2008
	Rice straw	Aditiya et al., 2015
	Animal Manure	Lee et al., 2021 Yan et al., 2018
Forest and Wood Biomass	Forest residues	Franko et al., 2016
	Forest residues	Hossain et al., 2021
Agro-Industrial Biomass	Sugarcane bagasse	Aita et al., 2011
	Potato peel waste	Chohan et al., 2020
	Starch milk	Katanski et al., 2024
	Sugar beet procesing juice	Dodić et al., 2009 Dodić et al., 2012 Vučurović et al., 2012
	Sugar beet pulp	Rezić et al., 2013 Vučurović et al., 2024
Other Biodegradable Biomass	Municipal Solid Waste (MSW)	Khraisheh and Li, 2020
	Sewage sludge	Manyuchi et al., 2020
	Kitchen Waste	Vučurović et al., 2014

Agricultural biomass, such as rice hulls, wheat straw, corn stalk, corn stover, and rice straw, has shown potential for bioethanol production through various pretreatment, hydrolysis, and fermentation processes. Pretreatment methods, including acid hydrolysis, hydrothermal, and alkali treatments, are used to break down the complex structure of biomass into fermentable sugars. Enzyme concentrations and conditions (e.g., temperature, pH, and residence time) during hydrolysis are tailored for each biomass type to maximize the sugar yield. Fermentation processes utilizing *Saccharomyces cerevisiae* vary in residence time and inoculum levels depending on the specific biomass. For example, rice hulls produced 11 g of ethanol per 100 g of biomass (Dagnino et al., 2013), while corn stover treated with NaOH yielded 35 g of ethanol per 100 g of carbohydrates (Zhao and Xia, 2009). These variations highlight the impact of pretreatment methods and biomass types on bioethanol production efficiency.

Forest biomass is a valuable resource for bioethanol production, encompassing various materials such as forest residues (including tops, branches, foliage, stumps, and roots), wood processing industry residues (like leaves, branches, bark, sawdust, and wood shavings), as well as wood waste from parks and gardens and discarded wood products such as pallets and furniture. These biomass sources are rich in lignocellulose, which must undergo pretreatment to break down their complex structure and release fermentable sugars. Effective pretreatment processes, such as mechanical, thermal, or chemical methods, are essential to enhance the accessibility of these sugars for fermentation, ultimately facilitating efficient bioethanol production and contributing to sustainable energy solutions.

Agro-industrial biomass, including sugarcane bagasse, potato peel waste, and sugar beet pulp, also holds promise for bioethanol production. Pretreatment strategies such as ammonium hydroxide, sulfuric acid, and ultrasound have been employed to enhance the breakdown of complex carbohydrates. For instance, sugarcane bagasse treated with ammonium hydroxide and fermented with S. cerevisiae resulted in a yield of up to 23 g of ethanol per 100 g of biomass (Aita et al., 2011). Pretreatment and hydrolysis of potato peel waste produced a variable ethanol yield of 0-33 g per 100 g of biomass, depending on solid loadings (Chohan et al., 2020). Similarly, sugar beet pulp underwent ultrasound and thermal pretreatment, leading to a bioethanol yield of 10 g per 100 g of biomass (Rezić et al., 2013). These findings demonstrate that the optimization of pretreatment and enzymatic hydrolysis steps is essential for improving bioethanol yields from agro-industrial biomass sources.

Other biodegradable waste such as Organic fraction of Municipal Solid Waste, sewage sludge, and kitchen waste are valuable raw materials for bioethanol production, OFMSW contains organic materials that can be processed to extract fermentable sugars, while sewage sludge, often rich in lignocellulosic content, can be treated to release sugars for fermentation. Utilizing these resources not only helps reduce environmental impact but also promotes the circular economy by converting waste into valuable biofuels.

1.3.2. Design of Bioethanol Fermentation Technology

The process of bioethanol production using various waste biomass of lignocellulosic or starchy origin is schematically shown in Figure 7.

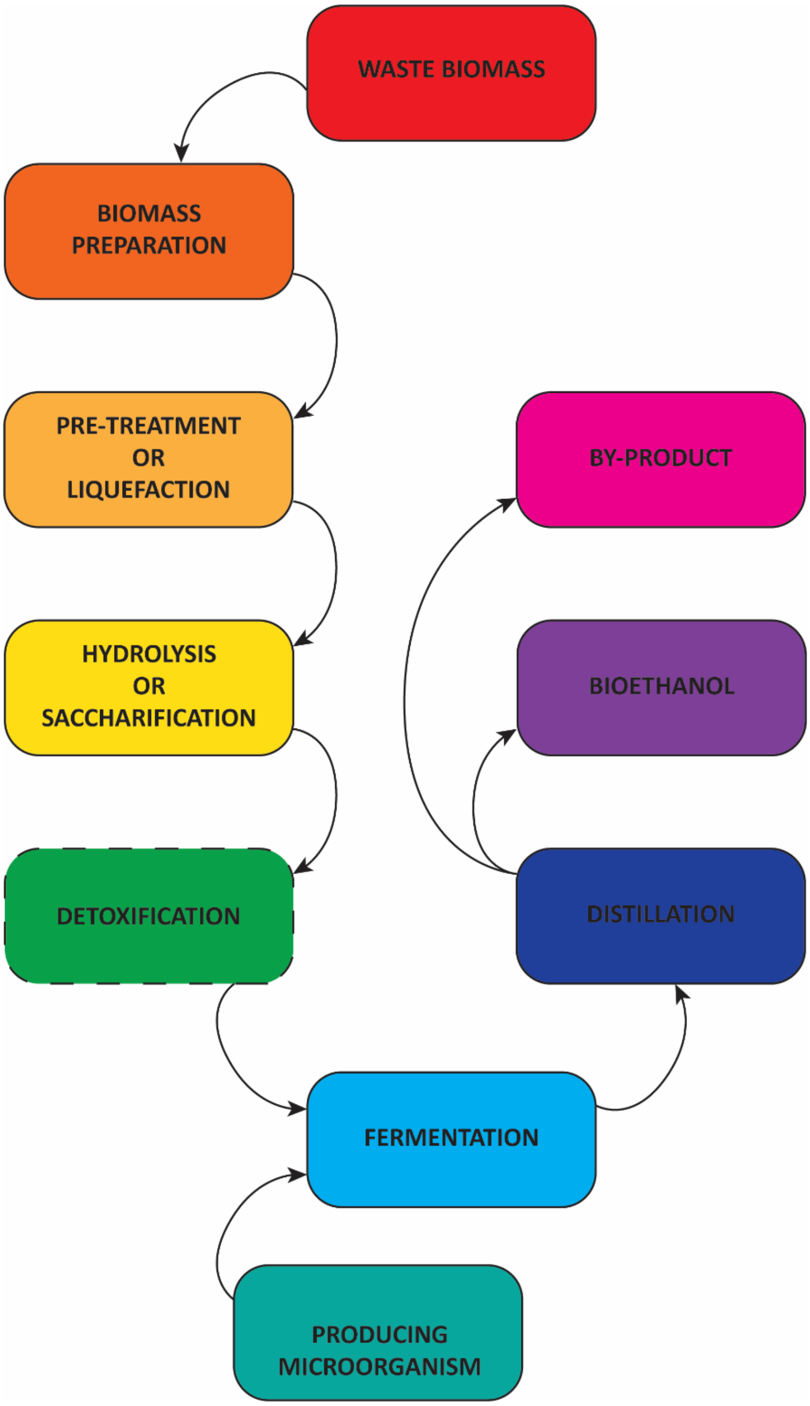


Figure 7. Bioethanol fermentation.

Although the specifics of the process vary depending on the type of biomass used, the general stages in the bioethanol production process are as follows (Nair et al., 2017, Trzcinski, 2018):

Preparation of waste biomass – size reduction through grinding, crushing, or cutting; preparing the raw material to reduce its volume; sometimes left out due to high energy costs and potential impacts on subsequent stages.

Pretreatment – physicochemical or biological processing (e.g. steam explosion, acid, alkaline, or microbiological pretreatment).

Release of fermentable sugars – through hydrolysis or saccharification using bacterial or fungal enzymes; In addition to enzymatic hydrolysis, concentrated acids can be used for hydrolysis. Acid hydrolysis requires harsher conditions, leading to more significant glucose degradation but also in a greater extent of hydrolysis.

Fermentation – using microorganisms, yeasts, bacteria, or fungi, in controlled conditions in bioreactors.

Distillation – separation of bioethanol from fermentation broth.

In ethanol production, fermentation can be conducted in a batch, semi-continuous, or continuous mode. The choice of bioreactor mode of operation depends on the characteristics and cost of the raw material, the price of the necessary equipment, and the productivity and yield of bioethanol, and the comparison of batch, fed-batch and continuous fermentation is given in the Table 4.

The bioethanol production process can be performed as

1. Separate hydrolysis and fermentation (SHF)
2. Simultaneous saccharification and fermentation (SSF) -
3. Simultaneous saccharification and co-fermentation (SScF) -
4. Consolidated bioprocessing (CBP)

The possibilities of combining and integrating certain phases in the production of bioethanol from starchy or lignocellulosic raw materials are shown in Figure 8. (Vohra et al., 2014).

Table 4. Comparison between batch, fed-batch, and continuous fermentation (Tse et al., 2021).

		Advantages:	Disadvantages
Batch	Microorganisms are provided with a fixed volume of medium (nutrients and other ingredients). Culture environment is consistently changing as nutrients are consumed.	Low cost Low risk of contamination Less control required Easier sterilization	Lower cell densities, ethanol production Longer downtime between batches due to cleaning, vessel setup, and sterilization
Fed-Batch	Media is inoculated with microorganisms which then grow under a batch regime for a certain amount of time, then nutrients are added incrementally throughout the fermentation.	Maintenance of maximum viable cell concentration Extended lifespan of cells Higher ethanol accumulation By-product accumulation is limited Control of factors (e.g., pH, temperature, dissolved oxygen)	Increased costs for process control Longer downtime between batches due to cleaning, vessel setup, and sterilization

Continuous	Fresh media is continuously added to the fermenter, replacing the consumed nutrients. Ethanol, used media, and toxic metabolites are continuously removed.	Less downtime for vessel cleaning Increased productivity Lower cost Higher degree of control Ability to automate, more cost-efficient and less sensitive to human error.	Less control for non-growth-related products Cell aggregation can prevent optimum steady-state growth Long growth periods can increase risk of contamination Can be difficult to maintain filamentous organisms due to viscosity and heterogeneity of the medium

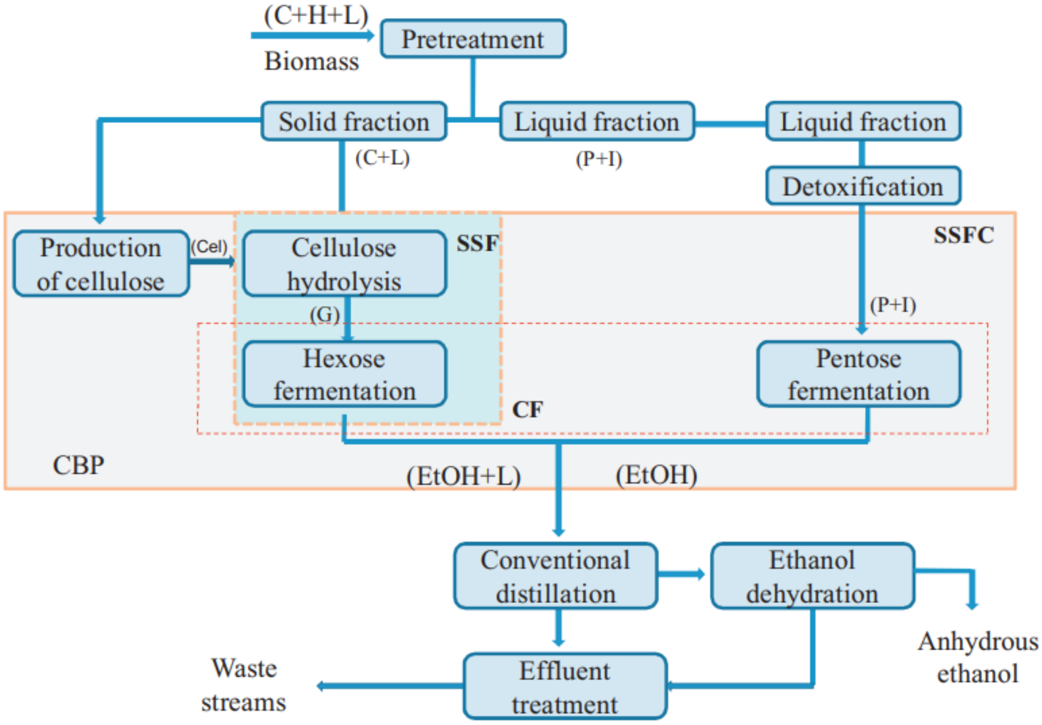


Figure 8. Process alternatives of bioethanol production (Vohra et al., 2014).

The bioprocessing 2nd and 3rd generation biomasses for bioethanol production is challenging compared to starchy biomasses. The bottlenecks of using lignocellulosic biomass for fermentative biofuel production is already well documented. Apart from the costly and strong pretreatment requirements, the formation of inhibitory substances that need detoxification, a mixture of pentoses and hexoses could adversely affect the process performance. However, intensive studies for bioethanol generation from lignocellulosic biomasses have been conducted and the results are promising. One of the problems is the fermenting culture to be used in 5C and 6C sugar mixture obtained from hydrolysis of cellulose and hemicellulose in lignocellulosic biomass. The most commonly used microbial cultures for bioethanol production from lignocellulosic biomasses are yeast namely *Saccharomyces* which is capable of utilizing only glucose with 120 g/L ethanol tolerance by Embden–Meyerhof–Parnas (EMP) pathway (Broda et al., 2022, Malik et al., 2022). The other yeast cultures *Pichia* genera can use xylose by pentose phosphate pathway, but low tolerance to ethanol (40 g/L), microaerobic condition requirement, low tolerance to acidic pH, catabolic repression in xylose utilization when glucose is available are the limitations of the culture (Broda et al, 2022). *Zymomonas* is a well-known ethanol producing bacteria by Entner–Doudoroff (ED) pathway with high tolerance to ethanol, and high rate of growth but no xylose utilization metabolism (Malik et al., 2022). Some other microbial cultures employed are bacteria as *Klebsiella, Aerobacter, Bacillus, Thermoanerobacter,* and *Aeromona*, yeasts cultures of *Pachysolen* and *Candida*,(Rastogi & Shrivastava 2017).

The initial sugar concentration in bioethanol fermentation is crucial. The higher the substrate utilization, the better product formation is desired on the industrial scale. On the other hand, the substrate inhibition problem in the microbial process is an issue. It can be controlled by running the process with high bacterial biomass. The yeast and bacteria can tolerate high sugar concentrations of up to 250 g/L (Rameshbabu et al., 2024). Bioprocess technologies such as fed–batch bioprocess, immobilized bioreactors, or repeated batch operation with cell recycle are widely used ones that can provide high biomass concentration to overcome substrate inhibition for running the process at high initial sugar concentrations (Bušić et al., 2018). These bioprocesses are conventional fermentation technologies known as separate hydrolysis and fermentation where sugar-rich supernatant of the pretreated lignocellulosic biomasses is used. Simultaneous Saccharification and Fermentation (SSF) is a single-stage process with enzymatic hydrolysis of biomass and then generation of the desired product by the fermentative organism. The enzyme used for this purpose is cellulolytic which could work well at 50 °C while fermentation occurs at 30-34 °C (Sharma et al., 2021). So the fermentation difference for hydrolysis and product formation is an issue to be solved. One of the suggestions is to develop genetically manipulated yeast cultures that can run the fermentation at high temperatures. Consolidated bioprocess uses a consortium or a single species of microorganism which is capable of hydrolysing the biomass and fermenting the generated sugar to ethanol. The process seems to be ideal considering the cost of pretreatment and the use of enzymes for hydrolysis purposes in the other strategies. However, the rate of hydrolysis is slower compared with that of bioethanol fermentation causing a reduction in the overall reaction rate of the process (Rastogi and Shrivastava, 2017, Singh et al., 2022). When lignocellulosic biomass is the raw material, the sugar syrup after enzymatic hydrolysis will contain glucose and xylose which may not be further processed for product formation in the fermentation strategies mentioned above. The alternative one is Simultaneous Saccharification and Co-Fermentation (SSCF) in which different microbial cultures for hydrolysis and processing generates xylose as well as glucose. The process has a complex nature like controlling the operating and environmental conditions for the cultures used in the process.

One of the commercial bioethanol producers is the United States from corn, accounting for 58% of global bioethanol production with 59 billion L in 2023 (Statista). The availability of corn makes it an excellent feedstock for bioethanol production. The two major methods for processing corn to bioethanol are dry and wet milling. In dry milling, milling, two-stage cooking in a jet cooker with enzymes for liquefaction and hydrolysis are applied, then sugar syrup is fermented to ethanol with the formation of co-products such as distillers' grains and carbon dioxide (Bušić et al., 2018). In wet milling, the corn is hydrolyzed by applying heat in a sulfurous acid solution for two days, the material is decomposed into starch, fiber, corn germ, and protein. The starch can then be used to produce ethanol, corn syrup, or food-grade starch. The process also generates additional products such as animal feed, corn oil, gluten meal, and gluten feed (Jain et al., 2024). The bioethanol share of Brazil is about 30% with 31.5 billion liters of ethanol from sugar cane (Statista). The process includes milling, the extraction and concentration of sugarcane juice to obtain a high sugar concentration necessary for high product formation and then followed by ethanol fermentation, distillation, and dehydration [Dias, et al., 2012, Wu et al., 2021). The baggase is the residue of the process. The recent studies concentrate on valorisation of baggase to bioethanol (de Araujo et al., 2019, Hor et al., 2022). The industrial sugarcane processing for ethanol generates vinasse which can be used as natural fertilizer. The other contributors to bioethanol production are the European Union and India followed by China.

EU bioethanol production biomass resources are wheat, corn, barley, rye, triticale, sugar beets, and cellulosic biomass. The number of refineries producing first generation fuel ethanol was 66 and decreased to 59 by the year from 2014 to 2023 with a total capacity of 8,519 million liters/ year. The refineries producing cellulosic fuel ethanol reached 5 with a total production capacity of 200 million liters/ year for the same period. The consumption of bioethanol is increasing in the EU whereas the production cannot satisfy the demand (USDA, 2023).

Wu et al. (2021) evaluated the current status of ethanol production in China. The existing bioethanol industries are using corn mainly with wheat, cassava and sweet sorghum as the raw materials. In the year 2021, the fuel ethanol production capacity in China was approximately 3.2 million tons (Mt), with an additional 5.88 Mt from projects under construction or planned, bringing the total capacity to 9.08 Mt. Of this, 6.54 Mt (72.03%) is derived from grain-based ethanol, 1.68 Mt (18.50%) comes from non-grain sources like cassava, and 860,000 tons (9.47%) is from cellulosic ethanol. As stated by Wu et al. (2021), the pressure of rising corn prices, declining ethanol prices, food security and needs in technological advancements are the shortcomings of China to develop corn fuel ethanol on a large scale in the future. It is suggested utilization of cellulosic ethanol in China.

The current status of India in bioethanol production from lignocellulosic biomass was summarized by Jain et al. (2024). The raw materials used for this purpose are bamboo, rice straw, sugarcane bagasse, and agricultural waste with the production capacity between 30-63 million liters/year. According to the U.S. Department of Agriculture (USDA), Foreign Agricultural Service report published in 2024 about the bioethanol production in India. It is expected India’s ethanol production for 2024 to reach 6.35 billion liters, a two percent drop from last year due to a projected decline in sugarcane production and a depleting rice grain supply (USDA, 2024).

The use of immobilized yeast cells in alcoholic fermentation for bioethanol production is a rapidly developing research area due to its numerous technical and economic advantages compared to the use of free cells, especially in the continuous fermentation process (Verbelen et al., 2006; Kourkoutas et al., 2006). By using immobilized yeast cells in alcoholic fermentation, it is possible to achieve a high concentration of active biomass, as well as good contact between the cells and the nutrient medium, thus achieving high ethanol productivity, improving the stability of the process, and obtaining a product of uniform quality (Mallouchos et al., 2007). Significant scientific attention is directed toward developing new immobilization methods and techniques, improving the construction of bioreactors with immobilized biocatalysts, and finding solutions to material and energy problems related to the immobilization technique. It is very important that, during the process of immobilization, the cells of microorganisms maintain their viability and metabolic activities. With this procedure, high concentrations of active biomass can be achieved in the bioreactor, which leads to high productivity and increased stability of the process, and obtaining a final product of uniform quality (Verbelen et al., 2006). Different aspects of the immobilization methodologies have been investigated in detail, including their impact on microbial growth and physiology, limitations of internal and external mass transfer, product quality, bioreactor design, and economics of the entire production process (Mussatto et al., 2010).

According to the nature of the interaction between biocatalysts (enzyme or microorganism) and the support, immobilization may be classified as chemical physical.

Chemical immobilization includes ionic and covalent bonds forming, intramolecular covalent bonding between biocatalyst molecules, incorporation in the polymer structure, and chelate forming with transition metals (Boross et al., 2008). Physical methods for yeast immobilization (Figure 9.) include the following techniques: (a) attachment to a surface, (b) entrapment within a porous matrix, (c) containment behind a barrier, and (d) self-aggregation (Verbelen et al., 2006).

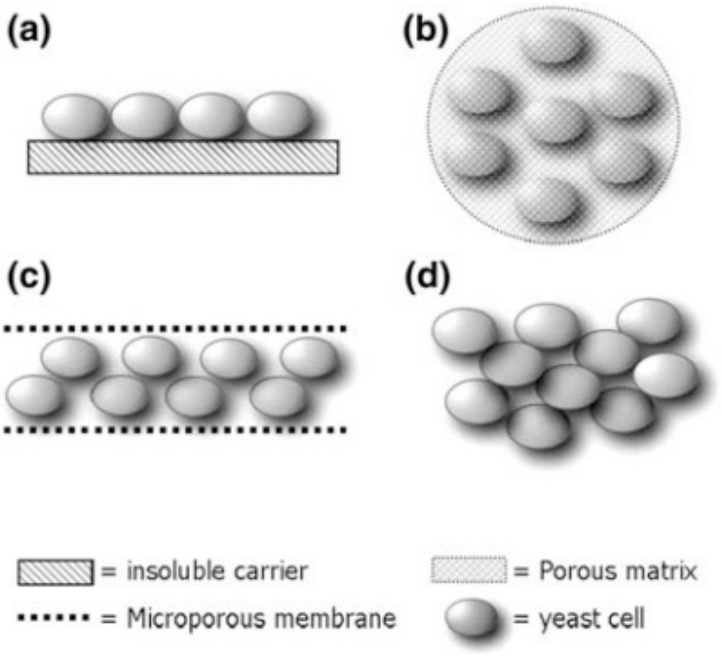


Figure 9. Basic methods of yeast immobilization: (a) attachment to a surface, (b) entrapment within a porous matrix, (c) containment behind a barrier and (d) self-aggregation (Verbelen et al., 2006).

Natural immobilization by attachment on the surface (Figure 9a) is very simple and takes place in mild conditions, but the intensity of cell attachment is significantly weaker compared to the cross-linking of cells in the polymer structure. Cell adsorption to insoluble supports can be caused by Van der Waals and electrostatic interactions between yeast cells and the surface of the support. The natural adsorption of yeast cells on supports has not yet been fully elucidated, but it is certainly the result of electrostatic forces or the result of the formation of covalent bonds between the surface of the support and the cell membrane (Figure 10) (Kourkoutas et al., 2004). Immobilization of yeast cells by natural adsorption on the surface is very simple, cheap and does not require special conditions, but the amount of immobilized cells per unit mass of the yeast carrier is significantly lower compared to cells immobilized by cross-linking in a polymer matrix (Verbelen et al., 2006). The thickness of the yeast film on the support surface varies depending on the thickness of monolayer cells to about 1 mm and depending on the nature and intensity of the force with which the cells are attached to the support. However, since there are no barriers between yeast cells and the solution, desorption and washing of yeast cells from the support is possible until the equilibrium between adsorbed and freely suspended yeast cells is reached (Kourkoutas et al., 2004).

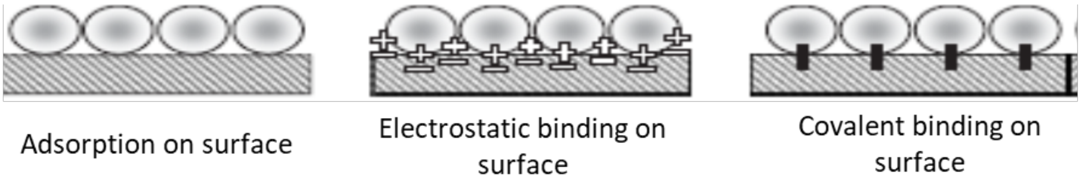


Figure 10. Immobilization of yeast cells by adsorption on the surface of insoluble carriers (Kourkoutas et al., 2004).

The immobilization of yeast by entrapment (Figure 9b) implies the formation of a porous matrix which is synthesized in situ around the cells. Natural and synthetic polymer hydrogels such as: Ca-alginate, k-carrageenan, agar, polyurethane, polystyrene, and polyvinyl alcohol are most often used for this purpose (Verbelen, 2006). Polymer carriers are usually formed as spherical beads, with diameters ranging from 0.3 to 3 mm. Although a very high concentration of biomass can be achieved, the application of polymer matrices is rare in industrial fermentation due to several disadvantages such as limited diffusion of nutrients, metabolites, and oxygen in the gel matrix, and an increase in cell density in the beads, chemical and physical instability of the gel, and inability to regenerate beads, which makes this category of immobilization quite expensive. In scientific research, great efforts have been made to solve these shortcomings, by introducing new techniques that are able to adjust the size and shape of the hydrogel (Verbelen et al., 2006).

S. cerevisiae strains have a natural ability to attach to inert surfaces or associate with each other, referred to as flocculation or self-aggregation. Yeast flocculation is a reversible, asexual, and calcium-dependent phenomenon, in which cells' surfaces bind to each other to form flocs containing thousands of cells. Due to their macroscopic size and mass, yeast flocs quickly sediment from the fermented medium, ensuring natural cell immobilization. The use of flocculent strains is attractive, due to its simplicity and low cost. The natural flocculation ability of certain microorganisms is influenced by numerous factors such as genetic characteristics, cell wall structure, surface charge and yeast growth phase, flow intensity, temperature, pH, concentration of Ca^{2+} ions, and concentration of nutrients in the fermentation medium. Thus, the content of glucose, sucrose, and nitrogen compounds in the fermentation medium can affect the success of the immobilization. Yeast flocculation depends on the expression of several specific genes such as FLO1, FLO5, FLO8, and Lg-FLO1, while genes, such as FLO11, confer adhesion to inert substrates and the formation of biofilms on nutrient sources (Verbelen et al., 2006).

In continuous immobilized yeast fermentation systems contain three phases: solid (the carrier or aggregate), liquid (the medium), and gas (air, oxygen, or other gas feeds). Different types of bioreactors (Figure 11) are being used depending on the type of immobilization, the metabolism of cells, and the mass and heat transfer requirements. In a packed bed reactor (Fig. 11A), the fermenting medium is passed either upward or downward through the reactor which is packed with immobilized yeast. In a fluidized bed reactor (Fig. 11B), intensive mixing of gas, liquid, and solids occurs by recirculating the fermenting substrate, resulting in less abrasion of the carrier particles compared with stirred reactors. In airlift (Fig. 11C) and bubble column (Fig. 11D) reactors, the circulation is performed by gas injection (Verbelen et al., 2006; Genisheva et al., 2014). In continuous fermentation system, immobilized cells show significantly higher productivity than free cells, particularly under VHG fermentation conditions (Pátaková et al., 2000; Bai et al., 2009).

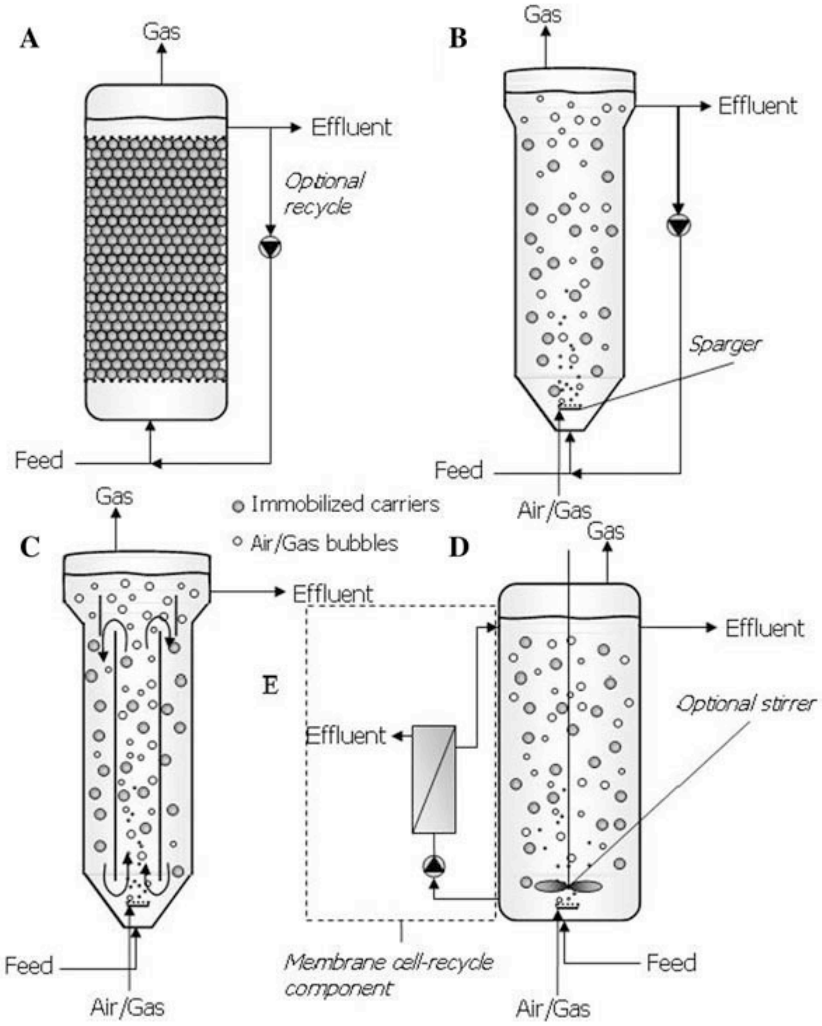


Figure 11. Common types of immobilized cell bioreactors: (A) packed bed reactor; (B) fluidized bed reactor; (C) gas lift reactor; (D) bubble column reactor (or stirred reactor if stirred); and (E)membrane cell-recycle reactor (Verbelen et al., 2006).

Immobilization technology is used in various fermentation processes for bioethanol production. Different immobilized yeast systems are used for the fermentation of a wide range of substrates for first-generation or second-generation bioethanol production. Some of the fermentation parameters reported by groups of researcers for the production of first-generation and second-generation bioethanol by immobilized yeast are depicted in Table 1 and Table 2.

Yeast immobilization with low-cost carrier materials is a suitable strategy to optimize the fermentation of lignocellulosic hydrolysates for the production of second-generation (2G) as well as first-generation (1G) ethanol. Using immobilized cells facilitates the enhancement of the fermentation performance, the resistance to inhibitors contained in the hydrolysates, and the co-utilization of sugars, along with facilitating separation operations and the reuse of yeast in new production cycles. As shown in Tables 5 and 6, the most common immobilization technology used calcium alginate as a yeast carrier but other supports such as different natural materials have emerged as interesting alternatives

Table 5. Immobilized cells system applied for first-generation bioethanol production.

Type of immobilization system	Yeast immobilization carrier	Immobilized yeast	Raw material	Sugar concentration (g/L)	Fermentation conditions	Ethanol production (g/L)	Ethanol productivity (g/Lh)	Ethanol yield (% w/w)	Fermentation efficency (%)	Reference
Cross-linking and covalent binding	Alginate-based MCM-41 mesoporous zeolite composite	*S. cerevisiae*	Sugar molasses	170	30 °C, 115 rpm, 12 h	78.6	6.55	46.24	90.66	Zheng et al. (2012)
	Bacterial cellulose-alginate (BCA) sponge	*S. cerevisiae* M30	Cane molasses	220	33 °C, 150 rpm, 48 h	92	1.92	41.82	82	Kirdponpattara et al. (2013)
Immobilization on a support surface	Sorghum bagasse	Mutant baker's yeast 3013	Glucose and sucrose	200	30 °C, 16 h	92.7	5.72	46.35	90.88	Yu et al. (2013)
	Thin-shell silk cocoon	*S. cerevisiae* M30	Blackstrap molasses	240	33 °C, 150 rpm, 48 h	80.6	1.85	33.58	65.85	Rattanapan et al. (2011)
	Sugar beet pulp	*S. cerevisiae* DTN	Sugar beet thick juice	120	30 °C, 48 h	52.3	1.09	43.58	85.46	Vučurović et al. (2012)
	Sweet sorghum stalks	*S. cerevisiae* NP 01	Sorghum juice	230	30 °C, 72 h	98.5	1.37	42.83	83.97	Ariyajaroenwong et al. (2012)
	Modified activated carbon									Chinwatpaiboon et al. (2023)
Entrapment in a porous matrix	Calcium alginate	*S. cerevisiae* CTCRI	Mahula flower	350	30 °C, 96 h	25.8	0.27	7.37	14.45	Behera et al. (2010)
	Calcium alginate	*S. cerevisiae* var. *ellipsoideus*	Corn meal	150	30 °C, 74 h, 150 rpm	88.9	2.34	59.27	116.21	Nikolic et al. (2010)
	Calcium alginate	*S. cerevisiae* G1	Glucose	250	28 °C, 120 h	43.4	0.36	17.36	34.04	López-Menchero et al. (2021)
	Penicillium chrysogenum fungal pellet	*S. cerevisiae* G1	Glucose	250	28 °C, 120 h	63.1	0.66	25.25	49.51	
	P. chrysogenum pellet + calcium alginate coat	*S. cerevisiae* G1	Glucose	250	28 °C, 120 h	55.2	0.58	22.09	43.32	
	P. chrysogenum fungal pellet	*S. cerevisiae* G1	Starch	5	28 °C, 24 h	2.4	0.1	47.34	92.82	Peinado et al. (2006)
	P. chrysogenum fungal pellet	*S. cerevisiae* G1	Sugar molasses	400	28 °C, 125 h	90.7	0.73	22.68	44.48	

		P. chrysogenum fungal pellet	*S. cerevisiae* Uvaferm BC	Glucose	180	28 °C, 10 h	78.9	8.4	43.83	85.95	García-Martínez et al. (2011)
		Silica gel	*S. cerevisiae* wild-type strain	Apple juice	100	Aerobic, 30C, 5 days	12.9	2.58	85	90	Martín-Morales et al. (2023)
		Sepiolite-based biohybrids	*S. cerevisiae* wild-type strain	Apple juice	100	Aerobic, 30°C, 5 days	7.1	1.42	50	55	
		Alginate/cellulose (from wood waste) beads	*S. cerevisiae*	Glucose	100	30°C, 24 hours	114.5	1.5	-	-	Pratama et al. (2023)
		Neat Alginate	*S. cerevisiae*	Glucose	100	30°C, 24 hours	85.5	-	-	-	
		Bacterial Nanocellulose	*S. cerevisiae* and amylases double freeze-dried	Starch (5%, w/v)	-	Simultaneous saccharification and fermentation	-	-	51	89.9	Drosos et al. (2023)
			S. cerevisiae and amylases single freeze-dried				-	-	46	81.1	
		Open-cell macroporous poly(acrylamide) (PAM) hydrogels	-	Glucose	-	-	-	-	-	68	Sun et al. (2024)
Auto-Immobilization	Biofilm	Biofilm-immobilized continuous fermentation (FLO5)	*S. cerevisiae* 1308-FLO5	Glucose	200	35°C, 37°C, continuous	Up to 705.61	-	-	-	Wang et al. (2023)
		Biofilm-immobilized continuous fermentation (FLO10)	*S. cerevisiae* 1308-FLO10	Glucose	200	35°C, 37°C, continuous	Up to 705.61	-	-	-	

Table 6. Immobilized cells system applied for second-generation bioethanol production.

Type of immobilization system	Yeast immobilization carrier	Immobilized yeast	Raw material	Initial substrate concentration (g/L)	Fermentation conditions	Ethanol production (g/L)	Ethanol productivity (g/Lh)	Ethanol yield (% w/w)	Fermentation efficiency (%)	Reference
Auto-Immobilization	Multispecies biofilm membrane or MBM (N-O)	*S. cerevisiae* and *Pichia stipitis*	Avicel	10*	Semi-continuous consolidated bioprocessing, 28 °C, 240 h	3.5	0.02	35	68.63	Brethauer and Studer (2014)
			Avicel	17.5*	Batch consolidated bioprocessing, 28 °C, 216 h	7.2	0.04	41.14	80.67	
			Wheat straw slurry	17.5*	batch consolidated bioprocessing using MBM with both yeasts, 28 °C, 144 h	9.8	0.07	56	109.8	
			Washed pretreated wheat straw supplemented with xylose	17.5* and 22 xylose		9.1	0.06	41.36	81.11	
	Self-flocculation (N)	*S. cerevisiae* KF-7	Diluted waste molasses	180	Continuous fermentation, 30 °C, 150 rpm, 840 h	80	6.6	44.44	87.15	Tang et al. (2010)
Entrapment in a porous matrix	Agar-agar cubes (O)	*S. cerevisiae* MTCC 174	Sugarcane bagasse enzymatic hydrolysate	50	Batch fermentation, 30 °C, 72 h	9.4	0.26	18.8	36.86	Singh et al. (2013)
		S. cerevisiae CTRI	Mahula flowers	350	Batch fermentation, 30 °C, 96 h	25.2	0.26	7.2	14.12	Behera et al. (2010)
	Alginate beads (O)	*Pachysolen tannophilus* MTCC 1077	Peels of pineapple *Ananas cosmosus*	51.7	Batch SSF supplemented with 5 FPU cellulase/g substrate, 50 °C for 24 h saccharification and 32 °C for 96 h fermentation	10.5	0.15	20.31	39.82	Bhatia and Johri (2015)

Pichia stipitis NCIM 3498		51.7	Batch SSF +5FPU cellulase/g substrate, 50 °C for 24 h saccharification and 30 °C for 96 h fermentation	10.9	0.15	21.08	41.34	
S. cerevisiae and Pichia stipitis	Wheat straw hydrolysate	30	Continuous fermentation, 30°C	10.42	9.8	34.73	68.1	Karagöz and Özkan (2014)
S. cerevisiae CTRI	Mahula flowers	350	Batch fermentation 30 °C, 96 h	25.8	0.27	7.37	14.45	Behera et al. (2010)
S. cerevisiae	Carrots discards	89.8	Batch fermentation,30 °C, 200 rpm, 4 h	24.5	7.17	27.28	53.5	Clementz et al. (2014)
Candida shehatae NCL-3501	Rice straw auto hydrolysate	23.1	Batch fermentation, 30 °C, 150 rpm, 120 h	11.55	0.24	0.03	0.05	Abbi et al. (1996)
		20		9.4	0.2	47	92.16	
S. cerevisiae MTCC 174	Sugarcane bagasse enzymatic hydrolysate	50	Batch fermentation, 30 °C, 72 h	11.8	0.32	23.6	46.27	Singh et al. (2013)
Xylose-fermenting *S. cerevisiae* T18	Undetoxified sugarcane bagasse hemicellulose hydrolysate	118	Batch fermentation, 35 °C, 150 rpm, 8 h	30	5.7	25.42	49.85	Milessi et al. (2020a)
S. cerevisiae Itaiquara bakers yeast with xylose isomerase	Crude sugarcane bagasse hemicellulosic hydrolysate	75.5	Continuous fermentation, 35 °C, 150 rpm, 24 h	23.88	1.8	31.63	62.02	Milessi et al. (2020b)
	Detoxified sugarcane bagasse hemicellulosic hydrolysate	98.7		23.17	1.9	23.48	46.03	
S. cerevisiae BY4743	Saccharified liquid of laccase delignified Aloe vera leaf rind	42.5	Continuous fermentation, 40 °C, 6 h	15.3	2.55	36	70.59	Rajeswari and Jacob (2020)
			Continuous fermentation in packed bed reactor, 40 °C for 6 h	16.5	2.75	38.82	76.12	

S. cerevisiae YPH499 and *Pachysolen tannophilus* ATCC 32691	Pretreated cotton stalk lignocellulosic biomass	20	Batch simultaneous saccharification co-fermentation, 30 °C, 150 rpm, 96 h	9.21	0.1	46.05	90.29	Malik et al. (2020)
Genetically engineered *S. cerevisiae* InvSc 1	Lime-retreated rice straw	92	Batch simultaneous saccharification and fermentation, 30 °C, 50 rpm, 240 h	35	0.13	38.04	74.6	Guan et al. (2019)
S. cerevisiae ATCC 26602	Rice husk hydrolysate	50	Batch simultaneous saccharification and fermentation, 30 °C, 24 h	17	0.71	34	66.67	da Silva et al. (2021)
	Detoxified rice husk hydrolysate			17	0.71	34	66.67	
Pachysolen tannophilus CCT 1891	Rice husk hydrolysate			9	0.38	18	35.29	
	Detoxified rice husk hydrolysate			8	0.33	16	31.37	
S. cerevisiae ATCC 26602 and *Pachysolen tannophilus* CCT 1891	Rice husk hydrolysate			17.5	0.73	35	68.63	
	Detoxified rice husk hydrolysate			17.5	0.73	35	68.63	
S. cerevisiae KCTC 7906 and *Scheffersomyces stipitis* KCTC 7228	Bamboo (*Phyllostachys pubescens*)	50	Separate hydrolysis and fermentation and sequential fermentation, 30 °C, 200 rpm, 48 h (*S. cerevisiae*), and 30 °C, 200 rpm, 120 h, 0.25 vvm (*S. stipitis*)	18	0.11	36	70.59	Song et al. (2022)
	Bamboo (*Sasa coreana*)			18	0.11	36	70.59	
	Bamboo (*Sasa borealis*)			17	0.1	34	66.67	
	Bamboo (*Phyllostachys pubescens* + *Sasa coreana* + *Sasa borealis*)			18	0.11	36	70.59	
Recombinant xylose-fermenting *S. cerevisiae* MDS130	Crude sugarcane bagasse hydrolysate + molasses	90.1	Repeated fed-batch fermentation, 35 °C, 5 h	50	22.8	55.49	108.81	Perez et al. (2022)

	S. cerevisiae SC90	Alkaline-pretreated oil palm trunk fibers	100	Batch simultaneous saccharification and fermentation, 40 °C, 150 rpm, 120 h	29.68	0.25	29.68	58.2	Wilaithup et al. (2022)
			200		52	0.43	26	50.98	
	Zymomonas mobilis ATCC 10,988 and *Pichia stipitis* ATCC 58,376	Synthetic glucose (30 g/L)/xylose (20 g/L) medium	0	Sequential fermentation, 30 °C, 150 rpm, 70 h	20	0.29	40	78.43	Kamelian et al. (2022)
	Genetically engineered *S. cerevisiae* T0936 with the ability to ferment xylose	Wheat straw	51.4	Batch SSF + 10 FPU cellulase/g suspended solids, 50 °C, 500 rpm (saccharification); and 30 °C, 150 rpm, 96 h (fermentation)	37.1	0.38	72.18	141.53	Ishola et al. (2015)
Alginate-chitosan capsules (O)	Genetically engineered *S. cerevisiae* T0936 with the ability to ferment xylose	Wheat straw	51.4	Batch SSF + 10 FPU cellulase/g suspended solids 35 °C, 96 h	21.9	0.23	-	-	Ishola et al. (2015)
	S. erevisiae TISTR 5339	Cassava pulp	60	Repeated-batch SSF, 50 °C, 150 rpm, 2 h (saccharification); 30 °C, 150 rpm, 120 h (fermentation)	20	0.17	33.33	65.36	Khanpanuek et al. (2021)

*cellulose, I: inorganic support, N: natural support, O: organic support; SSF: simultaneous saccharification and fermentation

1.3.3. The Technology Status of Bioethanol Fermentation

The technology status of bioethanol production is directly dependent on the used feedstock. According to the used feedstock, bioethanol is classified into four generations. First-generation bioethanol is produced from sugary or starchy crops such as sugar cane, sugar beet, cereals, potatoes, etc. These crops are also food and feed, with enhancing costs due to food scarcity. They provide high ethanol yields, have lower processing costs, and good industrial practices to efficiently use all secondary and by-products. Second-generation bioethanol uses low-cost lignocellulosic feedstocks with the potential to be applied widely. However, despite the significant research and technological development in second-generation bioethanol, it is still not economically and energy efficient, and hence it is uncompetitive with fossil fuels. Third-generation bioethanol is produced from algae, while fourth-generation bioethanol uses genetically modified algae to enhance bioethanol yield. Currently, 99% of global bioethanol production comes from the first-generation route by developed industrial production corresponding to a technology readiness level (TRL) of 9. Second-generation bioethanol is slowly developing and is currently produced in several first-of-the-kind plants (TRL 7-8). Third- and fourth-generation bioethanol production is still in the lab and pilot stages (TRL 1-4). Although 3G bioethanol may be produced on non-arable lands it still does not fulfill energy efficiency and carbon footprint requirements. Key challenges for the development of bioethanol production are using low-cost renewable raw materials by applying efficient processing technology to utilize all feedstock constituents with low energy input and obtain high ethanol yield and productivity, without negative influence on the environment.

Bioethanol fermentation, also referred to as alcoholic fermentation (AF) is a complex conversion of organic substrates into products by enzyme-catalyzed biochemical reactions that are an integral part of the metabolism of microorganisms, primarily yeasts. The simplified definition of alcoholic fermentation states that it is the conversion of low molecular weight sugars into ethanol and carbon dioxide by yeast cells with the release of energy (Stanzer et al., 2023). Bioethanol is obtained by alcoholic fermentation from raw materials of biological origin using freely suspended, or more recently immobilized cells of yeast *Saccharomyces cerevisiae*.

Bioethanol is widely used as a modern biofuel or bioenergy source (Figure 12.) and replacement to fossil fuels with a constant increase in global production during the past few decades due to its renewable, nontoxic, environmentally friendly, and carbon-neutral nature. It is also traditionally used as a solvent, antiseptic, chemical, and raw material in medicine, chemical, food, and pharmaceutical industries (Devi et al., 2023).

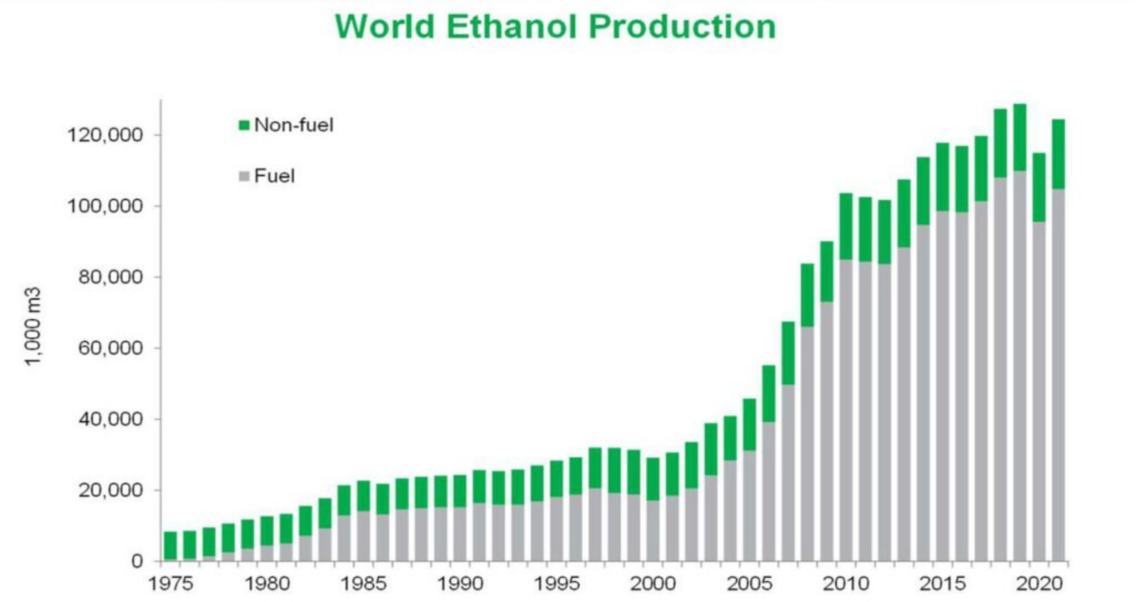


Figure 12. World fuel and non-fuel bioethanol production in the last few decades. Adapted from Khaitan Bio Energy (2024).

Bioethanol is one of the most prospective renewable modern biofuels worldwide (Li et al., 2022; Bušić et al., 2018). According to reports from the American Renewable Fuel Association (RFA) the global world annual bioethanol production (Table 7. and Figure 13.) in 2021 was 27.290 million gallons, while it reached a maximum of 29.330 million gallons in 2019 (RFA). The USA is the leader in world production with a share of more than half (53%) of the global bioethanol supply, primarily from corn grains, followed by Brazil with a share of 28% in the worldwide production of bioethanol from sugar cane. EU countries produce about 5% of the world's bioethanol, mainly from sugar beet, corn, and wheat. According to the second revision of the EU Directive 2018/2001 (RED III) new goals for renewable energy in the EU by 2030 are aiming to share at least a 45% of renewable energy including bioethanol in the overall energy consumption (EU Directive EU Directive 2018/2001).

Table 7.Annual World Fuel Ethanol Production (Mil. Gal.) Adapted from (RFA, 2024).

Region	**2019**	**2020**	**2021**	**2022**	**2023**	**% of World Production**
United States	15,778	13,941	15,016	15,361	15,620	53%
Brazil	8,860	8,100	7,320	7,400	8,260	28%
European Union	1,380	1,330	1,410	1,460	1,440	5%
India	500	520	870	1,230	1,430	5%
China	1,020	940	900	920	950	3%
Canada	497	429	434	447	460	2%
Thailand	430	390	350	370	370	1%
Argentina	290	210	270	310	300	1%
Rest of World	645	620	680	722	760	3%
Total	29,400	26,480	27,250	28,220	29,590	

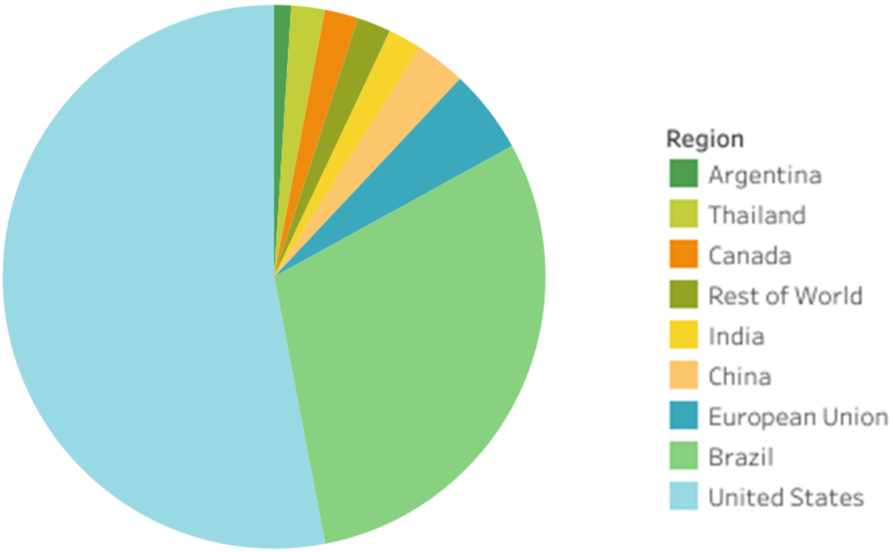
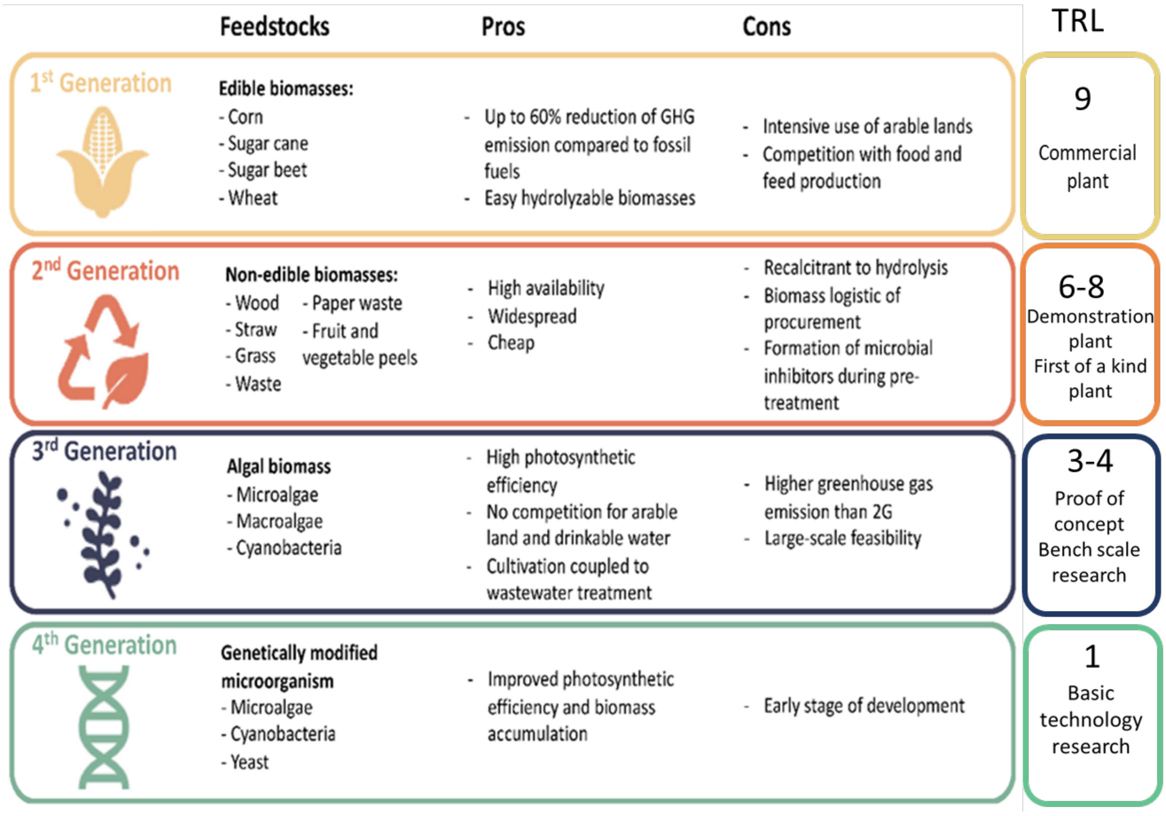


Figure 13. World Fuel Ethanol Production by Region. Adapted from (RFA, 2024).

Depending upon used feedstocks, bioethanol is classified into four generations (Figure 14). Currently, 99% of the global bioethanol production is the first generation bioethanol (1G) obtained from starch raw materials (corn, wheat, barley, potatoes, rice, etc.) and sugary raw materials (juices from sugar cane or sugar beet processing and molasses). Nowadays about 60% of the global bioethanol is produced from corn, about 25% from sugar cane, 3% from wheat, and 2% from molasses, and the rest is obtained from various other kinds of cereals, cassava, and sugar beet (Hoang and Nghiem, 2021). The 1G bioethanol is produced worldwide at an industrial commercial level, especially in the EU implying the technological readiness level (TRL) 9.

In recent decades, significant efforts have been made in scientific research and technological development of the production of second-generation (2G) bioethanol from various cheap lignocellulosic materials (straw, grass, wood, wood processing residues, waste paper, etc.). However, the industrial production of 2G bioethanol is still not significantly established and is measured by several first-of-a-kind commercial-scale lignocellulosic ethanol plants due to various techno-economic and environmental and energy-consuming limitations of this technology (Bušić et al. 2018; Moonsami et al., 2022). Within the EU in 2021 only 1% of the total bioethanol was produced from lignocellulosic biomass (Flach, Lieberz and Bolla, 2022). Currently, the bioethanol production from lignocellulose is still at a technological readiness level 7–8, with only a few plants reaching an early commercial case (Vasilakou et al., 2023).



	Feedstocks	Pros	Cons	TRL
1st Generation	**Edible biomasses:** - Corn - Sugar cane - Sugar beet - Wheat	- Up to 60% reduction of GHG emission compared to fossil fuels - Easy hydrolyzable biomasses	- Intensive use of arable lands - Competition with food and feed production	9 Commercial plant
2nd Generation	**Non-edible biomasses:** - Wood - Straw - Grass - Waste - Paper waste - Fruit and vegetable peels	- High availability - Widespread - Cheap	- Recalcitrant to hydrolysis - Biomass logistic of procurement - Formation of microbial inhibitors during pre-treatment	6-8 Demonstration plant First of a kind plant
3rd Generation	**Algal biomass** - Microalgae - Macroalgae - Cyanobacteria	- High photosynthetic efficiency - No competition for arable land and drinkable water - Cultivation coupled to wastewater treatment	- Higher greenhouse gas emission than 2G - Large-scale feasibility	3-4 Proof of concept Bench scale research
4th Generation	**Genetically modified microorganism** - Microalgae - Cyanobacteria - Yeast	- Improved photosynthetic efficiency and biomass accumulation	- Early stage of development	1 Basic technology research

Figure 14. Technological readiness level of four bioethanol generations (Zuliani et al., 2021; Kowalski et al., 2022).

A third generation of bioethanol (3G) can be produced from microalgae, macroalgae, and cyanobacteria. 3G bioethanol is currently at TRL 3-4 implying proof of concept and banch scale research.

The fourth generation of bioethanol (4G) is still in the scientific research phase and involves the utilization of genetically modified organisms such as cyanobacteria and algae (Zulijani et al. 2021).

Regardless of the nature of the raw material, any bioethanol production process tends to fulfill major goals such as sustainability by using renewable biomass and not fossil fuels, global climate change, biodegradability, urban air pollution regarding greenhouse gas (GHG) benefits, carbon sequestration, national security, and the farm economy by cultivation of feedstock crops and utilization of all by-products (Balat and Balat, 2009).

1.3.4. Identification of key challenges faced by bioethanol technology

In general, the industrial bioethanol production process may be divided into three main stages (Figure 15) raw material preparation to obtain substrate containing fermentable sugars, alcoholic fermentation by yeast, ethanol recovery by distillation, rectification, and dehydration (Li et al., 2022). Therefore, the development of bioethanol technology is aimed to increase the efficiency of all stages of production. This includes several directions of development such as (i) the application of cheap and easily available raw materials and their preparation and decomposition with as little energy investment and as little enzyme consumption as possible, (ii) increasing the efficiency of fermentation by using improved enzymes and producing microorganisms with the best performance, (iii) application of the best fermentation technique in bioreactors of improved construction to achieve the highest ethanol yields, (iii) application of highly efficient systems for recovery and purification of ethanol.

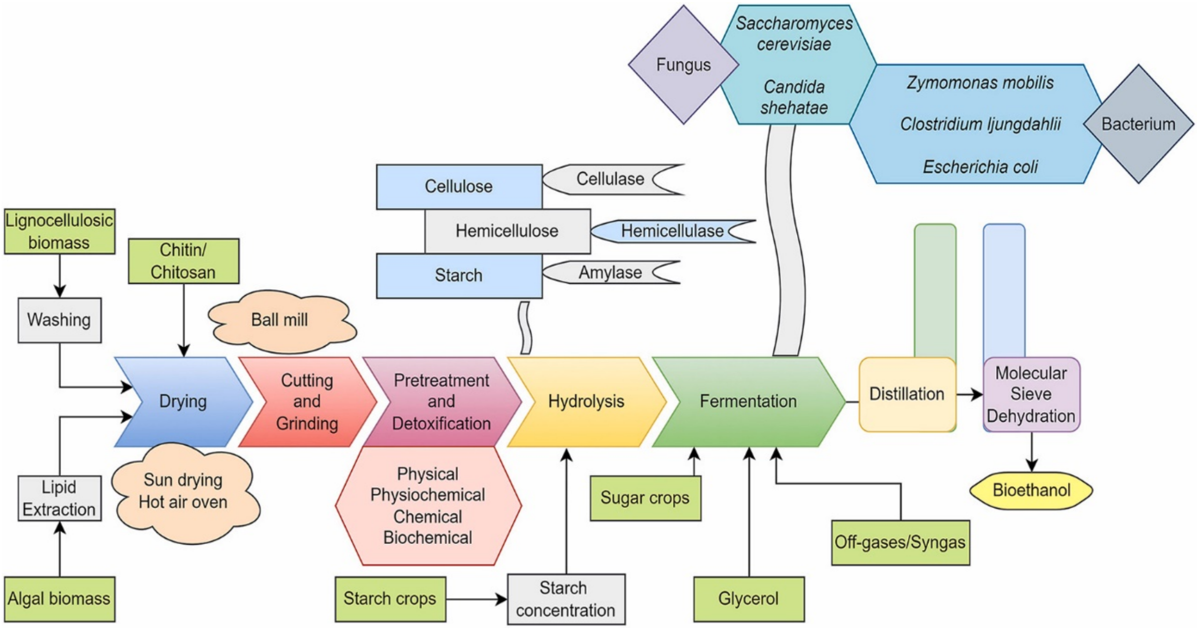


Figure 15. Bioethanol production stages (Jain and Kumar, 2024).

The cost and efficiency of pretreatment and the entire production process depend highly on the nature of the raw material. The main advantage of sugar-containing raw materials for bioethanol production is the presence of readily fermentable sugars which do not require enzymatic hydrolysis in contrast to starch and lignocellulosic biomass, enabling significant cost savings. Hence, the preparation of these raw materials mostly includes mechanical pretreatment and sugar juice extraction (Bušić et al., 2018).

For bioethanol production from starch-containing feedstocks, it is necessary to perform the hydrolysis of hydrated starch (Figure 16). Starch is a mixture of linear (amylose) and branched (amylopectin) polyglucans which is usually hydrolysed by a combination of α-amylase and glucoamylase, into glucose syrup, which can be fermented into ethanol by yeast *Saccharomyces cerevisiae*. Some cereals (wheat, ray, barley, triticale) contain autoamylase which can be used for the hydrolysis of a certain amount of starch. However, modern bioethanol industries usually use α-amylase and glucoamylase commercially obtained as biotechnological products. α-amylase is a metabolic product of bacteria such as *Bacillus licheniformis* and genetically modified strains of the *Escherichia coli* and *Bacillus subtilis*. Glucoamylase is produced by molds *Aspergillus niger* and *Rhizopus sp.* Glucose is then converted into bioethanol by yeasts (Bušić et al., 2018). The choice of the hydrolysis–fermentation strategy influences bioethanol production, affecting ethanol concentration, yields, and productivity, which significantly affects the economic performance of the entire production process (Katanski et al., 2024).

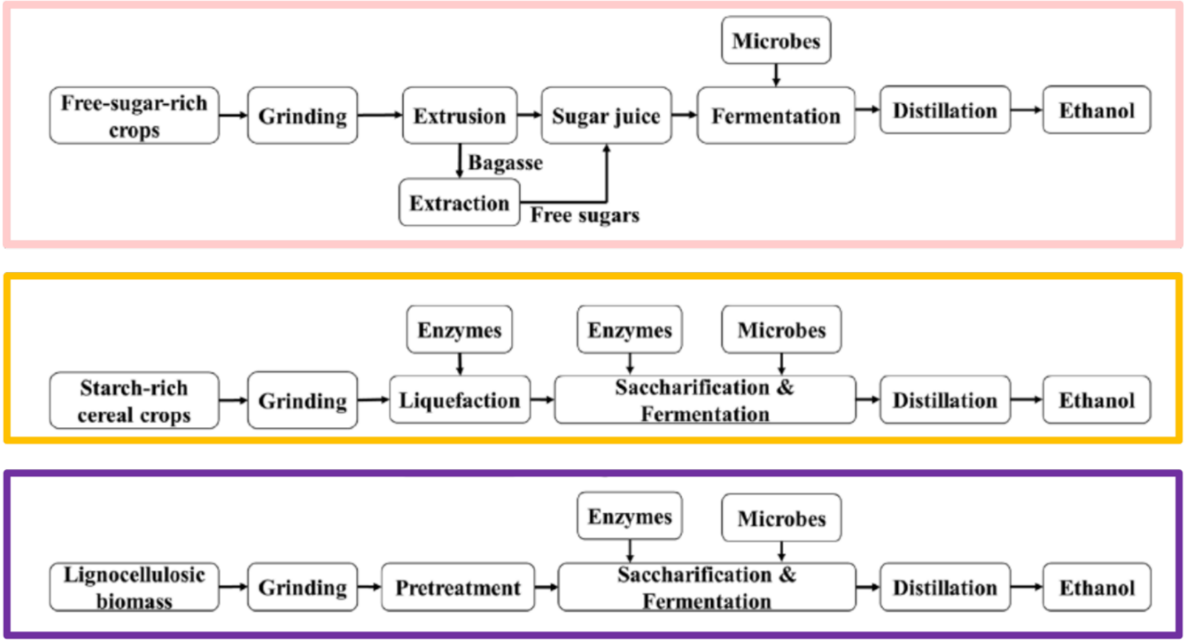


Figure 16. Bioethanol production stages (Zuliani et al., 2021).

Lignocellulosic biomass is the most abundant source of renewable biomass and is seen as a high-potential replacement for 1G raw material for bioethanol production (Zuliani et al., 2021). However, the conversion technologies to bioethanol are still at a low maturity level, thus allowing for future cost reductions through technological learning. Despite remarkable research efforts to improve pretreatment processes the industrial production of 2G bioethanol remains a challenge, mainly due to the costs associated with the pretreatment process (Vasilakou et al., 2023).

Lignocellulose consists of cellulose (C6 sugar polymers), hemicellulose (C5 sugar polymers), and lignin (aromatic alcohol polymers). Firstly, a pretreatment of raw material is applied to the raw material to separate these three different constituents. Separated lignin is usually dried and used as a fuel for the process or power generation. The next step is the saccharification of polysaccharides through enzymatic hydrolysis using cellulases and hemicellulases. The common yeasts are used for the fermentation of C6 sugars while C5 sugars need specific microorganisms such as genetically modified yeasts which are developed in recent years. For 2G bioethanol production, considerable efforts have been made to develop effective pretreatment methods, efficient enzymes, and the effective conversion of pentose sugars. However, the high cost of lignocellulose pretreatment is still the key issue and drawback for commercializing 2G bioethanol production.

3G bioethanol can be produced from algae and microalgae grown on non-arable lands without competition with food and feed production. Although microalgae cultivation may contribute to wastewater remediation by the uptake of inorganic nitrogen and phosphorous, currently the biomass yield does not meet industrial requirements for profitability and energetic input (Zuliani et al., 2021).

The 4th generation bioethanol combines genetically engineered feedstock and genomically synthesized microorganisms such as microalgae, yeasts, fungi, and cyanobacteria with the final goal of enhancing the overall biomass yield and reducing the carbon footprint of the conversion process. However, there are significant environmental concerns raised about the use of genetically modified organisms posing some limitations (Zuliani et al., 2021; Jain and Kumar 2024).

As the price of the raw material accounts for 55-75% of the selling price of bioethanol, the production of alcohol from cheap and easily available raw materials plays a crucial role in the profitability of this technological process, where the costs of preparing the raw material for fermentation should be taken into account, as well as the achieved yield of ethanol (Cardona and Sanchez, 2007). Although significant research and development of the technological process is done to improve the yields of all biofuel generations the availability and price of feedstocks, pretreatment procedures, environmental concerns, and final profitability remain to be the key factors influencing the commercialization of bioethanol production and its contribution to the regional economy.

1.4. Biobutanol fermentation

Biofuels offer several advantages over other renewable energy sources. Their energy originates from biomass, a concentrated form of solar energy. Microorganisms produce biofuels under mild conditions, requiring minimal nutrients to generate valuable products. This process contributes to maintaining atmospheric CO_2 balance by capturing the CO_2 released during production and converting it into new biomass, effectively achieving net-zero CO_2 emissions. Additionally, using waste materials in biofuel production has added benefits, as traditional waste management often requires substantial energy, infrastructure, and generates environmentally harmful by-products like leachate.

The most prominent biofuels include bioethanol, biomethane, biobutanol, and biohydrogen. Among these biofuels, biobutanol production from biomass is rather new and promising. It is the only biofuel that shares characteristics similar to gasoline, making it a suitable alternative as a fuel source. Physicochemical properties and certain advantages of butanol are given in Figure 17. Its key benefits include low volatility, reduced corrosiveness, and the capability to power fuel-driven engines. Additionally, biobutanol can be blended with either gasoline or diesel, offering the potential to reduce the automobile industry's dependence on traditional fuels (Pugazhendhi et al., 2019, Jin et al. ,2011, Dürre, 2008).

Butanol

Flash Point: 35 °C
Motor Octane Number:78
Oxygen content: 22%
Calorific Value:29.2 MJ/L
Melting Point:-89.8 °C
Auto ignition temperature:343 °C
Boiling Point: 117.7 °C
Viscocity: 2.578 mPA.s (25 °C)

Advantages of butanol as a biofuel

1. Direct use in pure form
2. It can be blended with gasoline
3. Safer to handle.
4. Less corrosive
5. Higher energy content
6. More similarity with real gasoline
7. Less likely to contaminate the groundwater if it spills
8. No modifications is required in exsting car to be able to use butanol as fuel

Figure 17. Physicochemical properties and advantages of using butanol as fuel.

Biobutanol research dates back to the 19th century, with production sites established during the World Wars in the early 20th century. However, these sites were eventually abandoned as interest shifted toward petroleum and its derivatives. Today, concerns about the environmental impact of petroleum, along with greenhouse gas emissions, have led to a renewed focus on biobutanol. Industrial butanol production involves ABE (Acetone, Butanol, and Ethanol) fermentation using Clostridial strains. By the mid-20th century, this process was successfully carried out using starchy materials like grain, molasses, and potatoes (Pugazhendhi et al., 2019, Dürre, 2008). Nowadays, varieties of biomasses, including lignocellulosic ones, are under consideration as a raw material for their suitablity in biobutanol production.

In light of the growing demand for biofuels and increasing interest in biobutanol, this section provides an overview of the current state of biobutanol research and identifies key areas for future exploration. It discusses the fundamentals of biobutanol fermentation, presents a comprehensive scientific review of various biomass types, and evaluates their suitability for biobutanol production. Biomass sources with the most favorable characteristics and the highest potential for biobutanol fermentation are highlighted. Additionally, the metabolic pathways involved are analyzed, with special attention given to strategies aimed at overcoming the challenges in biobutanol production.

1.4.1. Evaluation of Biomass Types for Biobutanol Fermentation

Feedstocks for biofuel production are categorized into three types: 1st generation, which includes starch-based biomass; 2nd generation, such as lignocellulosic waste; and 3rd generation, like algae biomass (Ndaba et al., 2015). The 2nd and 3rd generation biomasses are considered more suitable for biofuel production due to their renewable nature. The monomeric units of biomass components serve as fermentation substrates for microorganisms in biobutanol production (Zheng et al., 2009). Thus, the first step in biofuel production is selecting a pretreatment method to break down biomass into a monomeric syrup that can be fermented. Each available pretreatment method has its advantages and drawbacks, as outlined in other sections of this report.

Similar to other biofuels, 1st to 3rd generation biomasses have been used as substrates for biobutanol production. The first generation of the ABE fermentation process utilized starchy biomass, such as maize, cassava, and others (Gottumukkala et al., 2017; Ndaba et al., 2015). Starch-based biomass is easy to generate monomeric units resulting in high biobutanol concentrations in fermentation. Since they do not produce interfering inhibitory compounds with fermentation as encountered in strong pretreatment methods with lignocellulosic. However, the use of starchy biomass in ABE fermentation was later discouraged due to the fuel-food debate, as these sources are predominantly food crops, prompting a shift toward non-food biomass for fermentable sugar production in the ABE process (Vivek et al., 2019).

The limitations of first-generation biomass led to the development of second-generation biomass research for ABE fermentation, focusing on the use of agricultural waste as fermentation substrates. Lignocellulosic biomass is non-edible, widely available, and abundant, which eliminates the concerns associated with the food-versus-fuel debate that surrounded first-generation biomass (Vivek et al., 2019). However, the primary drawback of lignocellulosic biomass is the need for costly pretreatment to release fermentable sugars for fermentation. This process involves removing lignin, which alters the structure of lignocellulose and allows enzymes to degrade it into fermentable sugars (Gottumukkala et al., 2017; Ibrahim et al., 2018).

The use of various food crops, lignocellulosic wastes, and algal biomass in ABE fermentation has been well documented. For instance, bagasse from Sotol spirit production, a lignocellulosic waste rich in cellulose, serves as an effective substrate for ABE fermentation. Fermenting Sotol bagasse with *Clostridium beijerinckii* yielded acetone, butanol, and ethanol concentrations of 0.94, 1.97, and 1.90 g/L, respectively (Piñón et al., 2022). In another study, Saadatinavaz et al. (2021) explored butanol production from hydrothermally pretreated orange waste, producing 42.3 g of biobutanol, 33.1 g of acetone, and 13.4 g of ethanol per kilogram of orange waste. Valdez et al. (2015) used a co-culture of *Clostridium beijerinckii* 10132, *Clostridium cellulovorans* 35296, and *Enterococcus* spp. in the ABE fermentation of wheat straw, yielding 3.7 g/L ethanol, 14.2 g/L butanol, and 5.4 g/L acetone. Wu et al. (2016) also studied ABE fermentation using *Clostridium acetobutylicum* with glucose, xylose, and glucose/xylose mixtures as carbon sources, achieving the best results with glucose/xylose mixtures, yielding 16.1 g/L of butanol and 25.9 g/L of total ABE.

Fruit residues, such as pulp, peels, and seeds, are also rich in sugars, proteins, and acids (Bikash & Sibi, 2017; Raganati et al., 2016). For example, peach pulp, a by-product of juice production, is abundant and contains high levels of sugar as well as ions like potassium, calcium, and phosphorus, which enhance solvent production (Argun & Dao, 2017; Raganati et al., 2016). Similarly, *Ficus carica*, a widely grown Mediterranean lignocellulosic fruit, is rich in carbohydrates and proteins. However, unprocessed waste figs are often contaminated with aflatoxin and incinerated. Due to their high sugar content, figs are an excellent biomass source for producing valuable energy products like butanol and biohydrogen (Aksoy, 2017). Abibu and Karapinar (2022) demonstrated the effectiveness of hydrolysis as a pretreatment for releasing fermentable sugars in Figs, using microwaving to achieve total sugar concentrations of 82.9 g/L from 100 g of dry figs per liter. Fermentation of hydrolyzed Fig by *Clostridium pasterianum* produced ABE concentrations of 6.3, 5.03, and 1.6 g/L, respectively (Abibu & Karapinar, 2024).

Algae, classified as third-generation biomass, are fast-growing microorganisms with minimal growth requirements. They mainly consist of cellulose and a small amount of hemicellulose, with no lignin, making them a more favorable option than lignocellulosic biomass. Algae-based biomass offers economic benefits, green technology advantages, and the potential to produce value-added products. However, a major challenge is the limited availability of algae and the high costs associated with reactors needed for algae cultivation (Demirbas, 2010; Foley et al., 2011). Research on biobutanol production from algae is limited. One notable study involved lipid-extracted algae (LEA), which were pretreated through acid hydrolysis to release fermentable sugars for converting organic waste into ABE. Hydrolyzed LEA produced 8.5 g/L of butanol, and the fermentation digestate from LEA has also been shown to have potential as a fertilizer for algae cultivation (Mao et al., 2023). *Chlamydomonas reinhardtii* CCAP 11/32C microalgae was fermented for ABE production by *Clostridium acetobutylicum* DSM 792 with pretreatment to remove chlorophyll pigments. The resulting butanol concentration was around 0.9 g/L

(Figueroa-Torres et al., 2020). The effects of the pretreatment method and heat shock protein overexpression were investigated for efficient butanol production from *Saccharina japonica* using engineered *Clostridium tyrobutyricum* (Fu et al., 2021). Pretreatment methods including acid hydrolysis, acid hydrolysis and enzymatic saccharification, and ultrasonic-assisted acid hydrolysis were employed to obtain the fermentable sugars, and the resulted hydrolysates were evaluated for butanol fermentation. The study showed that ultrasonic-assisted acid hydrolysate produced the highest butanol concentration of 12.15 g/L. The effects of heat assisted acid and alkaline pretreatment with different concentrations, reaction times, and temperatures for hydrolysis of *Rhizoclonium* spp. were studied (Salaeh et al., 2019). ABE fermentation of hydrolysate with *Clostridium beijerinckii* TISTR 1461 with the addition of enzyme resulted in 2.43 g/L butanol. A successful butanol production method using alkali and acid pretreated biomass of *Chlorella vulgaris* JSC-6 was achieved by Wang et al. (2016) with a butanol titer of 13.1 g/L.

In summary, the biobutanol concentration and the yield substantially variy with the biomass type and the applied pretreatment methods. Bacterial culture is another issue with the optimization of media composition, fermentation conditions, and the bioprocess technology used. Table 8. summarizes some of biobutanol production results from different biomasses, applied pretreatment, and hydrolysis method.

Table 8. Pretreatments and biobutanol production from different biomass.

Biomass	Microorganism	Pretreatment	Butanol (g/L)	References
Cassava starch and chips	*C. saccharoperbutylacetonicum* N1- 4	NA	15.5-16.9	Zheng et al., 2009
Gelatinized Sago starch	*C. acetobutylicum* strain P262	NA	18.82	Wyman et al., 2005
Gelatinized cassava Starch	*C. acetobutylicum* strain ART18	NA	15.80	Li et al., 2014
Cassava starch	*C. acetobutylicum* DSMZ 792	NA	4.37	da Silva et al., 2022
Sugarcane molasses	*Clostridium beijerinckii TISTR 1461*		11.19	Narueworanon et al. 2020
Banana peel	*Clostridium beijerinckii YVU1*	Sequential dilute alkali and acid pretreatments, Enzymatic hydrolysis	14·0	Reddy et al. 2020
	S. cerevisiae and Pichia sp	Physicochemical, Enzymatic hydrolysis	15.7	Mishra et al. 2020
Orange peel	*C. acetobutylicum NRRL B-591*	Hydrotherma, lEnzymatic hydrolysis, Detoxification	43.2 g/kg OW	Saadatinavaz et al.2021
Spoiled Fig (Ficus carica)	*C.pasteuranium DSM 525*	Microwave	5.03	Abibu & Karapinar, 2024
Apple pomace	*Clostridium beijerinckii CECT 508*	Thermal pretreatment Enzymatic hydrolysis	6.27	Hijosa-Valsero et al. 2017
Potato peel waste	*C.acetobutylicum* PTCC 1492	Dilute Acid, Enzymatic hydrolysis	N/A	Abedini et al, 2020
		Solvent extraction, Dilute Acid, Enzymatic hydrolysis	6.22	
		Organosolve Enzymatic hydrolysis	12.6	
Sweet potato waste	*C. acetobutylicum* CICC 8012	Enzyme application to reduce viscosity	11.39	Jin et al., 2022
Sugar beet pulp	*C. beijerinckii* DSM 6422	Microwave-assisted extraction, Enzymatic hydrolysis	8.3	Del Amo-Mateos et al. 2022
Cauliflower waste	*C. acetobutylicum*	Dilute acid-autoclaved, Detoxification	6.54	Khedkar et al. 2017
Peapod waste	*C. acetobutylicum B 527*	Dilute acid-autoclaved, Detoxification	3.82	Nimbalkar et al. 2018
Sugarcane bagasse	*C. acetobutylicum ATCC 824*	Alkaline, Enzymatic hydrolysis	8.40	Tsai et al. 2020
Sugar beet pulp	*C. beijerinckii* DSM 6422	Dilute acid-autoclaved, Enzymatic hydrolysis	7.8	Bellido et al. 2015

Brewer’s spent grain	*C. acetobutylicum* DSMZ 792	Enzymatic hydrolysis	7.93	Giacobbe et al., 2019
	Clostridium beijerinckii DSM 6422	Acid-autoclaved, Enzymatic hydrolysis	6.0	Plaza et al. 2017
Rice straw	*C. acetobutylicum ATCC 824*	Alkali and enzymatic	9.10	Tsai et al. 2020
	Clostridium beijerinckii DSM 6422	Simultaneous saccharification, fermentation	24.80	Valles et al. 2021
Chicken feather and wheat straw	*C.beijerinckii* NRRL B-598	Alkaline	4.21	Branska et al 2020
	C.saccharoperbutylacetonicum	Alkaline	3.81	
Municipal solid waste	*C. acetobutylicum* NRRL B-591	Enzymatic hydrolysis	1.24	Farmanbordar et al. 2018
		Organosolv at high temperatures, Enzymatic hydrolysis	8.57	
Microalge	*C. acetobutylicum ATCC 824*	NA	4.32	Tsai et al. 2020
Sugar maple	*C. acetobutylicum* ATCC824	Alkali Nano-membrane concentrated hemicellulosic hydrolysate	7	Sun & Liu 2012

N/A: not applied

1.4.2. Design of Biobutanol Fermentation Technology

The biobutanol production process involves three stages as pretreatment of feedstock, ABE fermentation, and separation of products. There are different methods for every stage. A convenient production process depends on the substrate structure and the feasibility of the selected method.

Clostridial strains are widely used in ABE fermentation under mesophilic conditions due to their ability to ferment a variety of carbohydrates and form spores under strict conditions (Harris et al., 2002; Poehlein et al., 2017; Pugazhendhi et al., 2019). Species such as *C. acetobutylicum*, *C. beijerinckii*, *C. saccharoperbutylacetonicum*, *C. aurantibutyricum*, *C. saccharoacetobutylicum*, *C. pasteurianum*, *C. sporogenes*, *C. cadaveris*, and *C. tetanomorphum* are commonly studied for their biobutanol production potential (Kumar & Gayen, 2011). Among these, *C. acetobutylicum and C. beijerinckii* are especially known for their high butanol and other neutral solvents production capability (Veza et al.,2021). Additionally, *C. saccharoperbutylacetonicum* and *C. saccharoacetobutylicum* have shown high yields in butanol production (Li et al., 2020). Beyond Clostridium species, genetically modified *E. coli*, *Pseudomonas* species, and *S. cerevisiae* have been used for butanol production (Rao et al., 2016). For example, while *E. coli* does not naturally produce biobutanol, metabolic engineering enables it to do so (Zheng et al., 2009). Moreover, *Lactobacillus* sp. was showen that it can naturally produce n-butanol during anaerobic sugar fermentation (Russmayer et al., 2019).

The ABE process is a biphasic fermentation that consists of two stages: acidogenesis (acid production) and solventogenesis (solvent production), and use fermentable sugar derived from biomass. The acidogenic phase generates acids (acetic and butyric) and hyrdogen, whereas ABE fermentation produces solvents (acetone, butanol, and ethanol) (Pugazhendhi et al., 2019). Lowering the pH in the acidogenic phase drives the fermentation into the solventogenic stage, in which products of acidogenesis are re-dissimilated to produce solvents acetone, butanol, and ethanol in the ratio 3:6:1, respectively (Jin et al., 2011).

Clostridial strains suffer from the cell membrane and cell wall damage, which leads to greater membrane fluidity and eventually cell death as biobutanol production increases. The variety of by-products produced during fermentation reduces butanol yield, and the inability of Clostridial strains to withstand solvent concentrations above 2% is a significant challenge in ABE fermentation (Lee et al., 2008; Nanda et al., 2017; Ibrahim et al., 2018). Utilizing continuous fermentation with suspended or immobilized cell growth could help mitigate solvent inhibition, potentially increasing yield. However, further improvements are required at the biochemical pathway level. A focused study of the ABE fermentation pathway suggests it should be optimized for butanol production over acetone, ethanol, hydrogen, or other organic acids. After careful examination of the ABE fermentation pathway (Figure 18), it should be directed toward butanol production rather than other products. For example, enzyme inhibitors for lactic acid formation can be added to the fermentation medium to prevent its production. Similarly, specific inhibitors for enzymes involved in ethanol and acetone production, along with co-factors for butyrate and butanol, could be incorporated in both phases of fermentation. Electron carriers can be used to divert the hydrogen to the butanol generation. These approaches would reduce the formation of acetone-ethanol or lactic acid-acetate and significantly boost biobutanol yield as the primary solvent product.

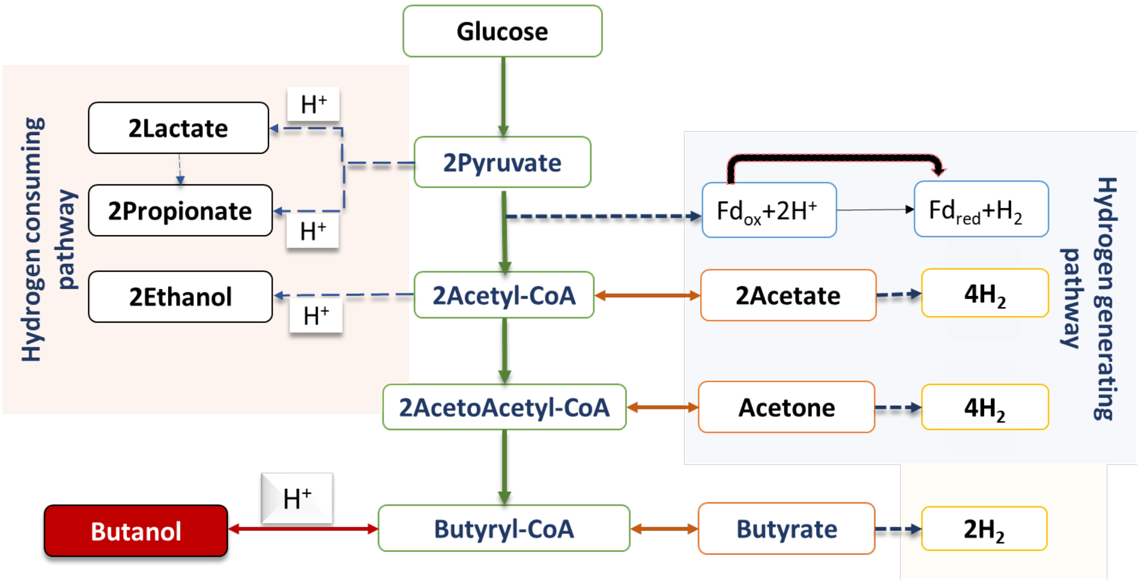


Figure 18. ABE fermentation pathway.

Microorganisms interact with several ions that affect the metabolic pathway for bioutanol production. The addition or limitation of these ions could increase or inhibit the enzymatic activity of Clostridium sp. In ABE fermentation pathway. Combined effects of zinc supplementation and magnesium deficiency could lead to enhancement in glucose conversion, reduction in ethanol concentration and early initiation of solvent production. Mukherjee et al. (2019) studied the individual or combined effects of Zn^{2+} supplementation and magnesium deficiency on butanol production. *Clostridium acetobutylicum* ATCC824 was used to perform batch fermentation with 89.6 g/L glucose concentration. The lowest butanol yield was 13.72 g/L for the Mg^{2+} starved condition. However, Zn^{2+} supplemented- Mg^{2} starved medium gave the highest yield of 19 g/L. Similarly, Wu et al. (2013) concluded that Zn^{2+} supplementation could enhance butanol productivity and cell growth. *Clostridium acetobutylicum* L7 was used to perform batch experiments, with 70 g/L glucose addition. Solvent production was triggered earlier with a time of 40 h when Zn^{2+} was added to medium. Without Zn^{2+} supplementation, solventogenesis was initiated at 64th hour of the fermentation. Consequently, final butanol concentrations were 12.6 and 11.7 g/L for Zn^{2+} supplementation and without Zn^{2+}, respectively. Abibu and Karapinar (2024) focused on the effects of important cations like Co^{2+}, Cu^{2+}, Mn^{+}, Fe^{2+}, Na^{+}, Mg^{2+}, Zn^{2+}, Ca^{2+}, K^{+}, Mo^{3+}, B^{3+}on biobutanol production from microwave hydrolyzed Fig by *C.pasteuranium* DSM 525. From the study, (Mo^{3+} and Na^{+}) and (Mo^{3+} and Fe^{2+}) were found to be the significant elements favoring ABE fermentation and organic acids respectively.

Adding calcium carbonate ($CaCO_3$) as a source of Ca^{2+} can enhance butanol production by acting as a buffering agent, which helps prevent excessive acid build-up in the fermentation medium. A study investigated the effects of $CaCO_3$ and yeast extract supplementation in the enzymatic hydrolysate of dilute acid-pretreated rice straw. The total ABE concentration reached 5.32 g/L, with a butanol yield of about 64.5%. The addition of $CaCO_3$ alone has been shown to increase butanol production by a factor of four (Gottumukkala et al., 2013). Moreover, $CaCO_3$ supplementation may enhance the growth, glucose utilization capacity, and butanol tolerance of Clostridium sp. (Richmond et al., 2011). The impact of $CaCO_3$ supplementation was studied for two microorganisms: *Clostridium acetobutylicum* ATCC824 and *Clostridium beijerinckii* 260. For *Clostridium acetobutylicum* ATCC824, butanol concentration rose from 11.43 to 14.78 g/L, and the total ABE concentration increased by 46% compared to the control group. Similarly, for *Clostridium beijerinckii* 260, butanol titer improved from 11.38 to 13.89 g/L, and the total solvent concentration increased by 31%. Additionally, $CaCO_3$ supplementation was found to enhance butanol tolerance in *Clostridium* species by over 40%, which likely contributed to the higher ABE concentrations. Likewise, Su et al. (2020) concluded that adding salts as sources of Ca^{2+} can improve sugar uptake and solvent production by enhancing enzymatic activity. Both $CaCO_3$ and $CaCl_2$ were tested as Ca^{2+} sources in butanol production from the enzymatic hydrolysate of acid-pretreated corn straw using *Clostridium acetobutylicum* CICC 8016. The addition of $CaCO_3$ alone led to complete sugar consumption and resulted in butanol concentrations three times higher than those achieved with $CaCl_2$ or in a salt-free medium. The study concluded that the absence of salt inhibited intracellular Ca^{2+} uptake due to non-sugary compounds in the medium, leading to lower ABE concentrations. Furthermore, additional Ca^{2+} enhanced enzymatic activity by increasing protein levels involved in glycolysis and maintaining redox balance.

Iron limitation can boost butanol production. In a batch experiment with *Clostridium acetobutylicum* ATCC824 using 66 g/L glucose, low levels of acetic acid were observed, with butanol being the primary fermentation product. The butanol-to-acetone ratio increased from 3.7 to 11.8 under iron-limited conditions, and the conversion of glucose to butanol improved from 20% to 30% (Junelles et al., 1988). However, in experiments using cheese whey as the substrate with *Clostridium acetobutylicum* ATCC824, iron supplementation was essential for butanol production. With an initial sugar concentration of 55 g/L, butanol titers were about 7.13 g/L. Iron deficiency in this case led to lactic acid production rather than solvents (Durán-Padilla et al., 2014).

Butanol production can be enhanced by adding butyric acid, which acts as an initiator to direct the metabolic pathway toward biobutanol production (Lin et al., 2015). Al-Shorgani et al. (2012) determined the optimal butyric acid-to-glucose ratio for *Clostridium saccharoperbutylacetonicum* N1-4. The highest butanol concentration of 17.76 g/L, with a productivity of 0.15 g/L.h, was achieved with the addition of 4 g/L butyric acid. However, a slight inhibitory effect was noted at 15 g/L butyric acid due to the strain's adaptation to high acid levels. In another study, Al-Shorgani et al. (2018a) explored the impact of adding 4 g/L butyric acid to the fermentation medium with and without pH control. Under uncontrolled pH conditions, butyric acid increased butanol concentration to 16.5 g/L, whereas pH control shortened the stationary phase and reduced bacterial growth, also inhibiting butyric acid consumption. Similarly, Yusof et al. (2010) investigated the effects of initial butyric acid supplementation using batch cultures of *Clostridium acetobutylicum* NCIMB 619. They found that adding 2 g/L butyric acid at the initial phase of ABE fermentation improved glucose conversion to 71% and increased acetone and butanol concentrations by 5 and 1.6 times, respectively, compared to the control medium.

Another factor influencing butanol production is the amount of NAD(P)/NAD(P)H generated during glycolysis, with 4 moles of NADH required to produce 1 mole of butanol from glucose. To overcome NADH limitations, electron carriers can be used to shift carbon conversion towards solvent production rather than acid formation. Methyl viologen and neutral red are effective electron carriers in this regard. For instance, neutral red can alter the NAD(P)/NAD(P)H ratio to favor alcohol production over acids (Wang et al., 2018, Zheng et al., 2015). Girbal et al. (1995) studied the effects of neutral red addition in the chemostat culture of *Clostridium acetobutylicum*ATCC 824. Without neutral red addition, products were mainly acids. When neutral red was supplemented to the medium, the main products were solvents with reduced acetate, butyrate yields. Furthermore, production of dihydrogen was 66.6 % lower which resulted in higher NAD(P)H activity. Peguin et al. (1994) investigated the effects of methyl viologen addition at different pH values. At a pH value of 4.5, 1 mM addition of methyl viologen to the broth remarkably increased the butanol production (0.65 mol/mol glucose) due to the enhanced NAD(P)H yield by prohibiting molecular hydrogen release. Moreover, acetone production decreased with increasing pH values, due to decreasing in acid consumption. In another study, *Clostridium acetobutylicum* ATCC55025 with the *hydA* gene disrupted was used to assess the impact of methyl viologen supplementation in media containing glucose or corn stover. The gene disruption alone resulted in a butanol yield of 0.24 g/g with a concentration of 12.9 g/L. When 0.5 mM methyl viologen was added, the yield increased to 0.28 g/g, with a butanol concentration of 13.8 g/L. Additionally, acetic acid and butyric acid levels decreased by 36% and 25%, respectively, leading to a reduction in acetone concentration from 3.2 g/L to 1.1 g/L. Similar outcomes were observed with corn stover as the carbon source, yielding 10.5 g/L butanol at 0.24 g/g. With an additional 0.2 mM methyl viologen, the butanol concentration and yield rose to 12 g/L and 0.28 g/g, respectively. Acid concentrations showed no significant changes with or without methyl viologen, and acetone production remained largely unchanged (Du et al., 2021).

In butanol production, *Clostridial* strains require key nutrients such as nitrogen and phosphorus to sustain their biological functions. To optimize cell growth, sugar absorption, and production efficiency, it is crucial to prevent nutrient deficiencies. However, excessive levels of these nutrients can negatively impact microbial activity and hinder butanol production. The optimal carbon-to-nitrogen (C/N) and carbon-to-phosphorus (C/P) ratios vary depending on the strain and medium used, so adjusting these ratios can enhance product yield (Del Pilar Anzola-Rojas et al., 2015; Rajagopalan, 2016). Al-Shorgani et al. (2018b) studied the optimization of C/N ratio to improve butanol production with *C.acetobutylicum* YM1. C/N ratios varied between 5 and 120 and the highest butanol concentration of 9.21 g/L was obtained at a C/N ratio of 12.8. Gu et al. (2009) investigated the effects of ammonium acetate as a nitrogen source and cassava starch as a carbon source with *C.acetobutylicum* EA2018. When 30 mM ammonium acetate was added to the medium, 19.4 g/L of total ABE concentration with 67 % butanol yield was obtained, due to increased acid reassimilation. Higher ammonium acetate concentrations did not significantly improve butanol production.

The bioprocesses for ABE fermentation are batch, fed-batch, and continuous as used in other bioprroduct formation by fermentation. Batch fermentation is mainly used in biobutanol production due to its operational simplicity and low risk for contamination (Birgen et al., 2019). In this process, all of the media composition is fermented in a reactor without any interference. The main drawback of this process is low productivity of butanol (<12g/L) might be observed with an average initial substrate concentration of 60-80 g/L (Ibrahim et al., 2018; Ranjan & Moholkar, 2012). Moreover toxicity of butanol accumulation and the required period for the preparation of the medium could be end in low productivity of butanol (Al-Shorgani et al., 2019).

Fed-batch fermentation is generally applied when substrate inhibition, due to the high concentration, might occur (Li et al., 2011; Ranjan and Moholkar, 2012). Initially, substrate in low concentration is added to the fermentation process. After consumption of the carbon source, more substrate is added system while keeping the concentration under toxic level (Dolejš et al., 2014; Visioli et al., 2014). Compared to batch culture, a fed-batch system could result in higher butanol concentrations (Ibrahim et al., 2018). However, simultaneous product elimination is necessary for an effective process (Lu et al., 2012).

The continuous fermentation (chemostat) process involves substrate addition with the simultaneous withdrawal of products. It has several advantages like decreasing equipment downtime, inoculation time and solvent toxicity (Ranjan & Moholkar, 2012). Nonetheless, the solvent quality and amount could fluctuate due to the problems with dilution and harvest (Pugazhendhi et al., 2019). Hence, several methods like two-stage, immobilized culture, and cell recycling are applied to chemostat system for improving butanol production (Birgen et al., 2019). Immobilized cells or cell recycling could be used for the avoiding the loss of cells during harvest (Bankar et al., 2013, Gottumukkala et al., 2017). Two-stage fermentation which involves the acidogenesis and solventogenesis separately may also allow enhanced substrate degradation and efficient conversion of acids to solvent(Bankar et al., 2012).

Product separation poses a significant challenge in biobutanol production. Butanol toxicity is a major issue as it inhibits bacterial cells and leads to reduced yields. To address this problem, effective product separation is essential (Lin et al., 2017). An ideal separation method should be cost-effective, highly selective, safe for microorganisms, and resistant to negative interactions with broth components (García et al., 2011; Staggs and Nielsen, 2015). Various methods have been proposed, including distillation, gas stripping, adsorption, liquid-liquid extraction, perstraction, pervaporation, reverse osmosis, and freeze crystallization (Abdehagh et al., 2014; Kujawska et al., 2015).

Distillation is a traditional method used to recover products in ABE fermentation (Xue et al., 2017). This technique relies on differences in volatility between components. Since biobutanol has a higher boiling point (118 ^{0}C) compared to water, the energy requirements and process costs can be high, particularly if the biobutanol concentration in the fermentation medium is low (Ezeji et al., 2004; Kamiński et al., 2011). Additionally, distillation has a low selectivity for butanol (Kujawska et al., 2015). These limitations have led to the exploration of alternative, more efficient separation methods. Among the various methods studied, gas stripping, adsorption, and pervaporation are the most commonly researched techniques for butanol separation (Pugazhendhi et al., 2019).

Gas stripping involves using gases such as H_2, CO_2, or N_2 to remove butanol from the fermentation broth. The process entails bubbling the gas through the medium, where the butanol adheres to the gas bubbles. These bubbles are then directed to a condenser, where the butanol is separated as it condenses (Abdehagh et al., 2014; Ezeji et al., 2004). The method is favored for its simplicity, non-fouling nature, and lack of toxicity to microorganisms (Kujawska et al., 2015; Xue et al., 2017). However, issues such as excessive foam formation and lower selectivity for butanol may occur (Pugazhendhi et al., 2019).

In the adsorption process, butanol is captured by an adsorbent within a packed column, and the solvent is then recovered either by increasing the temperature or by replacing the adsorbent (Xue et al., 2017). Common adsorbents for butanol separation include activated charcoal, polyvinylpyrrolidone, and silicates, with silicate being the most frequently used due to its zeolite structure and hydrophobic nature (Qureshi et al., 2005; Vane, 2008). This method is noted for its high selectivity for butanol and ease of use (Pugazhendhi et al., 2019). However, it has several limitations, including biofouling, the need for high solvent concentrations to achieve efficient recovery, and the generally low capacity of adsorbents, which poses a challenge for industrial applications (Kamiński et al., 2011; Kujawska et al., 2015).

Pervaporation is an effective separation method that uses a selective membrane to recover solvents from the fermentation medium (Ezeji et al., 2004). This technique involves the selective diffusion of the medium through a hydrophobic membrane, aided by vacuum application (Kamiński et al., 2011; Pugazhendhi et al., 2019). The permeated solvents, now in the gas phase, are then captured as vapor and condensed into liquid form in cold traps (Abdehagh et al., 2014). Commonly used membranes include polydimethylsiloxane and silicon rubber sheets, with polydimethylsiloxane being particularly favored for its high butanol selectivity and physical stability (Pugazhendhi et al., 2019; Xue et al., 2017). Key benefits of pervaporation include low energy consumption, minimal impact on microorganisms, prevention of medium content loss, low process temperature, and a favorable operation-to-cost ratio. However, achieving the necessary low pressure for condensation can be costly (Abdehagh et al., 2014; Kamiński et al., 2011).

1.4.3. The Technology Status of Biobutanol Fermentation

Although biobutanol production has been known since 1895, the technology for large-scale production is recently on the agenda. The fact that advanced and known bioethanol technology limits the production of biobutanol on an industrial scale. Two provisions of the Clean Air Act permit blending up to 12.5% biobutanol by volume with gasoline. Additionally, a waiver from the U.S. Environmental Protection Agency (EPA) allows for a 16% biobutanol blend, making it a legal equivalent to E10 (a 10% ethanol, 90% gasoline mix). Biobutanol blends up to 12.5% must meet the ASTM D7862 fuel quality standard. As of June 2018, the EPA approved biobutanol blends of up to 16%. It's crucial to ensure that these blends do not exceed the EPA oxygen content limit of 3.7%. The approval assumes no other oxygenates, such as ethanol, are present in the fuel mix (USDE, 2024).

Several companies claim to produce renewable butanol by fermentation from lignocellulosic biomass which is technically mature, abundantly available, and low cost. DuPont declared its significant investment in biofuels with three major projects. The most ambitious project of Dupont's involved using biotechnology to convert plant sugars into butanol considering its several advantages over ethanol. The company evaluated biobutanol as a fuel worth investing in due to its ability to be transported by piping systems in the existing infrastructure, its high calorific value, and the generation of other valuable by-products during production. It is also emphasized that biobutanol production will provide diversity in renewable energy sources (Rome, 2019). Butamax, a joint venture of BP and DuPont, announced developing isobutanol technology, retrofitting ethanol plants, and running a demonstration plant in the UK, in 2017. The other company is Gevo which has operated a commercial plant in Luverne, USA, since 2014, producing isobutanol alongside ethanol in a side-by-side operation from biomass (gevo®, 2024).

Although these companies are working on industrial-scale biobutanol production, the technology readiness level can be stated as TRL4. Apart from bacterial metabolic limitations, bioreactor technology is another issue. Attached bacterial growth bioreactor systems are preferred because they provide high microorganism retention capacity and low retention times. For this purpose, packed column, fluidised bed and expanded bed etc. bioreactors can be used. The choice of microorganism support particles in attached growth systems is important in terms of solid-liquid contact in the reactor, in-reactor canalization, and biomass retention capacity. While porous microorganism support particles are preferred, the durability of the particle is another factor. Clogging and in-reactor channeling are operational problems observed in attached growth systems. These types of reactors are suitable for liquid feeding, it is not possible to feed the waste biomass directly into the reactor. Therefore, it is necessary to hydrolyze the biomass by physical or chemical methods to transfer the fermentable sugar content to the liquid phase and to separate the biomass particles as upstream process. Solid phase fermentation, simultaneous saccharification and fermentation, or extractive fermentation are other bioprocess approaches used for the direct fermentation of solid biomass. However, the reaction rate slows down and the product formation time (retention) is prolonged. Mixing, homogeneity, product separation technologies, and scaling up in such bioreactors are open areas for research.

1.5. Biohydrogen fermentation

Biohydrogen, a renewable and environmentally friendly alternative to fossil fuels, is gaining attention due to its potential for sustainable energy production. Produced via biological and biochemical pathways, biohydrogen offers a carbon-neutral approach to energy generation, emitting only water as a by-product during combustion. This report reviews the advanced biotechnological processes for biohydrogen production, emphasizing the recent developments and technical challenges associated with each method.

The main biological processes for hydrogen production (Figure 19.) can be categorized into direct and indirect photolysis, photofermentation, dark fermentation, and hybrid methods such a microbial electrolysis cells (MECs). Each method exploits specific metabolic pathways of microorganisms to convert organic substrates into hydrogen gas.

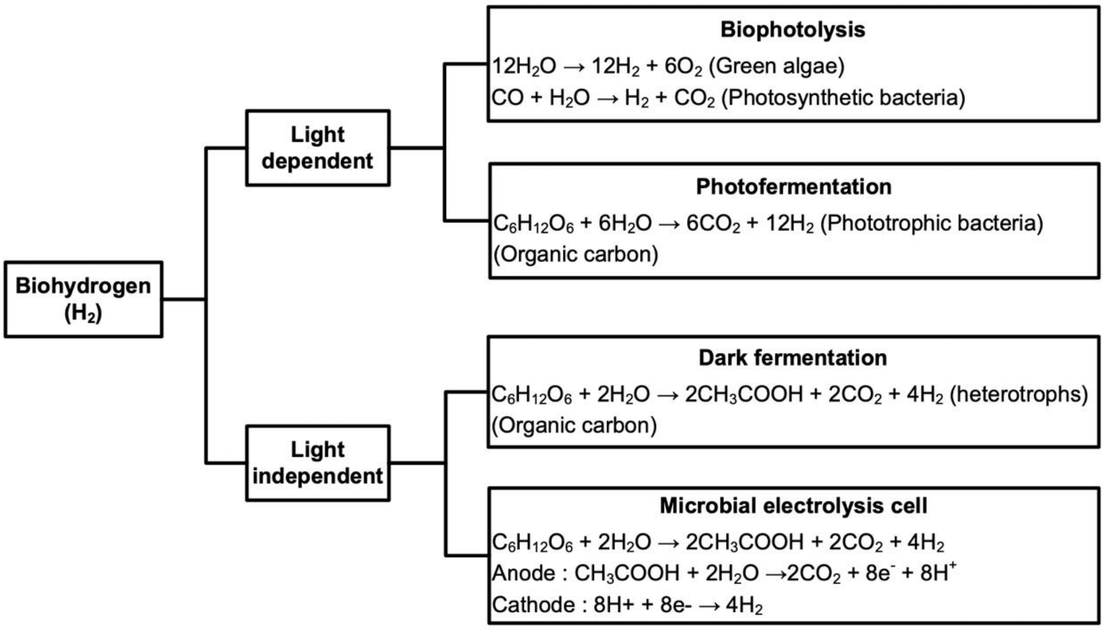


Figure 19. Biological pathways to produce hydrogen (Ghimire i sar., 2015).

Direct and Indirect Water Photolysis utilizes the photosynthetic capabilities of cyanobacteria and algae to generate hydrogen under light conditions. Photolysis is divided into direct (splitting water into oxygen and hydrogen using sunlight) and indirect (using intermediate electron carriers) processes (Wang & Yin, 2017). The primary challenge is the oxygen sensitivity of the hydrogenase enzymes, which leads to enzyme inhibition and low hydrogen yields. Current research focuses on genetically engineering strains to enhance hydrogen production and reduce oxygen sensitivity.

Photofermentation uses photosynthetic bacteria, such as *Rhodobacter sphaeroides*, to convert organic acids into hydrogen under light. The bacteria utilize light energy to drive the conversion of volatile fatty acids, such as acetic and butyric acids, into hydrogen. Although photofermentation can achieve high hydrogen yields, the requirement for continuous light input makes it economically challenging for large-scale applications (Arimi et al., 2015).

Dark Fermentation is considered one of the most promising methods for biohydrogen production due to its simplicity and independence from light. It involves the anaerobic degradation of organic substrates by various bacterial species, such as Clostridium and Enterobacter. The process yields hydrogen and organic acids as by-products. The key advantage of dark fermentation is its ability to utilize a wide range of organic waste materials, making it suitable for waste valorization (Karimi, 2015). However, the accumulation of by-products such as lactate, propionate, and ethanol can inhibit hydrogen production. Strategies to overcome these limitations include continuous removal of hydrogen from the fermentation broth and metabolic pathway engineering of the involved microorganisms.

Microbial Electrolysis Cells (MECs) combine the principles of dark fermentation and electrochemical processes to produce hydrogen. In MECs, an electric current is applied to overcome the thermodynamic limitations of the reactions, allowing for the simultaneous production of hydrogen and methane in separate chambers. This hybrid technology can enhance hydrogen yields but requires further optimization for commercial feasibility (Singh et al., 2015).

Figure 20. shows biodegradation steps and biological processes involved in fermentative hydrogen production from organic wastes (Wang at al. 2017), while Figure 21. represents diagram of the conversion of cellulose-based biomass to fuels and value-added chemicals (Wang at al. 2017).

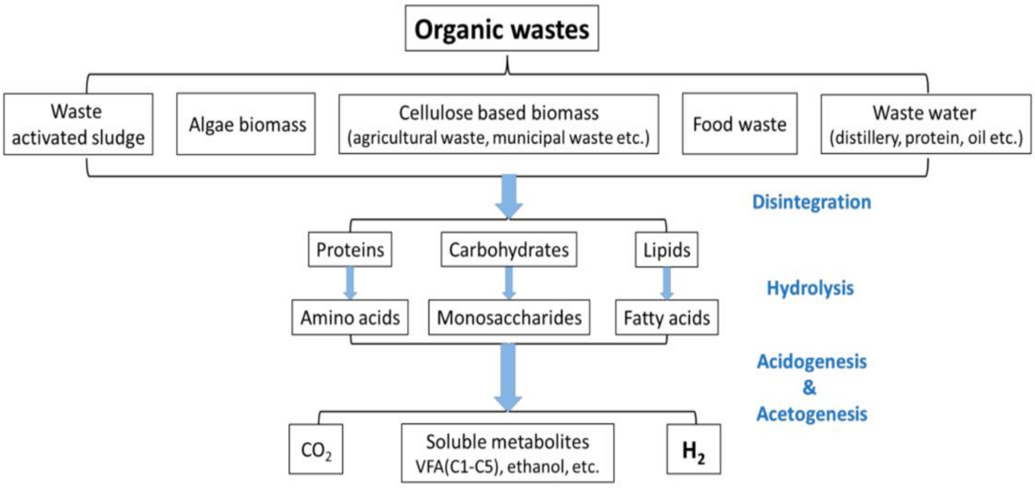


Figure 20. Biodegradation steps and biological processes involved in fermentative hydrogen production from organic wastes (Wang at al. 2017).

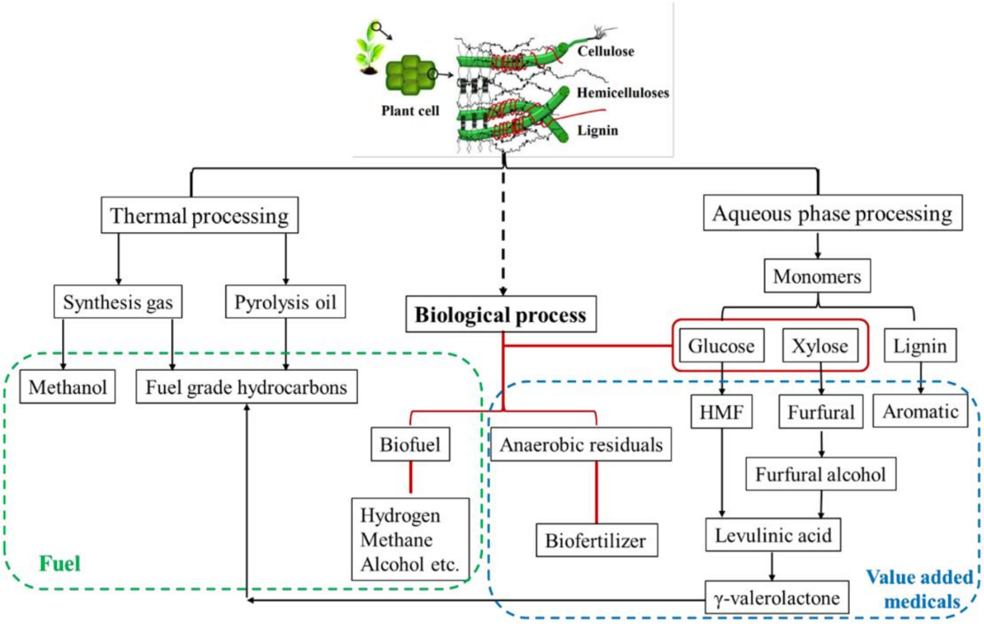


Figure 21. Diagram of the conversion of cellulose-based biomass to fuels and value-added chemicals (HMF: 5-hydroxymethylfurfural) (Wang at al. 2017).

The future of biohydrogen production lies in overcoming the economic and technical barriers associated with current processes. Integrating biohydrogen production with other renewable energy systems, such as bio-refineries and waste-to-energy plants, can significantly improve process economics. Furthermore, advances in genetic engineering, synthetic biology, and nanotechnology have the potential to revolutionize biohydrogen production, making it a viable alternative to conventional energy sources.

1.5.1. Evaluation of Biomass Types for Biohydrogen Fermentation

The choice of biomass for biohydrogen fermentation plays a critical role in the efficiency and yield of hydrogen production. This section reviews and evaluates various biomass types, focusing on their suitability for biohydrogen fermentation, with particular attention to agricultural, forest, agro-industrial, and other biodegradable biomass sources.

Agricultural Biomass. Agricultural biomass, including crop residues, animal manure, and agro-industrial by-products, stands out as a highly promising feedstock for biohydrogen fermentation due to its widespread availability, renewable nature, and rich organic content. Crop residues, such as wheat straw, rice husk, and corn stover, are particularly attractive because they are abundant and contain significant amounts of cellulose and hemicellulose (Table 9.).

Table 9. Overview of the types of biomass waste used for hydrogen fermentation, the necessary pretreatment methods, and the associated references.

Biomass waste		Required pretreatment	References
Agricultural Biomass	Wheat Straw	Mechanical grinding, steam explosion, acid hydrolysis	Wang & Wan (2008)
	Rice Husk	Alkali treatment, steam explosion	Wang & Wan (2008)
	Corn Stover	Dilute acid hydrolysis, enzyme treatment	Kaparaju & Rintala (2013)
	Animal Manure	Co-digestion, pH adjustment	Luo & Angelidaki (2013)
Forest and Wood Biomass	Wood Chips	Steam explosion, acid hydrolysis	Li & Zhang (2014)
	Sawdust	Steam explosion, enzymatic hydrolysis	Li & Zhang (2014)
Agro-Industrial Biomass	Molasses	No significant pretreatment required	Kiran & Liu (2015)
	Food Waste	pH control, co-digestion	Kim & Kim (2013)
Other Biodegradable Biomass	Municipal Solid Waste (MSW)	Separation, mechanical pretreatment	Chong et al. (2009)
	Sewage Sludge	Thermal hydrolysis, pH adjustment	Chong et al. (2009)

These complex carbohydrates can be effectively hydrolyzed into simple sugars, which are readily fermentable by microorganisms during the biohydrogen production process (Wang & Wan, 2008). Additionally, animal manure, especially from livestock like cattle and poultry, represents another viable biomass source for biohydrogen fermentation. The high content of volatile fatty acids (VFAs) and organic matter in animal manure makes it conducive to microbial activity and hydrogen production. However, the application of animal manure often requires co-digestion with other biomass types to optimize the carbon-to-nitrogen (C/N) ratio, which is crucial for maintaining the microbial balance and enhancing fermentation efficiency (Luo & Angelidaki, 2013). This approach not only improves hydrogen yields but also offers a practical solution for managing agricultural waste, contributing to a circular economy.

Forest and Wood Biomass. Forest biomass, including wood chips, sawdust, and lignocellulosic waste, is a potential feedstock for biohydrogen fermentation, though its high lignin content limits cellulose and hemicellulose accessibility. Pretreatments like steam explosion or acid hydrolysis are necessary to enhance bioavailability (Li & Zhang, 2014). Despite these challenges, effective pretreatment can yield hydrogen comparable to agricultural biomass, with pretreated sawdust producing around 2.0 mol H_2/mol hexose (Li & Zhang, 2014).

Agro-Industrial Biomass. Agro-industrial biomass like fruit and vegetable peels, molasses, and whey, is an abundant and highly valuable resource for biohydrogen production due to its rich content of fermentable sugars. One significant advantage of agro-industrial biomass is the minimal pretreatment requirement before entering the fermentation process (Kiran & Liu, 2015). This is exemplified by molasses, a by-product of sugarcane processing. Due to its high sugar concentration, molasses can achieve hydrogen yields with studies reporting up to 3.0 mol H_2/mol glucose in continuous fermentation setups. Additionally, food waste, rich in carbohydrates and generated during food processing, is a promising feedstock for biohydrogen production. Its high sugar content makes it ideal for co-fermentation, which can boost hydrogen yields by creating a more balanced, nutrient-rich environment for microbes (Kim & Kim, 2013). This process not only improves production efficiency but also helps address the issue of food waste by converting it into a valuable energy resource. Thus, agro-industrial biomass is crucial for biohydrogen production, offering significant environmental and economic benefits through the effective use of waste materials.

Other Biodegradable Biomass. Other biodegradable biomass sources, such as municipal solid waste (MSW) and sewage sludge, also hold potential for biohydrogen fermentation. MSW, particularly the organic fraction, is abundant and can be utilized effectively after separation and pretreatment. Similarly, sewage sludge, rich in organic compounds, has been shown to produce biohydrogen under anaerobic conditions, although its application is often limited by the presence of inhibitory substances (Chong et al., 2009).

Among the various biomass types reviewed, agricultural and agro-industrial biomass emerge as the most promising candidates for biohydrogen fermentation due to their high availability, rich organic content, and relatively low pretreatment requirements. Crop residues and agro-industrial by-products, such as molasses, exhibit particularly high hydrogen yields and are well-suited for scalable biohydrogen production. In contrast, forest biomass, while abundant, requires more intensive pretreatment, and its suitability depends on the efficiency of these processes. Overall, agricultural biomass, with its wide availability and favorable characteristics, presents the greatest potential for future applications in biohydrogen fermentation.

1.5.2. Design of Biohydrogen Fermentation Technology

Biohydrogen fermentation involves the breakdown of complex organic molecules by microorganisms in the absence of oxygen. The process can be categorized into two main types: dark fermentation and photofermentation. In dark fermentation, organic substrates such as glucose or organic waste are metabolized by bacteria like *Clostridium spp*., producing hydrogen and organic acids (e.g., acetic and butyric acids).

The primary product of biohydrogen fermentation is hydrogen gas (H_2), which can be used as a clean fuel for various applications. The major by-products include organic acids such as lactic acid, ethanol, propionate, and acetate. The accumulation of these by-products can inhibit hydrogen production by altering the pH and creating a toxic environment for the microorganisms. Therefore, maintaining optimal operational conditions is crucial for maximizing hydrogen yields.

Biohydrogen has several applications, particularly in the fields of renewable energy and sustainable waste management. It can be used as a fuel in fuel cells to generate electricity or as a precursor for producing synthetic fuels through the Fischer-Tropsch process. Additionally, biohydrogen production from organic waste materials helps in waste valorization, contributing to circular economy principles.

The efficiency of biohydrogen production is influenced by various factors such as substrate type, pH, temperature, and hydrogen partial pressure. In dark fermentation, yields are typically lower due to the thermodynamic limitations of the metabolic pathways.

One strategy to improve efficiency is to couple dark fermentation with photofermentation, which combines the strengths of both processes to increase hydrogen production (Arimi et al., 2015).

Biohydrogen fermentation technology offers a number of benefits as well as some limitations that must be addressed to improve its commercial feasibility. Advantages include the environmental benefits associated with using biohydrogen as a carbon-neutral energy source. The technology can leverage a wide range of organic wastes as feedstock, contributing to environmental sustainability by reducing pollution and greenhouse gas emissions (Demirbas, 2009). Moreover, biohydrogen fermentation processes, especially dark fermentation, are characterized by their operational simplicity and lower energy requirements compared to conventional hydrogen production methods, making them more accessible for small-scale and decentralized applications (Karimi, 2015). The scalability of biohydrogen fermentation is another advantage, as the process can be optimized and scaled up for industrial applications with proper reactor design and process control (Arimi et al., 2015).

On the other hand, the disadvantages of biohydrogen fermentation primarily revolve around its relatively low hydrogen yield, which is often hindered by the accumulation of inhibitory by-products like organic acids (e.g., lactic and propionic acids). This not only reduces hydrogen production efficiency but also complicates downstream processing (Wang & Yin, 2017a). Another major challenge is the high production cost associated with biohydrogen fermentation. Pretreatment of feedstocks, bioreactor operation, and product recovery contribute to substantial capital and operational expenses (Karimi, 2015). Furthermore, the stability of the microbial communities within the bioreactors is a critical factor for consistent process performance. Preventing contamination and maintaining the activity of hydrogen-producing microorganisms over extended periods can be difficult, leading to fluctuations in hydrogen yield and reduced system reliability (Singh et al., 2015).

The cost analysis of biohydrogen production includes both capital and operational expenses. Capital costs are associated with the construction of bioreactors, equipment for gas separation, and necessary infrastructure. Operational costs include feedstock acquisition, pretreatment, microbial culture maintenance, and energy input for reactor operation. A detailed cost comparison presented by Karimi (2015) suggests that while biohydrogen fermentation is more cost-effective than chemical hydrogen production in terms of raw material costs, the overall production cost remains high due to low hydrogen yields and expensive downstream processing.

1.5.3. The Technology Status of Biohydrogen Fermentation

The technology status of biohydrogen fermentation, a promising approach for renewable hydrogen production, has made considerable progress in recent years. However, it remains in the developmental phase, facing various technological, economic, and scalability challenges. Both dark and light fermentation processes are hindered by low yields and production rates, making them less competitive compared to other high-rate chemical and physical methods of biohydrogen production from biomass.

The current state of fermentative biohydrogen production technology is focused on developing bioreactor systems tailored to different types of waste, including the necessary pretreatment processes, fermentation methods, and microorganisms at the laboratory scale. There is significant scientific research being conducted in these areas. The main goal is to identify the optimal operating conditions for producing hydrogen through dark fermentation in completely mixed or attached bacterial growth fermentation systems after waste pretreatment. The aim is to enhance both production yield and rate. Theoretically, hydrogen yield from dark fermentation is 4 mol

H_2/mol glucose when glucose is converted to acetic acid, and 2 mol H_2/mol glucose for butyric acid formation. However, the commonly accepted yield in the literature is around 2.5-3.0 mol H_2/mol glucose. The production rate depends on the type of substrate, fermentation technology, and operational parameters.

It is evident that single stage dark and light fermentation will not be sufficient for high rate biohydrogen production. To further improve process efficiency and achieve complete conversion of organic waste into CO_2 includes sequential or combined fermentation technologies. Sequential dark and photofermentation is one of the options. The aim of this method is to generate hydrogen from the volatile fatty acids present in the dark fermentation effluent through photohermentation (Niño-Navarro et al., 2020, Rao and Basak, 2022). Combined dark and light fermentation in the same bioreactor as a co culture is another option to achieve the complete conversion of fermentable sugar to biohydrogen. The process seems to be simple but the rates of biochemical reaction carried out for biohydrogen generation by two cultures are different which causes operational problems. a high yield of 6.4 mol H_2/mol glucose which corresponds to more than half of the theoretical maximum was reported by Das and Basak (2022). As an alternative to photofermentation, the electrohydrolysis process can be implemented after dark fermentation in a sequential setup to produce hydrogen from volatile fatty acids (Ndayisenga et al., 2022, Phan et al., 2023). Unlike photofermentation, electrohydrolysis can handle wastewater with high nitrogen and salinity levels. Additionally, electrohydrolysis require only a minimal electrical energy input, rather than light, reducing overall energy demand. It is possible to reach 9.95 mol H2/mol glucose, which corresponds to 83% of the theoretical H2 yield as reported by Lalaurette et al. (2009) However, challenges remain in scaling up electrohydrolysis for large-scale applications. Considering the difficulties and limitations in photofermentative hydrogen production, it is economically advantageous to convert the organic acid-rich effluent into methane as a secondary product. In order to increase the process efficiency and to ensure the complete conversion of organic wastes to CO_2, the biomethane process can be applied as a second step with up to 75% methane purity (Ramos and Silva, 2020, Mozhiarasi et al., 2023). This sequential biohydrogen-biomethane process produces a high-energy gas mixture, "biohitane," which can be directly used for combustion or electricity generation.

Pretreatment of biomass is one of the most important problems due to the cost and the toxic compounds formed after the treatment affecting the fermentation efficiency. Consolidated fermentation states that single-stage biohydrolysis of biomass to fermentable sugars and H_2 production from the generated simple sugars through hydrolysis in the same bioreactors (Nagarajan et al., 2019).

Nanotechnology-supported hydrogen production technologies are emerging as a promising and innovative approach. Hydrogen production involves the transfer of electrons from electron donors to hydrogenases, enzymes responsible for the reduction of protons to molecular hydrogen. Nanoparticles can serve as electron carriers, improving the efficiency of this transfer (Elreedy et al., 2019, Sindhu et al., 2024). The role of nanoparticles in biohydrogen production involves their interaction with microorganisms, enzymes, and the biochemical pathways that lead to hydrogen generation. Nanotechnological advancements, such as increasing surface area, enhancing enzyme stability, and improving saccharification efficiency, can contribute to efficient biohydrogen production. Additionally, these applications can promote faster cell growth, shorten the lag phase, and shift the microbial community and metabolic pathways towards acetate synthesis, reducing side products and boosting hydrogen yield (Sindhu et al., 2024, Elreedy et al., 2019, Awogbemi and Von Kollon, 2024).

The purity of the hydrogen can constitute up to 60% of the total gas produced through fermentation, which is considerably lower than other hydrogen generation methods like water electrolysis, steam methane reforming, pyrolysis, and gasification etc. The generated gas mixture needs purification systems to make it viable for energy applications, which can increase operational costs.

Cost-economy perspective of dark fermentative biohydrogen from different biomasses and bioprocesses was reviewed by Srivastava et al. (2024). The cost of biohydrogen production through dark fermentation varies significantly depending on the substrate, operation mode, and processing parameters. Technoeconomic analyses show diverse cost estimates. For example, Tapia-Rodríguez et al. (2019) reported a maximum biohydrogen productivity of 1.88 L H_2/L with a cost of \$2.58/L H_2 using agave bagasse. Economical analysis of biohydrogen production from distillery effluent in a pilot scale bioreactor was estimated as \$37,070/year, with a hydrogen productivity yield (HPY) of 2.76 mol/mol glucose (Vatsala et al., 2008). The cost of dark fermentative biohydrogen using waste water was reported as 2.57 US \$/kg with a maximum HPY of 7.1 mol H_2/mol glucose. However, there are also reports about the cost of production up to 26.72–41.77 \$/kg H_2 (Sanchez et al., 2020). It is advised that the cost of producing biohydrogen through dark fermentation be reduced to \$0.30 per kg to make it a viable alternative to gasoline (Srivastava et al., 2024).

1.6. Composting

Composting is a natural biological process through which organic matter is decomposed and transformed into a stable, humus-like product known as compost. This process occurs under aerobic conditions, with microorganisms breaking down organic material into a valuable soil amendment. Composting has been utilized for centuries in agriculture to enhance soil fertility, reduce waste, and promote sustainable farming practices. With the growing emphasis on sustainability, composting has emerged as a critical technology for managing organic waste and mitigating environmental impact.

Composting consists of four primary stages: mesophilic, thermophilic, cooling, and maturation. The process begins with the mesophilic stage, where temperatures range between 20-40°C. Microorganisms initiate the decomposition of organic material, releasing heat and transitioning the process to the thermophilic stage (40-70°C). The high temperatures in this stage facilitate the breakdown of complex compounds, destroy pathogens, and eliminate weed seeds (Elango et al., 2009). The cooling stage follows, during which the temperature decreases as the microbial activity stabilizes. Finally, the maturation stage ensures the stabilization of the compost and the development of humus, resulting in a nutrient-rich soil conditioner (Fourti et al., 2013).

Several factors influence the efficiency and success of the composting process. Key parameters include the oxygen content, water content, temperature, nutrients, pH level, and the Carbon/Nitrogen (C/N) ratio of the feedstock (Wu et al., 2017). Monitoring these factors is crucial to ensure the optimum conditions for microorganism activity and efficient composting.

Composting systems are generally categorized into two main types: open (static) systems and closed (dynamic) systems (van der Wurff et al., 2016). Additionally, they can be further classified based on scale into small-scale and medium- to large-scale composting. The choice of a suitable composting system depends on several factors, including the volume of organic waste, available resources, and the desired quality and quantity of the final product.

Small-scale composting methods are typically used in household or community settings and include backyard composting, vermicomposting, and passive windrow composting. Backyard composting involves the use of simple piles or containers to decompose food scraps and garden waste through natural or manual aeration. This method is cost-effective and requires minimal infrastructure. Vermicomposting, on the other hand, relies on worms to break down organic materials, resulting in high-quality compost with limited space requirements. However, it requires careful maintenance to provide the right conditions for the worms. Passive windrow composting involves stacking organic materials in long rows without active mixing. Aeration occurs naturally, making it suitable for small quantities of organic waste and reducing labor needs.

In contrast, medium- and large-scale composting systems are designed to handle higher volumes of organic waste and are often implemented in municipal or industrial contexts. Transfer windrow composting, one of the most common methods, involves piling organic material in long rows and turning it periodically to introduce oxygen. This method is low-cost and straightforward but requires a substantial area. Aerated static windrow composting, another medium- to large-scale method, uses forced aeration via fans or air ducts, which accelerates the decomposition process and provides better odor control. However, it involves higher equipment costs. Closed system composting, which is performed in reactors or tunnels, allows for strict control of environmental conditions, making it ideal for processing organic waste with high moisture content. This system is more compact and efficient, requiring less space and providing better odor and emission management compared to open systems.

The effectiveness of composting depends on various factors, such as the quality and preparation of raw materials, particle size, pile size, temperature, humidity, ventilation, pH, and the duration of the process (Lazcano et al., 2008). The ideal C/N ratio is between 20:1 and 35:1, while humidity should be maintained at 55-65% (Lazcano et al., 2008). Proper ventilation ensures the supply of oxygen, preventing anaerobic conditions that can lead to odor issues. Monitoring these parameters allows for adjustments that optimize compost quality and process efficiency.

Composting is a sustainable waste management practice that contributes to environmental and economic well-being. By diverting organic waste from landfills, composting reduces methane emissions and promotes carbon sequestration in the soil. The finished compost enhances soil structure, increases water retention, and provides essential nutrients, making it an excellent soil amendment for agriculture and landscaping (Lakhdar et al., 2009).

The economic benefits of composting include reduced waste disposal costs, income from compost sales, and the potential for creating job opportunities in waste management and agriculture. However, composting operations face challenges such as maintaining consistent feedstock quality, managing odors, and ensuring public participation. Addressing these challenges through public education, regulatory support, and innovative technologies is crucial for the success of composting initiatives.

Recent advancements in composting technology focus on increasing process efficiency and scalability while minimizing environmental impact. Innovations include the use of the Internet of Things (IoT) for real-time monitoring, automation, and data analytics to optimize composting conditions. Additionally, specialized microbial cultures and biochar additives are being developed to accelerate decomposition and improve compost quality.

Closed systems, hybrid methods, and integration with renewable energy systems such as anaerobic digestion are gaining traction. These approaches enable composting operations to become more energy-efficient and environmentally friendly. The development of odor control technologies, biodegradable packaging, and urban composting solutions also reflects the growing interest in making composting accessible and acceptable in various contexts.

Composting is a versatile and sustainable waste management strategy that transforms organic waste into a valuable resource. It offers numerous environmental and economic benefits and aligns with circular economy principles. As technological advancements continue to improve the efficiency and scalability of composting, its adoption across various sectors is likely to increase, contributing to a more sustainable future.

1.6.1. Evaluation of Biomass Types for Composting

The selection of biomass for composting is a crucial factor that directly impacts the efficiency of decomposition, microbial dynamics, and quality of the final compost. Biomass types are primarily characterized based on their Carbon-to-Nitrogen (C/N) ratio, lignin content, and moisture levels, all of which play critical roles in microbial metabolism and humification processes (Zhou et al., 2022).

Carbon-rich materials, such as dry leaves, sawdust, straw, and wood chips, serve as energy sources for microbial communities involved in composting. Their high C/N ratio (ranging from 50-500:1) ensures that microorganisms have a steady supply of carbon for cell wall synthesis and metabolic processes. These materials provide structure and aeration within the compost pile, preventing compaction and facilitating oxygen diffusion (Zhong et al., 2023). However, the high lignin and cellulose content of such materials requires prolonged decomposition times, which can be accelerated through mechanical pre-treatment such as shredding to increase surface area and microbial accessibility (Silva et al., 2018).

Nitrogen-rich materials, including fresh grass clippings, kitchen scraps, and animal manure, are essential for protein synthesis and enzyme production in microbial cells (Zhu et al., 2021). With a lower C/N ratio (10-30:1), these materials promote rapid microbial growth and heat production (Nigussie et al., 2017). Their high moisture content and nutrient availability can, however, lead to ammonia volatilization and odor issues if not properly balanced with carbon-rich biomass. Nitrogen-rich materials, when combined with lignin-containing substrates, contribute to the formation of humic substances (HSs), enhancing soil fertility and stability.

Lignocellulosic biomass, such as agricultural residues (corn stalks, wheat straw) and woody materials, are rich in lignin and cellulose, which are more resistant to microbial degradation (Wu et al., 2022). These materials are crucial for the production of humic substances during composting, as their complex molecular structures undergo oxidative and microbial transformation, leading to the formation of stable, high-molecular-weight humic substances.

Humic substances significantly contribute to soil health by enhancing nutrient retention, water-holding capacity, and cation exchange capacity (Ansari et al., 2023).

The decomposition rate of different biomass types is influenced by their chemical composition, particle size, and environmental conditions such as moisture, pH, and oxygen availability. For optimal composting, maintaining a C/N ratio of 25-30:1, along with 50-60% moisture content, is recommended (Sundberg et al., 2008). Particle size reduction through shredding increases the surface area and improves microbial colonization, thus accelerating the breakdown of lignocellulosic materials (Kulcu et al., 2004). Additionally, maintaining an aerobic environment with adequate ventilation prevents the formation of anaerobic zones, which could inhibit microbial activity and slow down the decomposition process.

Advanced pre-treatment techniques, such as hydrothermal processing or the addition of microbial inoculants, can significantly enhance the decomposition of complex organic materials like lignin. Blending various biomass types to achieve a balanced C/N ratio, appropriate moisture levels, and optimal pH is essential for creating a conducive environment for microbial metabolism. Incorporating biochar or other amendments can further enhance the microbial activity and humic substance formation, leading to higher-quality compost.

Overall, the selection and evaluation of biomass types for composting should consider their C/N ratio, lignin content, moisture levels, and potential for humic substance formation. An optimal combination of these factors results in efficient decomposition, minimizes environmental impact, and produces compost that is rich in humic substances and beneficial for soil health.

1.6.2. Design of Composting Technology

Composting is a biological treatment method that takes place under aerobic conditions. Composting has been used in farming for centuries to improve soil fertility and crop health (Mehta et al., 2014). Organic matter is decomposed by microorganisms in an oxygenated environment and converted into a valuable soil amendment (Equation 1). This recycling process consists of four main stages (mesophilic, thermophilic, cooling and maturation). It also contributes to reducing global warming by sequestering carbon into the soil (Pergola et al., 2018).

$$\begin{array}{l}\text{Proteins}\\ \text{Amino acids}\\ \text{Lipids}\\ \text{Carbohydrates}\\ \text{Cellulose}\\ \text{Lignin}\\ \text{Ash}\\ \text{etc.}\end{array} + O_2 + \text{Nutrients} + \text{Microorganisms} \rightarrow \textbf{Compost} + \text{New cells} + \text{Dead cells} + CO_2 + H_2\text{O} + NO_3 + SO_4^{-2} + \text{Heat}$$

Equation 1

There are several factors that influence the recycling process. Some of these factors (oxygen and water content) play a very important role in the process. Others (microorganism, temperature, nutrients, pH, C/N ratio, feedstock size, mixing, etc.) affect the variation of important factors. Temperature is a result of microbial activity. Nutrients and pH are the most important limiting factors in the system. The general flow chart of the composting process is given in Figure 22. (Öztürk, 2010).

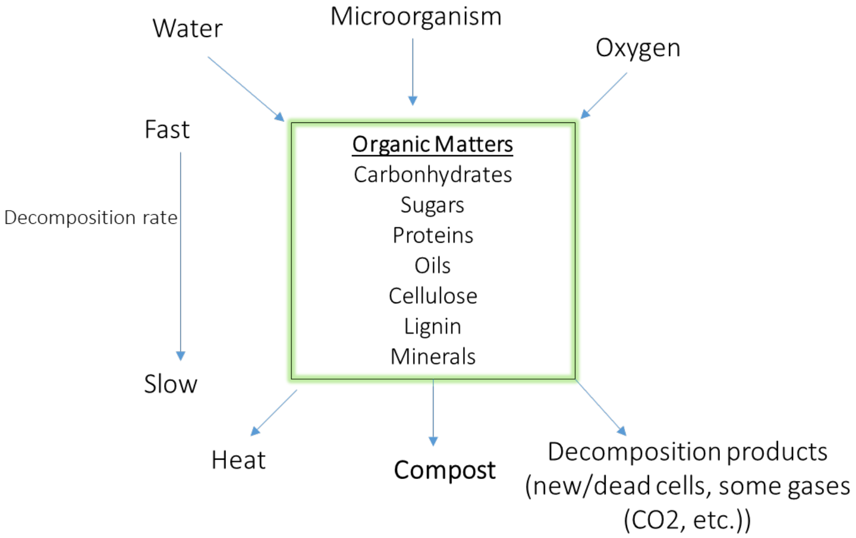


Figure 22. Composting process (Epstein, 1997; Öztürk, 2010).

1.6.2.1. Composting Systems

The design of composting technology is the engineering process of the methods and equipment used for the efficient decomposition of organic waste. There are many parameters (system scale, economic and environmental conditions, materials to be used, type and quantity of raw materials to be composted, targeted output, available equipment, manpower, etc.) that affect the design (Öztürk et al., 2015; Engin, 2022). Composting systems are mainly divided into two groups: open (static) and closed (dynamic). According to the scale, it is possible to divide them into two groups: household-small scale and medium-large scale. Information about the most commonly used composting systems is given below according to scale:

A. Home and Small Scale Composting

This includes backyard composting, vermicomposting and passive windrow composting. These systems are used in homes/gardens. Vermicomposting is carried out with red worms. These systems ensure that waste is reduced and recycled at source. The design features, advantages and disadvantages of these systems are given below.

Backyard Composting

Simple systems for household waste.

- **Design Features:** Usually simple piles or containers are used. Examples are pit composting, surface composting, green waste composting, crate-bank composting, etc. Aeration in these systems is provided by natural means or manually.
- **Materials to be used:** Food scraps, garden waste, leaves and grass cuttings.
- **Advantages:** Low cost, recycling at source, easy to implement.
- **Disadvantages:** Odor and pest control is required. Although they are small-scale systems, there are space limitations.

Vermicomposting

Vermicomposting is a worm-mediated composting.

- **Design Features:** Bins/beds are used, providing a moist and dark environment. Red worms (*Eisenia fetida* or *Eisenia andrei*), a suitable container and appropriate environmental conditions are sufficient. Waste is not mixed. Suitable temperature for the reproduction of worms is 22-27°C.
- **Materials Used:** Kitchen waste (especially fruit and vegetable scraps), cardboard, paper and garden waste can be used. Meat, bones and dairy products can cause odour problems.
- **Advantages:** High quality compost production, low odour, suitable for all climates, very small space requirement.
- **Disadvantages:** Labor intensive due to worm care and temperature control. It is a slower process (Öztürk, 2010; Christensen, 2011).

Passive Windrow Composting

It is an open system.

- **Design Features:** Open field systems where organic material is stacked in long rows. There is no mixing. Therefore, small piles should be created. Pile height should generally not exceed 1.5 m. It is ventilated by natural air movement.
- **Materials Used:** Animal carcasses (especially poultry), animal manure, garden waste, agricultural waste (Ölmez, 2013)
- **Advantages:** Low cost, easy installation, and simple
- **Disadvantages:** Depending on pile size and organic matter content, anaerobic environment and odour may occur, weed seeds may not be destroyed.

B. Medium and Large Scale Composting

They are open (static) or closed (dynamic) systems. Most common systems:

Transfer Windrow Composting

The oldest, simplest and most widely used method. Organic material is piled in long rows and turned periodically for aeration.

- **Design Features:** Open field systems where organic material is piled in long rows (triangular or trapezoidal). Aeration is achieved by periodic mixing. There is transfer. Typical pile height depends on the material but is usually 3.0-4.0 m wide and 1-3 m high. The length of the pile depends on the amount of waste and available facility space (Christensen, 2011).
- **Materials Used:** Garden waste, municipal solid waste, agricultural waste, municipal green waste and sewage sludge.
- **Advantages:** Simple and low cost, requires large area.
- **Disadvantages:** Dependent on weather/environmental conditions, odour control is difficult.

Aerated Static Windrow Composting

- **Design Features:** Systems in which organic material is held in place and pressurized aerated by fans or air ducts. Typical pile height is 3 m and floor width 12-15 m (Christensen, 2011). There is no transfer.
- **Materials Used:** Sewage sludge, municipal solid waste, garden waste
- **Advantages:** Faster process, odour control is easy, labor is less than in transfer batch composting.
- **Disadvantages:** High initial costs due to the equipment used, energy consumption due to aeration.

Closed System Composting: It can be carried out in-vessel, in reactor and in tunnel.

- **Design Features:** Composting is carried out in a closed container or vessel (channel/cell type, vertical flow reactor, container type reactor, horizontal flow tunnel type reactor, rotating drum type reactor, etc.) under controlled environmental conditions (Christensen, 2011). Compost is obtained faster than the other two composting processes (Waqas et al., 2018).
- **Materials Used:** Organic wastes with high moisture content, food waste, biosolids.
- **Advantages:** Fast and controlled composting, easy odour and emission control, low labor costs, less space required.
- **Disadvantages:** High capital and operating costs and system complexity (Tchobanoglous et al., 1993; Öztürk, 2010; Öztürk et al., 2015).

1.6.2.2. Factors to Consider When Composting

The efficiency of the composting process depends on several factors and these factors play an important role in evaluating the process performance. The main factors to consider when assessing the efficiency of the composting process:

Raw Material Mixture and Preparation

- **Quality of Feedstock:** The variety and quality of organic materials to be composted greatly affects the efficiency of the composting process. Materials with high carbon content (e.g. dry leaves, sawdust) and materials with high nitrogen content (e.g. kitchen waste, grass) should be mixed in a balanced ratio. All biodegradable wastes can be composted. Only hazardous wastes should not be used. One of the important aspects of feedstock quality is that the waste is collected separately (not mixed with other waste) (Christensen, 2011).
- **C/N Ratio**: It is important to balance the Carbon/Nitrogen ratio; ideally it should be 20-35:1 (Haug, 1993). Too high a carbon ratio slows down the composting process, while too low a ratio releases excess nitrogen as ammonia, which causes nutrient loss and odour problems (Christensen, 2011; Engin, 2022). To ensure the ideal ratio, wastes should be mixed and composted.
- **Particle Size**: Particle size between 1 and 2 inches in diameter is preferred for composting. Shredding organic materials into small pieces increases surface area, accelerating microorganism activity and accelerating decomposition. Small particles decompose faster, but very small particles can also impede air circulation (Ayilara et al., 2020).
- **Size of the Compost Pile:** The size of the compost pile affects its capacity to retain heat and moisture. Too small piles do not heat up sufficiently, while too large piles can lead to oxygen deficiency and anaerobic conditions.

Operating Conditions

- **Temperature:** Temperature is an important indicator in the composting process. Mesophilic (20-40°C) and thermophilic (40-70°C) stages are necessary for the destruction of pathogens and rapid decomposition of organic matter. The thermophilic temperature range (40-70°C) should be maintained to optimize microorganism activity. Temperature monitoring indicates whether the compost pile is functioning correctly. Temperature also helps to eliminate unwanted weed seeds.

- **Humidity:** 55-65% humidity is ideal. Humidity levels should be monitored and adjusted as necessary. It is recommended not to reduce the humidity below 35-40% (Christensen, 2011). Material that is too dry reduces the activity of microorganisms, while material that is too wet can lead to anaerobic conditions, resulting in bad odours and slow decomposition.
- **Ventilation:** Adequate oxygen should be provided; anaerobic conditions should be avoided (Ayilara et al., 2022). Regular aeration of the compost pile (usually by mixing) ensures that oxygen is evenly distributed throughout the pile. Maintaining aerobic conditions supports the efficient functioning of microorganisms. The oxygen supply for aerobic decomposition can be passive or forced. Oxygen concentration in the range of 5-15% is important for compost formation (Erdener, 2010).
- **pH:** The pH of the compost pile should generally be between 6.5 and 8. This range is ideal for the activity of microorganisms (Öztürk et al. 2015; Christensen, 2011; Onwosi et al., 2017). At low pHs, it can be increased by adding CaO (Fernandes et al., 1988).

Time and Monitoring

- **Composting Time:** It varies depending on the type of material and system design, usually ranging from a few weeks to several months. Assessing the final compost product for maturity indicators such as stable temperature, neutral pH and absence of recognizable feedstock particles can determine when the composting process is complete. Chemical analysis, testing the nutrient content of the finished compost (e.g. nitrogen, phosphorus, potassium), can provide information on its quality and suitability for use as soil amendment. Biological analysis, assessing microbial activity and diversity in the compost, can provide information on the health of the composting process. By monitoring these parameters and making necessary adjustments, the efficiency of the composting process can be maximized and high quality compost can be obtained.
- **Monitoring and Control:** Temperature, humidity and oxygen levels need to be monitored and controlled regularly.

Environmental Impacts and Regulations

- **Odour and Emissions:** Should be controlled by methods such as biofilters and coatings.
- **Waste Management Regulations:** Compliance with local and national environmental regulations should be ensured (Öztürk et al., 2015).

1.6.2.3. Steps in Composting Technology Design

Selection and Settlement

Proximity to sources of raw materials and end-users and accessibility for transport should be taken into account in site selection. There should be sufficient space for composting operations including pre-treatment, composting, curing and storage. Depending on the operating conditions and compost production capacity, an area of 1.2-2.5 m^2/t. year is required for a biowaste processing transfer windrow composting facility; 1.0-2.2 m^2/t.y for a closed or reactor type composting facility with a compost production capacity of 12,000 t. In low-traffic areas, the area requirement for a closed or reactor-type composting facility with a production capacity of 50000 t/y is only 0.4-0.8 m^2/t.y (Christensen, 2011). Impact assessments should be carried out, including soil, water and air quality management.

Process Design

After the site selection and layout of composting is determined, the raw material(s) and quantity(s) to be used in composting are determined. Usually different raw materials should be mixed. Firstly, pre-treatment (separation, shredding, grinding, mixing, etc.) is applied to the raw material. Then composting is done according to the selected method. After composting, curing and storage is done. The method and equipment to be used are decided according to site-specific factors, budget and desired output.

- Separation: Cyclone separator, dust collection system, fluidised bed air separators etc are used.
- Size reduction: Grinders, shredders etc are used (Öztürk et al., 2015)

Equipment Selection

- Raw material transport: Loaders, dump truck, conveyors, belt conveyors, etc are used.
- Raw material preparation: Chipper, shredder, shredder, mixer drum, hammer mill, etc. can use.
- Composting Equipment: Inverters, aerators (blowers, fans, pipes, thickeners), in-vessel systems, etc. are used.
- Control Systems: Automation for aeration, humidity and temperature control are used.

- pH control: Additives, aeration system are used.
- Biological reaction/mixing: Mixer, kneader, water addition system, water tanker are used.
- Screening: Fixed, vibrating, disc, rotating or drum sieve are used. (Öztürk et al., 2015)

Infrastructure and Auxiliary Facilities

- Water adding system: There should be water tanker and water adding system to maintain the humidity level.
- Electricity and Fuel: Required to operate machinery and control systems
- Drainage Systems: Required to manage leachate generated during composting.

Environmental and Regulatory Compliance

- Permits: Ensure compliance with local, state and federal regulations
- Environmental Impact: Assessments should be made for emissions, leachate and noise and necessary measures should be taken (Öztürk et al., 2015)

Cost Analysis

- Capital/Investment Costs: Costs required for initial set-up, equipment purchase and infrastructure development
- Operating Costs: Consists of labour, utilities, maintenance and administration costs.
- Revenue Streams: Consists of compost sales and potential tipping fees for waste reception

Application and Operation

- Construction and Installation: It is the process of construction of the compost facility and installation of equipment.
- Staff Training: Ensuring that the personnel are trained on composting processes and equipment usage. In addition, occupational health and safety training is provided against possible hazards.
- Operating Protocols: Establishment of standard operating procedures for efficient operation.

1.6.2.4. ındustrial application areas and purposes of composting technology

Composting technology has a wide range of applications in many industries. Organic materials that do not contain hazardous substances and can decompose are used in composting. With the developing composting technologies, product quality is increased and therefore the value of compost in the market is increasing rapidly. Compost is used in the reclamation of agricultural areas, gardens, forest areas, soil reclamation (soil cover, mining sites, roadbed creation), environmental control (biofilter, erosion control, wetland improvement, roadside stabilisation), and other uses (airports, cemeteries, schools, golf courses, green areas, holiday resorts) and many other places (Öztürk et al., 2015).

Agriculture

- **Agricultural Waste Management:** Soil fertility is increased by composting agricultural residues
- **Soil Improvement:** Using compost improves soil structure and nutrient content

Municipal Waste Management

- **Processing of Organic Waste:** Composting and disposal of food waste, green waste and sludge
- **Urban Waste Management:** It is ensured that organic wastes in cities are recycled by composting. It ensures zero waste management and sustainable waste management.

Food Processing and Retail

- **Food Waste Management:** Composting of organic waste from food production and distribution.
- **Closed Loop Systems:** It is aimed to include food waste back into production cycles as organic fertiliser.

Forestry and Landscape

- **Utilisation of Forest Waste:** Composting and utilisation of sawdust, bark and other forest residues.
- **Landscape Management:** Improving the soil structure of urban and rural landscapes by using compost

Livestock Breeding

- **Animal Waste Management:** Composting of manure and animal bedding into organic fertiliser
- **Pathogen Reduction:** It is ensured that animal wastes are disposed of safely and pathogens are reduced.

The usage areas of the produced compost according to its conformity to the standards and quality are summarised in Figure 23.

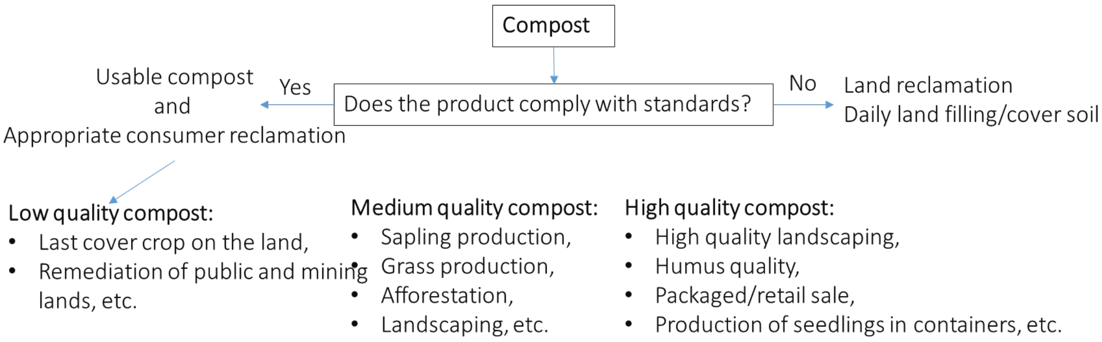


Figure 23. Uses of compost according to quality class (Öztürk et al., 2015).

1.6.3. The Technology Status of Composting

Composting is the decomposition of organic matter under aerobic conditions into a stable and humus-like product. Composting is becoming an increasingly familiar and preferred method. Composting of organic solid waste is a useful practice for soil restoration and an effective strategy for organic waste recycling (Yang et al., 2018). High quality compost can be produced from well managed (separately collected at source) organic wastes. In the well-managed composting process, pathogens harmful to plants are killed and weed seeds can be destroyed (Kugbe et al., 2021).

1.6.3.1. Technology Readiness Levels of Composting

The technological status of composting has improved significantly in recent years thanks to advances in engineering, microbiology, environmental science and policy frameworks. It is also an increasingly favoured method in terms of sustainability. Information on composting technology readiness levels (TRLs), recent innovations, challenges and costs is provided.

Technology Readiness Level (TRL) is a systematic measure that assesses the maturity of a particular technology. The TRL level ranges from 1 (observation of basic principles) to 9 (actual system proven in operational environment). TRLs framework, first developed by NASA and widely adopted by various industries, provides a systematic metric for assessing the maturity of technologies (Miller et al., 2016). TRLs have been applied in various fields such as biomanufacturing (Kedia et al., 2022), bio-industrial production (Smanski et al., 2022) and nuclear fuel development (Carmack et al., 2017). They provide a common vocabulary for stakeholders to assess technology maturity, prioritise objectives and assess risks in the development and commercialisation processes (Smanski et al., 2022). TRLs can help monitor the transition of emerging technologies into production (Moni et al., 2019). Composting technologies are found in different TRLs depending on the method and scale (Table 10.):

Table 10. TRL levels of composting technologies.

Composting Method	TRLs	Description
Backyard Composting	9	9- Actual system proven in an operational environment (commercially available).
Vermicomposting	8-9	8- Completion and qualification of the system through testing and demonstration 9- Actual system proven in an operational environment (commercially available).
Passive Windrow Composting	9	9- Actual system proven in an operational environment (commercially available).
Transfer Windrow Composting	9	9- Actual system proven in an operational environment (commercially available).
Aerated Static Windrow	8-9	8- Completion and qualification of the system through testing and demonstration 9- Actual system proven in an operational environment (commercially available).
Closed System Composting	7-8	7- Demonstration of the system prototype in an operational environment. 8- Completion and qualification of the system through testing and demonstration.

Small-scale composting methods (backyard composting, vermicomposting and passive windrow composting) have TRLs 9. They are real systems used commercially. Of the medium- and large-scale methods, transfer windrow composting is frequently used (Işık, 2009). Closed system methods are slightly less developed compared to other methods. Because it requires more equipment. In closed systems, less space is required, rapid decomposition is achieved, they are not sensitive to environmental conditions and odour control is easier.

Composting technology has advanced significantly, offering a variety of innovative approaches to organic waste management. Traditional thermophilic composting has been extensively studied and is a mature technology known for its ability to reduce waste, mineralise organic matter and promote humification (Wang and Wu, 2021). Furthermore, vermicomposting using earthworms as natural bioreactors has emerged as an environmentally friendly method to convert organic wastes into nutrient-rich compost useful for crop production (Karmakar et al., 2015).

Composting technology is evolving significantly every day, using advanced techniques and equipment to increase efficiency and effectiveness. Composting has been shown to contribute to economic, social and environmental well-being by efficiently managing biodegradable waste streams (Marmolejo-Rebellón et al., 2020). Composting technologies have also been associated with soil quality improvement, with organic fertilisers produced through composting improving soil physical properties and nutrient availability for plant growth (Yadav et al., 2023). The circular economy framework emphasises the importance of composting in waste management strategies, promoting resource recovery and environmental protection (Diéguez-Santana et al., 2022; Xu et al., 2023). As a result, composting technologies have evolved significantly and offer various solutions for organic waste management, soil fertility enhancement and sustainable agricultural practices. These technologies play an important role in promoting environmental sustainability, resource efficiency and circular economy principles (Xu et al., 2023).

1.6.3.2. Recent Innovations and Future Trends in Composting Technology

Population, technological development and urbanisation are increasing rapidly and as a result organic waste is also increasing rapidly. Composting, a natural process that converts organic waste into nutrient-rich soil amendments, offers a sustainable solution. Recent developments have focussed on increasing efficiency, scalability and environmental sustainability. Recent innovations and future trends in composting technology are given below:

1.6.3.3. Smart Composting Technologies

The Internet of Things (IoT) can be used for real-time monitoring and control, and artificial intelligence and machine learning can be used to scale the optimisation process (Aydin Temel, 2023; Zhou et al., 2022). IoT technologies and sensors monitor critical composting parameters such as temperature, pH, humidity and oxygen levels in real time. This data enables precise control and optimisation of the composting process. Automation reduces labour requirements and increases the efficiency of composting operations. Automated systems can manage tasks such as aeration and moisture adjustment (Manley et al., 2022; Xu et al., 2023). Big data analytics can be used to optimise composting processes, predict problems and improve operational efficiency (Xu et al., 2023). In a study that considers patent studies related to composting technology, it was stated that since managing organic waste at the source has become more important in recent years, automatic composters have become more prominent than manual ones. The review of patent documents revealed a marked shift from manual composting technology to automated composting technology (sensors and control feedback); composting technologies mainly focus on the aerobic composting process (>86%) and deal with general organic waste, which may include food waste (Azis, et al., 2022). Aerobic composting is highly favoured due to its lower capital requirements and generally faster composting process (Azis, et al., 2022).

Additives

Specialised microbial cultures are being developed to accelerate decomposition and improve compost quality (Xu et al., 2023). Specific species of bacteria, fungi and actinomycetes are used to target different types of organic waste. Enzymes/biostimulants can be used to break down complex organic compounds faster. Inoculation with thermo-tolerant Actinomycete strains such as *Streptomyces sp. H1, Mycobacterium sp. G1, Micromonospora sp. G7* and *Saccharomonospora sp. T9* has shown promising effects in enhancing degradation of resistant components such as lignocellulose (Zhou et al., 2023).

Additives are often added to improve the composting process by reducing leaching, greenhouse gas emissions and odour while at the same time increasing microbial activity and hence composting rate (Awasthi et al., 2020). Biochar, ashes, zeolites, or vermiculite are frequently used as additives (Zhou et al., 2022). The use of biochar as a compost additive to improve compost properties is increasing (Xu et al., 2023). There is research on the benefits of combining biochar with compost, such as improved nutrient retention, enhanced microbial activity and carbon sequestration. Compost-biochar mixtures are being developed for agricultural, horticultural and landscape uses. The use of biochar in combination with compost has been found to be a successful approach for the recovery of contaminated soils, especially for conventional pollutants (Liu et al., 2023). Other additives such as zero valent iron, carbon nanoparticles and montmorillonite also have various roles in composting (Xu et al., 2023).

Advanced Closed Systems

Continuous flow reactors allow continuous input and output of materials and increase efficiency. Rotary drum composters improve mixing and aeration, reducing processing time.

Hybrid Systems

Hybrid systems cover new and advanced composting methods to increase efficiency and reduce environmental impact. Integration with anaerobic digestion prior to composting can be applied for energy recovery from organic waste. For energy-neutral operations, composting can be combined with renewable energy systems such as biogas and solar energy. It may be possible to combine vermicomposting with conventional methods to evaluate the benefits of both systems.

Odour and Emission Control

There are improved methods to alleviate odour problems associated with composting. These include the development of advanced biofilters and bioscrubbers that use specific microbial communities to neutralise odours. Coating and encapsulation systems are being used to effectively control and treat odours. Biofilters can be used to remove ammonia and volatile organic compounds from composting of animal waste and carcasses (Shang et al., 2020; Khoshnevisan et al., 2021; Zhou et al., 2022).

Biodegradable Waste Packaging

Packaging that can be composted with organic waste is being developed. Thus, it is aimed to be a more environmentally friendly method. Zero waste approach will be applied.

Integration with Circular Economy Models

Composting will play an important role in circular economy strategies focussing on waste reduction and resource recovery. Integration with anaerobic digestion, wastewater treatment and bioenergy production is feasible. It covers the use of technologies to recover nutrients from compost for use in agricultural fertiliser and soil amendment (Xu et al., 2023).

Urban Composting Solutions

Compact and efficient composting systems specially designed for urban environments are being developed. Channel/enclosed systems are compact, odourless and automated composting units for residential and commercial buildings. Community compost centres are decentralised, small-scale composting facilities serving neighbourhoods or districts.

Quality Assurance and Standardisation

More stringent quality standards and certification systems for compost products should be established. Robust protocols for testing compost maturity, nutrient content and pathogen levels should be developed. Certification programmes should be established to ensure compost quality and safety and to increase market confidence and acceptance.

Regulation and Policy Support

Regulations and policies should be strengthened to promote composting as a sustainable waste management practice. Government incentives for composting infrastructure, research and adoption should be increased. Policies should be prepared that mandate the diversion of organic waste from landfills and promote composting as a preferred treatment method.

Industrial Applications

Composting practices need to be extended beyond traditional agriculture and horticulture to a variety of sectors. Composting can be used to treat pharmaceutical and nutraceutical waste. Biodegradable textiles and bioplastics can be composted as part of sustainable waste management practices. On-site composting systems for food waste processing enhance sustainability credentials. Further research is needed to understand its potential in controlling emerging pollutants such as per- and polyfluoroalkyl substances and microplastics etc.

1.6.3.4. Key Challenges in Composting Technology

Alongside progress, composting technology faces some challenges. These are:

Raw material variability

- Issue: Unsuitable quality and consistency of organic waste materials

- Impact: Decomposition in composting may not be sufficient. As a result, the desired quality of compost may not be obtained.

- Solution: Organic waste should be meticulously collected separately at the source (Kanat ve Ergüven, 2020).

Waste that is not collected separately should be sorted thoroughly and pre-treatment steps such as water content, shredding and sieving should be applied to ensure the required properties such as C/N, pH, moisture and size.

Odour Management

- Issue: Composting organic waste can produce unpleasant odours (Kanat ve Ergüven, 2020). A composting process is not possible without the release of odorous substances. Another cause of odour formation is the way the composting plant is operated (Bidlingmaier and Müsken, 2007).

- Impact: Odour problems can lead to deterioration of employee and environmental health, community complaints and legal challenges.

- Solution: The use of aeration systems, biofilters and appropriate feedstock management can help control odours. Closed systems may also be preferred for odour control (Christensen, 2011). Carbon should be added to the compost to intervene in the formation of pungent ammonia and pH should be controlled below 8.5 (Engin, 2022). Good odour control is an essential prerequisite for successful and environmentally friendly composting (Bidlingmaier and Müsken, 2007).

Public Perception and Participation

- Issue: Lack of public awareness and participation in composting programmes

- Impact: Low participation rates can affect the overall efficiency of composting operations by reducing the quantity and quality of feedstock.

- Solution: Education campaigns, incentives for participation and community engagement programmes can increase public participation. Demonstrating the environmental and economic benefits of composting can generate more public support (Anonymous, 2024).

Market Development for Finished Compost

-Issue: Develop and maintain a stable market for the finished compost product.

-Impact: Lack of demand can affect income and the sustainability of composting.

-Solution: Marketing efforts, quality assurance and demonstration of the benefits of compost can help develop a stable market.

Contamination from non-organic materials

- Issue: Presence of non-compostable plastics, metals and other non-organic pollutants in the feedstock.
- Impact: Contamination can reduce compost quality and lead to environmental hazards.
- Solution: Implement effective sorting and screening processes and educate waste generators (the public) on correct sorting. Advanced separation technologies, such as optical sorters and AI-assisted systems, can improve the purity of organic waste streams (Anonymous, 2024).

The future of organic waste composting technologies lies in innovation, integration and community involvement. As technological advances continue to improve the efficiency and scalability of composting, the potential to achieve sustainable waste management increases. By adopting innovative solutions, integrating composting into circular economy models and engaging communities, we can transform organic waste management and deliver significant environmental, economic and social benefits (Anonymous, 2024).

Cost of The Composting Technology

A detailed cost analysis for composting includes both capital/investment and operating costs. Capital costs consist of land acquisition, site preparation, infrastructure and buildings, composting equipment (such as mixers, shredders, screens and turners), utilities installation (installation of water, electricity and sewerage systems), permits and licences. Operating costs include staff salaries/labour, raw material procurement (collection, transport), utilities (water, electricity and fuel to be consumed), maintenance and repairs, insurance premiums, monitoring and testing (laboratory tests for quality control and environmental compliance), marketing-distribution (advertising, packaging, finished product transport), and other miscellaneous costs. The main factors affecting the cost of composting are the plant capacity and the level of technology used. Of course, the energy, construction and machinery purchase costs of the location of the facility are also effective on the cost. In a study conducted by Külcü and Yaldiz (2005), the investment cost of a static windrow composting plant where 50.000 t of waste will be processed annually was calculated as 1.372.436 $. Product costs for composting systems with 10000-150000 t/year capacity were reported to be 11-29 $/t (Külcü and Yaldiz, 2005). In cost-based studies conducted for open systems, composting costs vary between 5-36.01 $/t depending on the plant capacity (Kashmanian et al., 1993; Renkow et al., 1993).In a study carried out in Turkey, the investment cost of a transfer windrow composting (open) system with a daily capacity of 50 t was calculated as $820,000. It was stated that 61% of the investment cost was for machinery and equipment and 27% was for construction costs and 50% of the planned annual cost of $50,000 was for personnel costs.With the annual profit from compost sales, the plant is expected to finance itself between 7-8 years (Engin, 2022).

Composting can create economic opportunities by creating employment in waste management and agriculture sectors besides compost production and sales (Anonymous, 2024).

Conclusion

The technology status of bioethanol production is dependent on the nature of the feedstock. 1G bioethanol obtained from raw materials containing sugar and starch that can be hydrolyzed to C6 sugars is at the highest technological readiness level (TRL 9) and is commercialized worldwide. 2G bioethanol from lignocellulose is at TRL 6-8 with only a few pilot and first-of-the-kind plants. 3G and 4G bioethanol is still in the research phase at TRL 1-4. Key factors influencing bioethanol production are availability and cost of raw material, followed by pretreatment cost and energy input for raw material preparation, fermentation feasibility by highly producing microorganisms in improved bioreactors for obtaining high ethanol yield, ethanol recovery by highly efficient systems, and the possibility of valorization of all by-products. The technological process's environmental influence, including its carbon footprint, is also crucial in determining bioethanol production's commercialization.

Immobilized yeast cells in bioethanol production are nowadays mostly applied in research or pilot fermentation processes. However, in the last decades, there has been an increased number of published works about the use of immobilized cells for first and second-generation bioethanol production. The focus is on searching for the appropriate support for cell immobilization or a method, which will not interfere negatively with the quality of ethanol. Most of the published data is about batch alcoholic fermentation. Few researches exist on malolactic fermentation of wine with immobilized cells. Most of the published work refers to batch fermentation processes as basic research with the final aim of performing repeated batch or continuous fermentation. The successful implementation of continuous fermentation by immobilized yeast for bioethanol production demands more investigation to be done for each specific raw material.

Advancing biobutanol technology requires conducting research to optimize metabolic pathways in increasing both production efficiency and rate. This includes developing genetic modifications and enhancing enzyme activity to overcome inhibitions, as well as applying selective separation methods that allow for the simultaneous extraction of biobutanol. Other areas for technological needs in the production of biobutanol from biomass are the development of continuously operated, energy-efficient, and scalable single-step biomass hydrolysis and fermentation bioprocess technologies. Finally, design and scale-up of novel attached and suspended bioreactors for high-efficiency production is necessary.

Biological hydrogen production is recognized for its cleanliness and cost-effectiveness, but existing microbial mechanisms have limitations that require enhancement. Genetic engineering can improve enzyme activities related to hydrogen production, address inhibition issues, and increase resistance to these inhibitors. While dark fermentation technology is well-established, large-scale applications have not yet been implemented. Advances in photobioreactor design and operation are needed to address key challenges in fermentative and photolytic hydrogen production. Alternative methods such as consolidated fermentation and sequential or combined dark-photofermentation offer potential for increased production and complete substrate conversion with minimal pollutant emissions. The application of nanomaterials in biohydrogen production and biomass pretreatment is a rather recent development, promising to address many current limitations.

Anaerobic digestion offers a robust and versatile approach to managing biodegradable waste streams while generating biogas as a renewable energy source. The technology not only reduces waste volume but also produces valuable by-products such as digestate for soil enhancement. AD’s potential for integration with energy and agricultural systems makes it a promising solution for sustainable waste management. However, challenges such as feedstock variability, process optimization, and biogas upgrading must be addressed to maximize its efficiency and commercial viability.

Composting is a well-established and sustainable organic waste management solution that efficiently converts organic matter into valuable soil amendments. The process promotes the recycling of nutrients, enhances soil fertility, and reduces landfill waste. By optimizing parameters such as moisture content, aeration, and carbon-to-nitrogen ratio, composting yields a high-quality end product, reduces greenhouse gas emissions, and mitigates environmental pollution. Despite its many benefits, composting requires careful management of process conditions to ensure optimal decomposition and minimize odors.

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KEY ENABLING TECHNOLOGIES ACCORDING TO FEEDSTOCK TYPE

Part II

Thermochemical Conversion Technologies

CA 20127

Waste biorefinery technologies for accelerating sustainable energy processes (WIRE)

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Thank you for your commitment and collaboration!

EUROPEAN COOPERATION IN SCIENCE & TECHNOLOGY

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Table of contents

List of acronyms

AAEMs	Alkali and alkaline earth metals
AFI	Ash Fusibility Index
BFB	Bubbling fluidized beds
BIGCC	Biomass integrated gasification combined cycles
CCHP	Combined cooling, heating, and power
CFB	Circulating fluid bed
CFBR	Circulating Fluidized Bed reactor
CHP	Combined heat and power
DFBs	Dual fluidised beds
DME	Dimethylether
ER	Equivalence ratio
FB	Fruit biomasses
FCC	Fluid catalytic cracking
FT	Fischer-Tropsch process
GHG	Greenhouse gas
HB	Herbaceous biomasses
HDO	Hydrodeoxygenation
HHV	Higher heating value
HRSG	Heat recovery steam generator
HT	Hemisphere Temperature
HTC	Hydrothermal carbonization
HTG	Hydrothermal gasification
HTL	Hydrothermal Liquefaction
IDT	Initial Deformation Temperature
ILs	Ionic liquids
LHV	Low heating value
LHW	Liquid Hot Water
LPG	Liquefied petroleum gas
MA	Mixed alcohols
MCFC	Molten carbonate fuel cells
MSW	Municipal solid waste
NOx	Nitric oxides
OFMSW	Organic fraction of municipal solid waste

ORCs	Organic Rankine Cycles
PAH	Polycyclic aromatic hydrocarbon
PCDDs	Polychlorinated dibenzodioxins
PCDFs	Polychlorinated dibenzofurans
PM	Particulate matter
POPs	Persistent organic pollutants
Pyro-CHP	Combined Intermediate Pyrolysis and CHP
SCFs	Supercritical fluids
SCR	Selective catalytic reduction
SER	Sorption Enhanced reforming
SMR	Steam methane reforming
SNG	Synthetic natural gas
SNCR	Selective non-catalytic reduction
SOFC	Solid oxide fuel cells
SR	Steam reforming
SS	Sewage sludge
TCR®	Thermo-Catalytic Reforming
TRLs	Technology Readiness Levels
VM	Volatile matter
VOCs	Volatile organic compounds
WB	Woody biomasses
WGS	Water-gas shift reaction
WTE	Waste-to-energy

List of figures

List of tables

Executive summary

Thermochemical conversion technologies are crucial in modern biorefineries, enabling a broad range of applications that contribute to the system at multiple scales. These processes are essential for maximizing the conversion of biomass into valuable products and can be adapted to achieve specific objectives, such as enhancing feedstock quality, improving product stability, and increasing energy efficiency. By tailoring these technologies to meet distinct goals, biorefineries can optimize their performance, reduce waste, and contribute to a more sustainable energy future.

Thermochemical conversion technologies offer a versatile and efficient means of transforming waste biomass into valuable energy carriers and bio-based products. These processes utilize high temperatures and chemical reactions to convert biomass into various forms such as bio-oil, syngas, bio-crude oil, hydro-char, and solid biofuels like torrefied biomass and bio-char.

Given the diverse nature of waste biomass, thermochemical processes are classified into several key methods: direct combustion, torrefaction, pyrolysis, gasification, hydrothermal processes, and plasma technologies.

Direct combustion technology is the most established and widespread method for energy recovery, involving the burning of waste biomass to produce heat and power. This technology is commonly used for low-moisture biomass like wood residues (e.g., sawdust, wood chips, wood pellets/briquettes), fruit waste (e.g., olive stones, cherry pits, nut shells). These types of waste biomass are commonly used and are emphasized as effective options for combustion. They have low moisture content and are less challenging to process compared to more complex materials like sewage sludge, organic part municipal solid waste, and animal-derived materials.

Pyrolysis is a foundational chemical process and a key precursor to both gasification and combustion of waste biomass. It involves the thermal decomposition of materials at high temperatures in an oxygen-free environment. During pyrolysis, complex organic compounds break down into simpler molecules, producing gases, liquids (such as bio-oil), and a solid biochar. These products serve as valuable intermediates that can be further utilized in bio-fuel production, bio-chemical synthesis, fertilizers, and various other applications. Pyrolysis is highly adaptable to various waste biomass types, including wood residues, agricultural residues, agro-industrial biomass (fruit peels, vegetable and fruit pomace, shells, fruit kernels/stones/pits etc) and can produce bio-char and bio-oil. Other, biomass wastes like sewage sludge, organic part municipal solid waste is more challenging, due to presence of contaminants, high moisture content, ash content, heterogeneity etc.

Biomass gasification is a promising approach for utilizing waste biomass within a biorefinery framework. Through this high-temperature process, waste biomass is transformed into syngas—a versatile energy carrier that can be further refined for power generation, bio-fuel production, and various bio-chemical applications.

Gasification is a versatile technology, adaptable to various types of waste biomass, including agricultural residues, forest and wood biomass, agro-industrial byproducts, and other biodegradable wastes such as kitchen scraps, food waste, the organic fraction of municipal solid waste (OFMSW), and sewage sludge. Among these, agricultural residues and forest biomass are often considered the most suitable for gasification due to their high energy content and relatively low moisture levels, which enhance the efficiency of the gasification process. OFMSW and sewage sludge are also viable for gasification, though they pose unique challenges. OFMSW has high moisture content and a heterogeneous composition, which can hinder gasification efficiency. Pre-treatment steps such as drying and the removal of inorganic contaminants are typically necessary to improve process outcomes. Similarly, sewage sludge requires pre-treatment to reduce moisture and remove inorganics, as its high ash content can lead to tar production and other operational issues. Effective pre-treatment is thus crucial for both OFMSW and sewage sludge to optimize gasification efficiency and reliability.

Torrefaction is a process performed at lower temperatures to produce solid biofuels such as torrefied biomass. Torrefaction offers several key benefits for upgrading biomass in bioenergy applications. First, it increases the energy density of biomass, providing a higher energy content compared to raw waste biomass and enhancing feedstock efficiency. Additionally, torrefaction improves storage and handling by making waste biomass hydrophobic, which prevents water absorption and reduces susceptibility to biological degradation. This process also enhances the combustion and gasification properties of biomass; the resulting material is more homogeneous and easier to grind, making it a superior feedstock for these applications. Torrefaction is a versatile technology, adaptable to various types of waste biomass, including agricultural residues, forest and wood biomass, agro-industrial byproducts, and other biodegradable wastes such as kitchen scraps, food waste, the organic fraction of municipal solid waste (OFMSW), and sewage sludge. Among the mentioned waste biomass types, agricultural residues (like straw and husks) and forest/wood biomass (such as sawdust and wood chips) are particularly suitable for torrefaction. These materials have relatively low moisture content and high lignocellulosic content, which makes the torrefaction process more efficient and produces high-quality torrefied biomass. The OFMSW, sewage sludge, kitchen scraps, and food waste can also be torrefied, but they come with some challenges: effective pre-treatment is essential to reduce moisture and remove undesirable components.

Hydrothermal Liquefaction (HTL) is a promising process for converting wet biomass, such as sewage sludge and food waste, into bio-crude oil under moderate temperatures and high pressures. Unlike other thermochemical processes that require dry feedstocks, HTL can efficiently process wet materials without the need for energy-intensive drying, making it particularly advantageous for high-moisture biomass. This capability addresses a key limitation of other technologies, expanding the range of biomass types suitable for sustainable biofuel production. Bio-crude produced from Hydrothermal Liquefaction (HTL) offers a diverse range of applications. It can be upgraded through processes like hydrodeoxygenation and catalytic cracking to produce transportation fuels such as diesel and biodiesel, which meet established fuel standards and support cleaner energy solutions. Additionally, bio-crude contains valuable compounds, including phenol derivatives, ketones, and cycloalkenes, making it a crucial feedstock for various industrial applications in the chemical and pharmaceutical sectors. With its high heating value, bio-crude is also suitable for heat and power generation, serving as a viable fuel for combustion in boilers and engines. The solid residue from HTL, known as biochar, can be utilized as a soil amendment, an adsorbent for water treatment, or a support material for catalysts, further contributing to sustainable waste management. Moreover, bio-crude contains platform chemicals that can be refined for further synthesis, enhancing its utility in bio-based chemical production. These applications underscore the versatility and value of HTL bio-crude in advancing renewable energy and sustainable industrial practices.

Hydrothermal carbonization (HTC) is a thermochemical conversion process that utilizes heat and pressure to transform wet biomass feedstocks into hydro-char. HTC is particularly advantageous because it can process wet feedstocks without the need for an energy-intensive drying step, making it suitable for handling biomass with high moisture content. This process effectively reduces the moisture content of the biomass while enhancing its energy density, making hydro-char a valuable product for various applications. Hydro-char functions as an effective adsorbent in wastewater treatment, helping to remove heavy metals and other contaminants from water sources. It also plays a role in carbon sequestration by capturing and storing carbon in the soil, thereby contributing to climate change mitigation. With its high carbon content and energy density, hydro-char can be utilized as a solid fuel for combustion, providing a renewable energy source. Furthermore, it can be processed into activated carbon for various industrial applications, including gas and liquid filtration. Hydro-char can also be incorporated into bio-fertilizers, supplying essential nutrients to plants and promoting sustainable agriculture. These diverse applications underscore the versatility and importance of hydro-char as a product of HTC.

Plasma technologies, especially plasma gasification, represent cutting-edge methods for converting waste biomass into valuable products such as syngas. Plasma gasification is highly versatile and can process a wide range of waste biomass types, such as forest and wood residues, agricultural residues, food waste, mixed organic waste streams from households and commercial sources, various organic waste materials from industrial processes, sewage sludge and other organic sludges. Also, should be mentioned, suitable feedstock for plasma technologies are contaminated waste, waste containing toxic or dangerous substances, non-biodegradable waste materials. Syngas can be utilized for energy production or as a chemical feedstock, providing a versatile solution for waste management and resource recovery. Plasma gasification operates at extremely high temperatures, effectively breaking down complex organic materials and facilitating the transformation of waste biomass into useful energy and bio-chemical resources. This innovative approach not only reduces the volume of waste biomass but also contributes to sustainable energy solutions.

Thermochemical technologies offer several key advantages, including flexibility in handling a wide range of feedstocks and the ability to produce diverse energy products, which contribute to a more sustainable energy landscape. Additionally, these technologies have the potential to reduce the environmental footprint by utilizing waste biomass and converting it into high-value products. However, there are also challenges and considerations associated with thermochemical technologies, such as high capital investment and operational costs, as well as ash-related issues like slagging and fouling, particularly when using low-quality feedstocks. Furthermore, there is a need for additional research to improve the efficiency and scalability of these processes, especially for emerging technologies like hydrothermal liquefaction (HTL) and plasma conversion.

In conclusion, thermochemical conversion technologies and biorefineries hold significant potential for sustainable energy generation and waste biomass valorisation. By selecting appropriate processes based on waste biomass characteristics, these technologies can help drive the transition to a circular bioeconomy.

2. General introduction to thermochemical conversion technologies

Thermochemical conversion is an energy intensive process that involves the thermal decomposition of compounds in waste biomass to produce high quality products (syngas, bio-char, bio-fuels, bio-chemicals, and bio-materials). The thermochemical conversion processes can be categorized into the following types based on temperature, heating duration, pressure, and the presence of oxygen:

1. pyrolysis (torrefaction, slow pyrolysis, fast pyrolysis, flesh pyrolysis and plasma pyrolysis),
2. gasification (fixed bad gasification, fluidized bed gasification, entrained flow gasification and plasma gasification),
3. direct combustion,
4. hydrothermal processes (liquefaction (HTL), hydrothermal carbonisation (HTC) and hydrothermal gasification (HTG)).

Each thermochemical conversion technology offers a unique array of products, has distinct input specifications, and utilizes various equipment configurations to recover the chemical value of waste biomass (Karmakar et al., 2023, Bosmans et al., 2013). Additionally, the diverse products and by-products generated by these technologies can serve as raw materials for producing a wide range of additional bioproducts."

A cleaned and conditioned syngas, main product from gasification process, can be used for the synthesis of many products such as methanol, ethanol, dimethylether (DME), Fischer-Tropsch diesel, mixed alcohols (MA), synthetic natural gas (SNG) and even pure hydrogen (Van der Drift and Boerrigter, 2006). Additionally, syngas can be used to produce fertilizers, particularly through the synthesis of ammonia derived from the gasification process. A common application of syngas is in combined heat and power (CHP) systems, where it is used to generate both electricity and thermal energy.

Slow pyrolysis and torrefaction processes convert waste biomass into solid fuels, such as bio-char and torrefied biomass respectively, with high heating values ranging from 21 to 29 MJ/kg (Biogreen and ETIA, 2018). Bio-char, a product of slow pyrolysis, can be utilized as a functional material in various applications, including soil enrichment, bioremediation, and filtration.

The liquid bio-oil produced from fast pyrolysis serves as a potential source for a range of valuable biochemicals, including resins, preservatives, biodegradable plastics, paints, adhesives, and flavoring agents (Jahirul et al., 2012). Bio-oil can also be used as a substitute for fuel oil or diesel in combined heat and power (CHP) systems (Jahirul et al., 2012) and after refining as a transportation fuel.

Bio-crude oil, as a main product from HTL, can be further refined into bio-fuels (e.g. gasoline, jet fuel, diesel) and bio-materials (e.g. engine lubricant) (Usman et al., 2024, Basar et al., 2021). Hydrochar, as a main product from HTC, can be used for energy production (trough combustion or gasification), as a or as a activated carbon or soil additive for soil nourishment (Yoganandham et al., 2020, Herklotz Benjamin, 2024).

An overview of thermochemical conversion technologies, their respective primary products and their end uses are shown in Figures 1.

This chapter aims to provide a comprehensive overview of thermochemical conversion technologies and their applications.

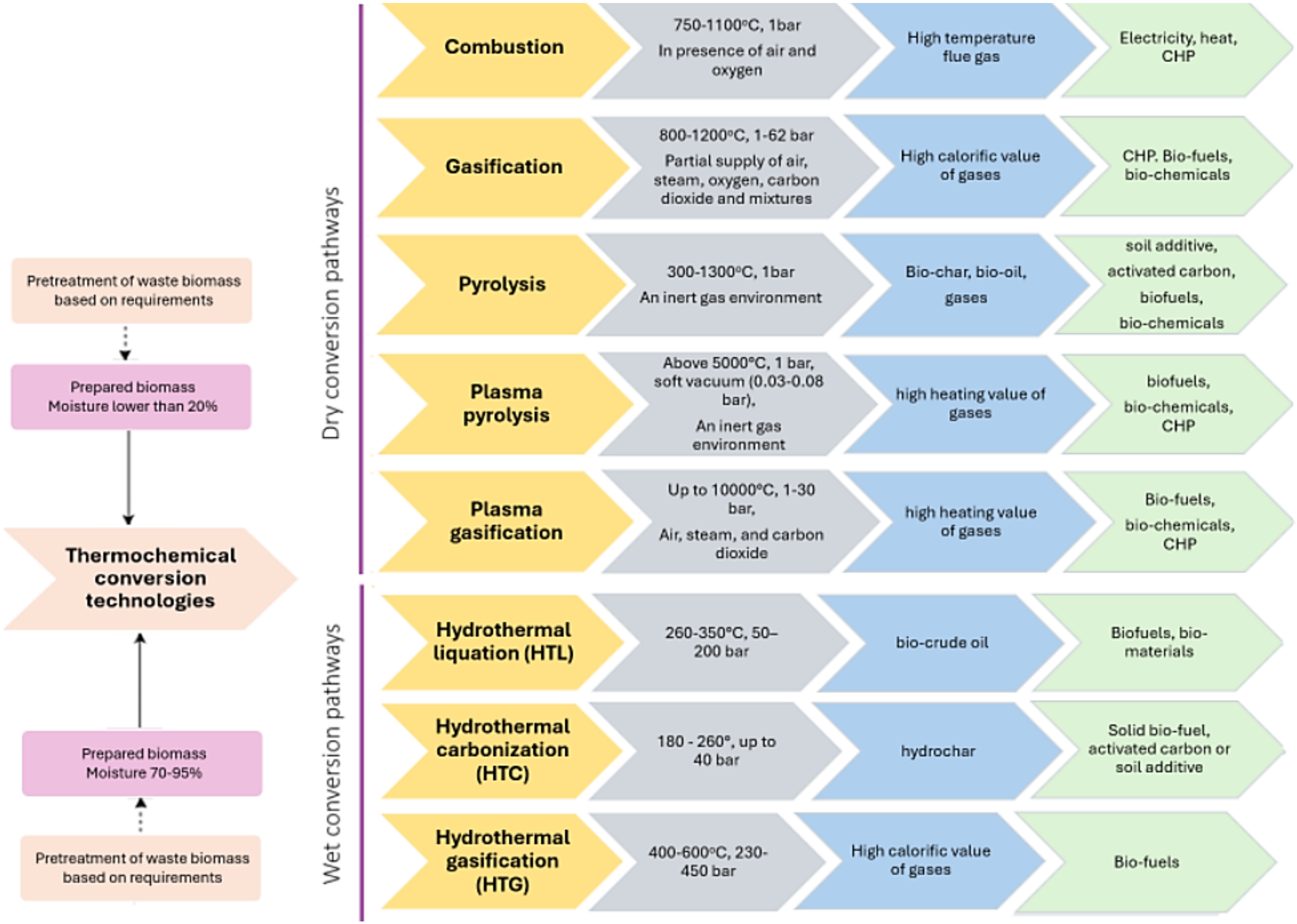


Figure 1. Different thermochemical conversion processes for biomass waste and their products.

2.1. Pretreatment of Waste Biomass used in Thermochemical Conversion Technologies

Summarized characteristics of biomass influencing the thermochemical conversion process is presented in Figure 2.

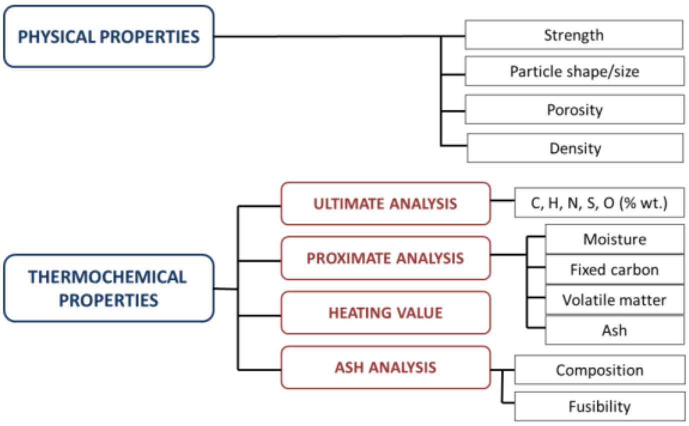


Figure 2. Biomass feedstock properties influencing the thermochemical conversion process (IEA Bioenergy, 2022)

The performance of the thermochemical conversion technologies and quality of the desired products are strongly affected by physical and chemical characteristics of waste biomass. Forest and woody waste biomass, typically of high quality with relatively low moisture and ash content, has been favoured over lower-grade biomass waste such as agricultural, agro-industrial, and other biodegradable materials. These lower-grade biomass wastes often have higher inorganic contents, low ash melting temperatures, high moisture content, large particle sizes, or irregular shapes and a low bulk density, and unwanted components like heavy metals (Koppejan and Cremers, 2019). These characteristics can pose operational challenges in feeding or converting the biomass waste into a desired products (Koppejan and Cremers, 2019). Inorganic materials can act as catalysts, altering the thermal degradation rate and changing the chemical pathways during pyrolysis, affecting the yield and quality of bio-char, bio-oil, and gases produced. During gasification, inorganics can form bed agglomerates, causing bed sintering and reducing the lifespan of gasification reactors. In combustion processes, inorganics can lead to slagging (formation of molten ash deposits) and fouling (deposition on heat exchange surfaces), decreasing efficiency and increasing maintenance requirements. Low ash melting temperatures can cause slagging and fouling in combustion, leading to operational issues such as reduced heat transfer efficiency and increased equipment wear. During gasification, low melting ash can create deposits that block reactors, reducing efficiency. High moisture content requires additional energy to evaporate, increasing the energy input and reducing overall process efficiency. Large particles hinder heat transfer and reaction kinetics, leading to incomplete conversion and lower product yields, potentially causing blockages in pyrolysis and gasification. In combustion, large particles may not burn completely, reducing efficiency, increasing emissions, and raising particulate matter levels. Waste biomass, such as agricultural residues, often has irregular shapes and low bulk density, leading to loose harvest formats and lower energy density compared to forest biomass. These properties cause processing inefficiencies and increase the volume and costs of conversion equipment and reactors for waste biomass processing. Heavy metals concentrated in the ash pose environmental risks and health hazards. They can also degrade reactor performance and lifespan through corrosion and catalyst poisoning.

Pretreatment of waste biomass used in thermochemical conversion technologies refers to the process of preparing biomass materials before subjecting them to thermochemical conversion methods such as torrefaction, pyrolysis, gasification, direct combustion, hydrothermal liquefaction (HTL), hydrothermal carbonization (HTC) and plasma (plasma pyrolysis and plasma gasification). Pretreatment steps such as physical (mechanical), chemical, thermal can significantly enhance the properties of waste biomass. These improvements make it feasible to use waste biomass more effectively, thereby broadening the resource base (Koppejan and Cremers, 2019).

2.1.1. Primary pretreatment methods

A. Physical (Mechanical) Pretreatment

Physical pretreatment methods involve mechanical processes to reduce the size and alter the physical properties of biomass.

Size reduction

Biomass is often bulky and heterogeneous. Pretreatment can involve grinding/milling, shredding, or chipping to reduce particle size, which improves handling and increases the surface area for subsequent processes. Size reduction is a crucial step in the pretreatment of waste biomass for thermochemical conversion technologies. Physical methods like grinding or shredding are commonly used to reduce the particle size of biomass feedstock, leading to increased conversion rates during thermochemical processes. Research has shown that physical size reduction can enhance conversion rates by up to approximately 50%, making the biomass more suitable for subsequent conversion steps (Vidal et al., 2011).

Reducing the size of biomass particles is essential for improving the accessibility of biomass components during thermochemical conversion processes like pyrolysis, gasification, and combustion. Smaller particle sizes can improve heat and mass transfer, resulting in more efficient conversion of biomass into energy-dense intermediates that can be further processed into bio-fuels and bio-chemicals (Liu et al., 2017).

By decreasing the size of biomass particles, the surface area available for chemical reactions increases, leading to enhanced conversion efficiency during thermochemical processes (Jin et al., 2014).

In conclusion, size reduction of waste biomass is a critical pretreatment step for thermochemical conversion technologies. Physical size reduction methods enhance the accessibility of biomass components, improves uniformity of feedstock, improve conversion rates, and optimize the efficiency of thermochemical processes to produce bio-fuels and chemicals.

Moisture Reduction

Many thermochemical processes require low moisture content for efficient operation. Pretreatment methods like drying or mechanical pressing reduce moisture levels, enhancing the energy efficiency of the conversion process. Moisture content is another critical factor in the pretreatment of waste biomass for thermochemical conversion technologies. Research has shown that reducing the moisture content in biomass feedstock can significantly enhance the efficiency and economics of thermochemical conversion processes. For instance, decreasing the moisture content from 45% to 35% can result in a substantial increase in the net present value of thermochemical projects, primarily by reducing the energy and cost associated with drying the biomass (Tanger et al., 2013). High moisture content in biomass can lead to decreased thermal efficiency and output fluctuation in boiler systems, underscoring the importance of dewatering as a crucial step in feedstock pretreatment for biomass power plants (Huang et al., 2023).

Various pretreatment methods are utilized to reduce moisture content and improve the efficiency of thermochemical conversion processes. Hydrothermal carbonization (HTC) or wet torrefaction is one such method employed to pretreat biomass before thermochemical conversion, particularly for biomass with high moisture content (Liu et al., 2017). Additionally, endeavours have been made to optimize waste heat recovery and mixed drying processes to effectively reduce fuel moisture content (Li Gang et al., 2022). Dewatering techniques, such as using liquid bio dimethyl ether, have demonstrated potential as energy-efficient methods for reducing moisture content in solid biomass feedstock (Öhrman and Pettersson, 2013).

hermochemical conversion processes, like pyrolysis and gasification, are employed to transform biomass into bio-oils, syngas, and other valuable products (Chundawat et al., 2011). These processes are influenced by the moisture content of the biomass, with low moisture content biomass being preferred due to enhanced heat and mass transfer during conversion (Nyakuma B. B. et al., 2014). Thermochemical conversion technologies are vital for converting biomass into bio-fuels and bio-chemicals, underscoring the significance of effective pretreatment methods to optimize the process (Zhao et al., 2022). Consequently, reducing moisture content in waste biomass through effective pretreatment methods is essential for enhancing the efficiency and economic viability of thermochemical conversion technologies. Dewatering techniques, pretreatment methods like HTC, and optimizing waste heat recovery processes are key strategies to reduce moisture content and enhance the overall performance of thermochemical conversion processes.

Densification

Various types of waste biomass, including wood and its residues (such as sawdust, chips, or shavings), agricultural waste (like straw), and food industry by-products, require densification (Vaish et al., 2022). Densified biomass offers uniform shape and properties, making it more suitable for thermochemical conversions such as combustion, gasification, and pyrolysis (Gong et al., 2023).

Biomass densification involves compressing biomass to increase its density by reducing volume. This is achieved by compressing the biomass through a die, where friction between the material and the inner die wall creates resistance that compacts the biomass (Li and Liu, 2000). Pressure and heat during this process, cause biomass particles to form attraction forces (Kaliyan and Vance Morey, 2009, Gong et al., 2023). Natural binders like lignin and carbohydrates soften, exit plant cells, and bind neighbouring particles (Gong et al., 2023). Elevated temperature and pressure during densification soften lignin, thereby enhancing biomass binding capabilities (Tumuluru, 2010). Upon cooling, these binders solidify into bridges, strengthening the densified product (Gong et al., 2023).

The three common densification technologies are extruding, pelleting, and briquetting (Gong et al., 2023, Tumuluru et al., 2011, Li and Liu, 2000). Extrusion uses temperature-controlled screws to compress and spin biomass into compact particles, involving rapid heating, compression, and shear forces that modify biomass components and cell walls (Gong et al., 2023). This method also serves as a physical-chemical pretreatment. In contrast, pelleting and briquetting primarily aim to increase biomass density.

In conclusion, compressing biomass into pellets or briquettes to increase bulk density improves uniformity of feedstock, and facilitates easier handling.

B. Chemical Pretreatment

Chemical pretreatments are often used for chemical modification of waste biomass and removal of impurities contained in biomass.

Chemical treatments are essential for modifying biomass composition, which involves removing or altering components that hinder conversion efficiency or introducing catalysts to enhance reaction rates. Chemical modification is a crucial step in the pretreatment of waste biomass for thermochemical conversion technologies. Altering the chemical composition of biomass feedstock can enhance the efficiency and effectiveness of processes such as pyrolysis, gasification, and combustion (Liu et al., 2017). These modifications can lead to the production of energy-dense intermediates that can be further converted into power, liquid fuels, and chemicals.

The chemical modification of biomass can significantly impact the quality of syngas produced during thermochemical conversion processes. The presence of oxygen during biomass conversion can influence the formation of syngas contaminants, emphasizing the importance of understanding the chemical reactions involved in thermochemical conversion (Schuetzle et al., 2015). Additionally, the composition of biomass can affect the quality of syngas generated, highlighting the need to consider the chemical properties of the feedstock for efficient conversion (Dai et al., 2019). Moreover, the use of catalytic thermochemical processes for biomass conversion to bio-fuels and chemicals highlights the importance of chemical catalysts in enhancing conversion efficiency (Mei Wu et al., 2014). Catalytic pyrolysis, gasification, and hydrothermal liquefaction (HTL) are key methods that utilize chemical catalysts to improve the conversion of biomass into valuable products.

Additionally, biomass often contains impurities like ash, minerals, and contaminants, which can negatively impact the efficiency of gasification, pyrolysis, and combustion processes. Pretreatment methods, such as washing or sieving, are essential to remove these impurities, reducing equipment fouling and improving product quality. The removal of impurities is a crucial step in the pretreatment of waste biomass for thermochemical conversion technologies. Impurities in biomass feedstock can have adverse effects on the efficiency and effectiveness of processes such as gasification, pyrolysis, and combustion. Various separation technologies help eliminate impurities from product streams during thermochemical conversions (Ibarra-Gonzalez et al., 2021).

Pretreatments play a significant role in eliminating impurities from biomass feedstock. Research has demonstrated that pretreatments can effectively remove alkali metals and other impurities from agricultural residues like wheat straw and rice straw, leading to the production of ash with lower loss on ignition and higher amorphous silica content (Ataie and Riding, 2013). Additionally, co-pyrolysis techniques have been employed to eliminate impurities from bio-oil fuels that cannot be upgraded using conventional pyrolysis processes (Bisen et al., 2022).

Impurities such as nitrogen, sulphur, alkaline compounds, and soot can affect syngas quality during gasification (Ufitikirezi et al., 2024). Effective pretreatment technologies are available to reduce inorganic contaminants in biomass to meet lower concentration limits and enhance the overall quality of the conversion process (Liu et al., 2017).

Chemical pretreatment involves using chemical agents at or near room temperature to alter biomass properties (Liu et al., 2017). Techniques include water leaching, and washing with acids, alkalis, or salts. Applying this pretreatment technologies impurities in waste biomass can be significantly reduced.

Water leaching is a pretreatment process that involves using water to remove soluble substances from biomass. Water leaching has proven effective in removing the majority of alkali metals, such as potassium (K) and sodium (Na), as well as some chlorine contaminants (Liu et al., 2017). The basic principle of this technology involves soaking or washing waste biomass with water, typically at ambient or slightly elevated temperatures. The duration of the leaching process varies based on the type of biomass and the concentration of impurities. Reducing inorganic content, such as alkali metals and chlorine, has several benefits: minimizes the risk of slagging, fouling, and corrosion in thermochemical conversion reactors; improve the quality of the syngas or bio-oil produced during conversion processes; lower the concentration of harmful substances in the biomass reduces the emission of pollutants during conversion.

Acid washing is a pretreatment process that uses acidic solutions to remove impurities and undesirable components from biomass. This method is particularly effective in eliminating minerals, metals, and other contaminants that can hinder the efficiency of thermochemical conversion processes. Waste biomass is treated with an acidic solution, such as hydrochloric acid (HCl) or sulfuric acid (H2SO4). The acid reacts with the impurities, dissolving them and allowing them to be washed away. Acid washing is an effective pretreatment method for improving the quality and reactivity of biomass by removing impurities such as minerals and metals.

This process enhances the efficiency of thermochemical conversion technologies, leading to better-quality products and reduced operational issues.

Base washing is a pretreatment process that utilizes alkaline solutions to remove impurities and undesirable components from biomass. This method is particularly effective in eliminating acidic compounds, certain metals, and other contaminants that can negatively impact the efficiency of thermochemical conversion processes. Waste biomass is treated with an alkaline solution, such as sodium hydroxide (NaOH) or potassium hydroxide (KOH). The base reacts with acidic impurities and certain metals, dissolving them and allowing them to be washed away. Base washing is an effective pretreatment method for improving the quality and reactivity of biomass by removing acidic impurities and certain metals. This process enhances the efficiency of thermochemical conversion technologies, leading to better-quality products and reduced operational issues.

As a result, chemical modification of waste biomass is also critical aspect of pretreatment for thermochemical conversion technologies. Understanding and manipulating the chemical composition of biomass feedstock can optimize thermochemical conversion processes, improve the quality of syngas produced, and enhance the overall efficiency of biomass conversion to bio-fuels and chemicals.

C. Thermal Pretreatment

Thermal pretreatment applies heat through steam, hot water, or other thermal carriers to initiate chemical reactions within the biomass. These reactions can break down complex organic molecules, reduce moisture content, and alter the chemical composition. Thermal pretreatment techniques, such as steam explosion, hot water extraction, torrefaction and hydrothermal carbonization, have proven effective in modifying biomass properties, including reducing ash content.

During steam explosion process biomass is treated with high-pressure steam, then rapidly decompressed, causing the material to undergo physical and chemical changes. Steam explosion treatment has been suggested to be used as pretreatment process in the pellets industry. Studies shows that the use of steam explosion pretreatment can improve the pellet durability in terms of mechanical strength and moisture sorption resistance (Lam, 2011). Pellets produced without this pretreatment are prone to disintegration into fines due to impact or moisture absorption during handling and storage. These fines can pose risks such as dust explosions during handling and self-heating of the pellets while in storage (Lam, 2011). Furthermore, steam explosion reduced the amount of alkali metals in the waste biomass, and the pressed pellets showed an increased density, impact and abrasion resistance (Stelte, 2013).

During hot water extraction, biomass is treated with hot water, which dissolves hemicellulose and other soluble compounds. This process helps to reduce impurities and improve the overall quality of the waste biomass. As for steam explosion, hot water extraction has a positive impact on pellets. Pellets made from treated biomass exhibited more resistance to moisture absorption compared to pellets made from untreated biomass due to the removal of hydrophilic hemicelluloses (Bujanovic B. et al., 2023).

As a result, the pretreatment of waste biomass used in thermochemical conversion technologies can be classified as mentioned above. In light of this information, optimizing the use of waste biomass in thermochemical conversion technologies plays an important role in making these processes more efficient, economically viable and environmentally sustainable. An effective pretreatment also positively affects the efficiency and economy of thermochemical conversion technologies. Herein, improving raw material compatibility with reactors, increasing product yield and quality, reducing energy consumption during conversion, minimizing equipment wear and maintenance, and facilitating integration into existing energy systems can be considered as important subtitles.

2.2. Direct Combustion

2.2.1. General review and evaluation of biomass types for direct combustion

Alternative resources for energy are in high demand due to the depletion of fossil feedstocks, rising oil prices, and environmental concerns related to CO_2 emissions. The energy production through direct combustion of biomass, that is CO_2-neutral, in place of fossil fuels can contribute to the clean energy transition goals. In the context of Directive (EU) 2018/2001, biomass is defined as "biodegradable fraction of products, waste and residues from biological origin from agriculture, including vegetal and animal substances, from forestry and related industries, including fisheries and aquaculture, as well as the biodegradable fraction of waste, including industrial and municipal waste of biological origin".

Regarding standardization, biomass as a fuel has been developed sectorally. The technical committee ISO TC 238, that developed several standards related to the use of biomass as solid bio-fuel and define biomass as "material of biological origin excluding material embedded in geological formations and/or fossilized" (ISO 16559:2022 Solid Bio-fuels — Vocabulary," 2022). Within the scope of ISO 16559:2022, the solid bio-fuels encompasses a wide range of fuels, including woody biomass (such as chips, hog fuel, firewood, wood pellets, and briquettes), herbaceous biomass (like straw, grass, miscanthus, etc.), fruit biomass (such as olive stones, cherry pits, grape waste, and nut shells), and aquatic biomass (including algae and seaweeds), as well as a category known as "blends and mixtures." Solid bio-fuel does not include any animal-based biomass, such as manure, meat and bone meal, and similar materials. Additionally, demolition timber is classified as hazardous waste and is not considered part of the solid bio-fuel category.

Despite direct combustion of solid bio-fuel be associated with vegetal biomass, the combustion of sewage sludge (SS), municipal solid waste (MSW), and animal-derived materials (e.g., fats, bones, and manure) for energy production offers also some advantages (Nanda *et al.*, 2021; Quan *et al.*, 2022). This process not only rapidly and substantially reduces waste volume but also completely destroys pathogens and microorganisms, aiding in waste stabilization and reducing its harmfulness (Quan *et al.*, 2022). In the context of limited land resources and rising energy demands, direct combustion is seen as an effective method to both decrease the quantity and toxicity of waste and recover valuable energy.

However, several challenges arise when combusting these wastes. The combustion of sewage sludge (SS) presents not only technical but also economic difficulties. Its high moisture content is a significant barrier, as it lowers reactor temperature and reduces the process's thermal efficiency. Removing this moisture is both energy-intensive and costly, leading to substantial CO_2 emissions. Moreover, the presence of harmful substances such as SOx, NOx, toxic polychlorinated dioxins, furans, and heavy metals requires more advanced downstream treatment, further increasing processing costs (Liang *et al*., 2021; Wang *et al*., 2020; Li *et al*., 2023). The direct combustion of municipal solid waste (MSW) faces additional challenges due to the heterogeneity of its composition. MSW typically includes both biodegradable and non-biodegradable materials from organic and inorganic sources, but its composition varies significantly across different municipalities worldwide. For example, the organic fraction can range from 15% in Berlin, Germany, to 75% in Dhanbad, India, (Babu eta al. 2021) influencing the choice of MSW treatment methods. Due to moisture's negative impact on the combustion process, the organic fraction of MSW, such as kitchen residues and yard waste, is usually better suited for biological conversion technologies (e.g., anaerobic digestion and composting). In contrast, MSW containing recalcitrant organic components (e.g., paper waste, packaging boxes, and cardboard) and non-biodegradable organics (e.g., plastics, rubber, polymers, and tires) is more appropriate for thermochemical conversion technologies (Nanda et al., 2021). Despite to the comprehensive content of the biomass concept, this general review is mainly focussed on the woody, herbaceous and fruit biomass combustion.

The direct combustion of biomass can be described in four stages, as follows:

i. Drying and heating of the particle: When the fuel particle is introduced into the reactor, usually a fluidized bed or grate-fired boilers, it absorbs heat through radiation and convection, with its interior receiving energy conducted through the particle. The drying process begins as soon as the particle's temperature reaches 100 °C, as the moisture transitions to a gaseous state and moves through the particle's pores to its surface. The phase change of the moisture can create cracks large enough to break the particle, especially if the vapour is not released quickly from the surface, thus reducing the internal pressure. Drying and heating are endothermic processes that depend on the temperature of the surrounding gases, as well as the size and moisture content of the particles (Lith, 2006; Loo et al, 2008).

ii. Devolatilization: This stage follows the drying process, where the volatile organic matter within the particle is released. The parameters influencing the quantity and type of products formed in this stage include temperature, heating rate, residence time, pressure, particle size, and the type of fuel used. The products of volatilization consist mainly of H_2O, CO_2, CO, H_2, and hydrocarbons. CO and CO_2 can be formed in significant amounts, in oxygen-rich fuels like biomass. The biomass devolatilization starts at 200-260°C (Demirbas, 2004; Demirbaş, 2005; Werther *et al.,* 2000). Hemicellulose is the first fraction to degrade and volatilize (225-325°C), followed by cellulose (325-375°C), while lignin degrades and volatilizes at a higher temperature range (until 500°C). Due to its high volatile matter content, a considerable fraction of the initial biomass particle mass is consumed during this stage.

iii. Combustion of volatiles: In the presence of oxygen, the combustion of the released volatile matter occurs, forming a visible flame around the particles (Demirbas, 2005). This stage is pronounced in biomass, where, in addition to the release of gaseous compounds, some more reactive compounds, particularly containing alkaline elements, are also released.

iv. Combustion of the char residue: After the volatile matter (VM) is released from the fuel particle, the combustion of the char residue begins. The char residue is mainly composed of fixed carbon and ash, with small amounts of hydrogen, oxygen, nitrogen, and sulphur. The oxidation of the char residue is facilitated by its porosity, which promotes the diffusion of oxygen into the particle, and in the presence of free radicals oxidation reactions occur, leading to the formation of CO and CO_2.The biomass moisture content is a critical aspect to the combustion efficiency. High levels of moisture in biomass substantially increase the energy required for moisture evaporation, which in turn influences negatively the temperature profiles (prolong the ignition time) and increases the greenhouse gases generation emissions (Lai *et al.,* 2024).

Despite the environmental and social benefits associated with using biomass for electricity production, the ashes from some types of biomasses can exhibit problematic behaviour, particularly due to the formation of deposits on the walls of boilers and gas ducts, justified by the low fusion temperature of some compounds (e.g. K-silicates), and high volatilization, followed by condensation, of alkali compounds (e.g. KCl), respectively. The accumulation of deposits in convective heat transfer zones (fouling) and in refractory areas of the boiler (slagging), as well as the sintering and agglomeration of the bed material in the case of fluidized bed combustion systems, and corrosion are issues that often hinder the proper functioning of combustion systems. Over time, the buildup of deposits in boilers and gas ducts affects their energy efficiency, and can also restrict the flow of gaseous compounds, leading to irreversible mechanical damage to the boiler. Ultimately, these problems may require frequent shutdowns of the boilers for maintenance.

In addition, pollutant emissions can be a problem if outdated technologies are used, flue gas cleaning is suboptimal, or if combustion conditions are not properly managed. To effectively minimize the pollutant emissions, it is crucial to ensure thorough mixing between combustible gases and combustion air, maintain an appropriate air-fuel ratio, provide sufficient residence time in the combustion chamber (greater than 0.3 seconds), and achieve a flame temperature of at least 800 °C. Failure to meet these conditions can lead to higher emissions of pollutants. For instance, incomplete combustion results in the release of flue gases from the combustion of biomass into the atmosphere, which include products like solid particles (such as biomass char, soot including adsorbed polycyclic aromatic hydrocarbon (PAH), and tars) and volatile organic compounds (VOCs), which have the potential to form secondary organic aerosols (Nussbaumer, 2017). Nitric oxides (NOx) and organic chlorine compounds are also released during the burning of biomass. It is necessary to employ cleaning technologies and biomass combustion conditions in a way that ensures the security of both the environment and human health.

Table 1 summarize the biomass direct combustion advantages and disadvantages.

Table 1. Biomass direct combustion advantages and disadvantages (Sivabalan et al., 2021; Teixeira et al., 2012)

Advantages	Disadvantages
● Several categories of biomass are available, such as unprocessed forest residues or wasted biomass from industrial processes ● CO_2 carbon neutral fuel, or in case of bioenergy with carbon capture and storage (BECCS) technologies, it can be considered a negative carbon emissions fuel ● Allow biomass mixtures and blends to produce less emissions of CO2, SOx and NOx, increase the combustion process efficiency, and reduce the occurrence of ash related problems.	● Most of lignocellulosic material had a high amount of moisture, and a drying step can be required before the combustion ● Slagging, fouling, corrosion and agglomeration due to the biomass inorganic composition ● Depending on the combustion system, a particle size homogenization and reduction can be required ● Densification can be required to reduce the transport costs ● The use in power generation can be limited by the cascade principle, that prioritizes reuse and recycling before the bioenergy applications. ● Limitations related with the economic viability, since it is mainly limited to the waste wood products and agro-processing operations

A Influence of biomass type in the occurrence of ash related problems

The inorganic composition and main types of chemical associations of elements in biomass are crucial in determining the behaviour of ash during combustion (Teixeira et al, 2012). Figure 3 identifies the main inorganic elements present in biomass, as well as the main types of chemical associations.

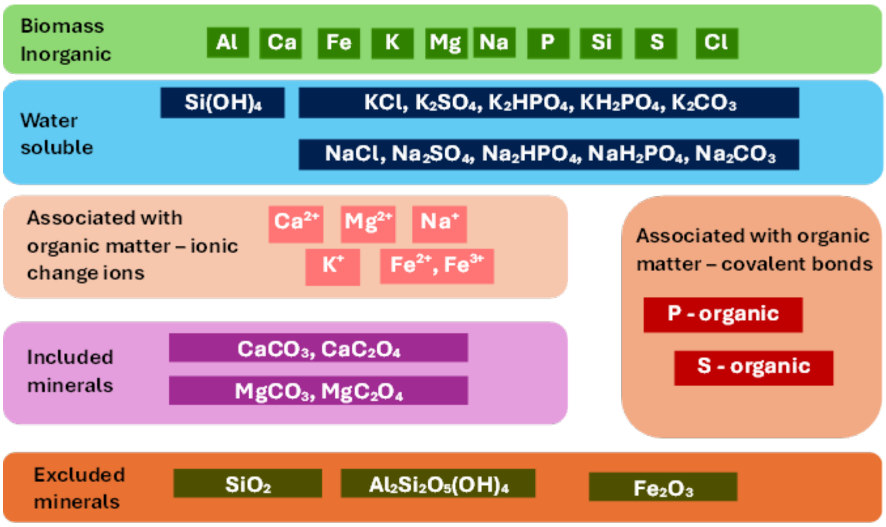


Figure 3. Inorganic Composition and key types of chemical associations among elements in biomass (Zevenhoven-Onderwater et al., 2000, Teixeira, 2012)

The chemical association of inorganic elements within the fuel matrix influences their behaviour during combustion due to the varying reactivity of the compounds. The most reactive compounds are water-soluble salts and inorganic elements associated with organic matter. The less reactive compounds are minerals included or excluded from the fuel matrix. In simplified terms, it is assumed that at high temperatures, the more reactive compounds are primarily responsible for the formation of deposits. Once volatilized, these reactive compounds are carried by the combustion gases, and as the gases cool down, the compounds can condense within the boiler or gas ducts, forming deposits, particularly in convective zones (fouling). These compounds may also react with the ash or interact with the bed material (in case of fluidized bed reactors), leading to bed agglomeration problems. In the flame zone, where high temperatures are continuously present, some compounds may melt or soften, contributing to bed agglomeration or the formation of deposits on heat exchange surfaces or refractory areas of the boiler (slagging) (Zevenhoven-Onderwater et al., 2000).

In addition to the nature and reactivity of the inorganic elements, their interaction and mass fraction in biomass during combustion determine the tendency for deposits formation and/or ash agglomeration.

Potassium (K) is likely the most relevant element concerning the formation of agglomerates and deposits (fouling and slagging), not only due to its reactivity with other fuel constituents but also because of the high levels typically found in various types of biomasses. However, it is important to note that the formation of potassium compounds always depends on the availability of other elements for these reactions to occur (Plaza et al., 2009). Although sodium (Na) behaves similarly to K during combustion, its contribution to deposit formation is less significant, as its content in plant biomass is typically low. Potassium (K) commonly reacts with **silicon (Si)** during combustion to form potassium silicates (which melt or soften at low temperatures) or reacts with **chlorine (Cl)** or **sulphur (S)** to form potassium chlorides or sulphates. These compounds can deposit on the internal surfaces of the boiler, gas ducts, and heat exchange areas (Lind et al., 2006; Öhman et al., 2000). Regarding the deposition of alkali salts, chlorine (Cl) is an important agent, as it determines the ease with which alkali metals are released into the gas phase during combustion (Johansen et al., 2011). It is commonly assumed that Cl evaporates easily and, at high temperatures, facilitates the transport of K, as evidenced by the frequent presence of KCl in deposits (Thy et al., 2006). Baxter *et. al*. (1998) argue that the concentration of Cl determines the amount of vapourised alkali metals during combustion, with the Cl content being more relevant than the actual alkali metal content in the fuel. Lind studied the effect of Cl and S on aerosol formation by adding HCl and SO_2 to a combustion reactor (Lind et al., 2006). They found out that the presence of HCl significantly increased the concentration of aerosols in the gas phase due to the formation of alkali metal chlorides, and consequently, a smaller fraction of alkali metals reacted with silicates and remained in the bed. Thus, in the presence of Cl, an increase in fouling and a reduction in slagging and/or bed agglomeration can be expected. On the other hand, the addition of SO_2 converts some chlorides into sulphates (sulfation), which helps reduce fouling since the condensation temperature of potassium sulphates (~1000 °C) is higher than the condensation temperature of potassium chlorides (~750 °C) (Iisa *et. al.,* 1999), thus occurring before the gases exit the combustion zone.

Lith *et. al.* (2008) observed that, in biomass, S is generally released in two stages. Organic Sulphur is released below 850 °C, with the majority being released below 500 °C. Between 850-1150 °C, inorganic S is gradually released, probably due to the incorporation of alkali and alkaline earth metals into silicates, which allows for the release of SO_2 (g). Practically all S is released at 1150 °C in the case of Si-rich fuels, whereas for fuels low in Si, about 50% of inorganic S is retained in the ash. Knudsen *et.al.* (2004) also mentioned that, in the presence of silicates, the stability of K_2SO_4 in the ash is reduced, as at high temperatures, Ca and K are preferentially incorporated into the silicate matrix rather than forming sulphates. Since the solubility of sulphur oxides in alkali silicates is low, only small amounts of S can be retained in the silicate matrix, resulting in low retention of S in bed ash. As the release of SO_2 (g) is more pronounced in Si-rich biomass, it is likely that sulfation is more pronounced in these cases.

Wiinikka *et.al.* (2007) emphasizes that the presence of alkali metals in the gas phase also depends on the (K+Na)/Si ratio in the fuel. During combustion, alkali metals can react with silicon (Si) in the fuel, producing alkali silicates with relatively low melting points, which causes the alkali metals to be retained in the molten ash rather than being vapourised.

Due to their ability to form compounds with higher melting points, the presence of **calcium (Ca),** as well as **magnesium (Mg), aluminium (Al), iron (Fe),** and **titanium (Ti),** typically helps to minimize the occurrence of agglomerates and deposits in the flame zone. However, the presence of the latter elements is usually insignificant in biomass. The presence of Ca can affect the equilibrium reactions of potassium, as Ca can bind with Si to form calcium silicates or calcium-potassium silicates, thereby decreasing the formation of potassium silicates (Risnes et al., 2003; Thy et al., 2000). In the fuels with high Ca content, the formation of calcium silicates may contribute to an increase in volatile potassium salts, consequently increasing the tendency for deposit formation in convection zones.

Summarizing, the formation of molten compounds is highly sensitive to the relative amounts of potassium (K) and calcium (Ca) in the fuels. If the K fraction is high and the Ca fraction is low, large amounts of molten compounds can form at temperatures below 900 °C. Conversely, if the K content is low and the Ca content is high, no molten compounds are observed at temperatures below 900 °C (Öhman *et al*., 2000).

The presence of **phosphorus (P)** as a component of the fuel or as an additive can influence deposit formation in the reactor during combustion. The chemical reactions involving phosphorus with silicon (Si), potassium (K), and calcium (Ca) at high temperatures are not fully understood (Sommersacher *et al.,* 2012). According to Grimm *et al.* (2011), the formation of potassium phosphates is thermodynamically favourable, followed by the formation of sodium (Na), calcium (Ca), and magnesium (Mg) phosphates. The authors also note that the formation of potassium phosphates is thermodynamically preferred over the formation of sulphates, chlorides, silicates, carbonates, and hydroxides. Apparently, when biomass contains a high amount of phosphorus (P), it can act as a sintering inducer since potassium phosphates melt at low temperatures (700 °C). However, the presence of calcium in the bed (as an additive or from the biomass) may promote the formation of stable calcium phosphates and calcium-potassium phosphates with high melting points (above 1000 °C), thereby minimizing deposit formation as less potassium will be available to react with silicon (Grimm *et al.,* 2011; Lindström *et al.,* 2007).

Figure 4 summarizes the ash content and chemical composition of various woody biomasses (WB), herbaceous biomasses (HB), and fruit biomasses (FB), based on data from ISO 17225-1:2021. To facilitate better comparison of the relative quantities of each element, a consistent x-axis scale was used across all graphs.

Briefly, the following are some of the mechanisms suggested in the literature to prevent ash related problems (Bartels *et al.,* 2008; Davidsson *et al.,* 2008; Elled *et al.,* 2010; Liao *et al*., 2012; Llorente *et al*, 2005; Lundholm *et al.,* 2005; Pettersson *et al.,* 2008; Risnes *et al.,* 2003; Teixeira *et al*., 2012):

i. **Decrease bed temperature and control temperature hot spots in the bed and/or freeboard** (*e.g.*, burning herbaceous biomass near 600 °C).
ii. **Fuel treatment** (*e.g.*, through washing to remove Na and K).
iii. **Retention of alkaline elements** by using additives *(e.g.,* limestone and dolomite) to minimize the formation of alkaline silicates with low melting temperatures.
iv. **Increase the content of refractory metals** (*e.g.*, Al and Fe) to enhance the formation of silicate compounds with higher ash melting temperatures.
v. **Combustion of mixed and blended biomasses** to reduce the formation of compounds with low fusion temperature and alkali compounds volatilization (e*.g.,* woody and herbaceous biomass).
vi. **Use of alternative materials in the bed** for biomass rich in Ca and K, replacing silica sand to reduce sintering (*e.g.,* olivine).

Although the influence of inorganic elements on deposit formation is well known, the variability in properties and composition of different types of biomasses- such as herbaceous biomass (which contains high levels of Si and K) and woody biomass (which contains a high level of Ca)—makes it difficult to predict the behaviour of biomass elements during combustion. Contamination with soil material is another issue (Knudsen *et al*., 2004b) that needs to be considered in these chemical evaluations. Additionally, the fact that various inorganic salts and oxides can interact and form compounds with significantly lower melting temperatures than the pure compounds further complicate the prediction of the behaviour of these elements during combustion (Arvelakis *et.al*, 2005; Olanders *et al,* 1995).

Despite the difficulties, over the years, various methodologies have emerged for predicting the formation of deposits and agglomeration of bed material. These include theoretical indices based on the biomass chemical composition or melting temperatures of the ash (Pronobis, 2005; Sommersacher *et al*., 2012; Visser *et al*., 2004; Zevenhoven-Onderwater *et al.,* 2000, Teixeira *et al*, 2012), the use of ternary diagrams containing the main oxides present in the ash (Öhman *et al.,* 2000, Teixeira *et al*, 2012), or simply an empirical assessment of the content of certain elements identified as problematic (Obernberger *et al.,* 2006). In addition, have been used methodologies based on chemical equilibrium calculations for phase prediction, which can help on the prevision of problematic compounds formation (e.g. with low fusion temperature) (Brus *et al.,* 2005; Gulyurtlu *et al.,* 2008; Nutalapati *et al.,* 2007; Plaza *et al*., 2009; Zevenhoven-Onderwater *et al*., 2000, Teixeira *et al*, 2014).

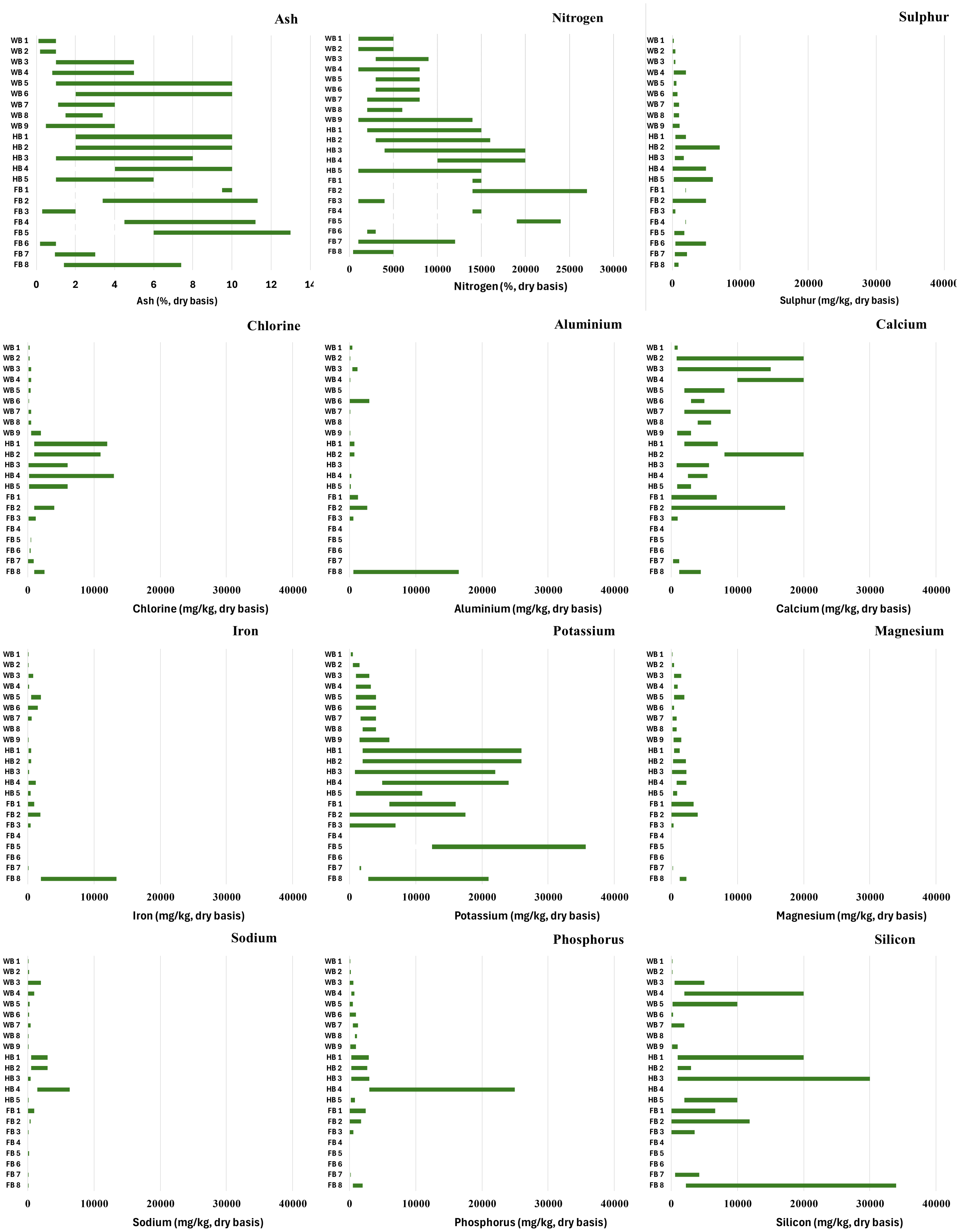


Figure 4. Ash content, net calorific value, and chemical composition ranges content of various woody biomasses (WB), herbaceous biomasses (HB), and fruit biomasses (FB) based on ISO 17225-1: 2021) data.

WB 1-Coniferous wood; **WB 2**-Broad-leaf wood; **WB 3**-Bark from coniferous wood; **WB 4**-Bark from broad-leaf wood; **WB 5**-Logging residues from coniferous wood; **WB 6**-Logging residues from broad-leaf wood; **WB 7**-Willow; **WB 8**-Poplar; **WB 9**-Eucalyptus; **HB 1**-Straw from wheat, rye barley; **HB 2**-Straw from oilseed rape; **HB 3**-Reed canary grass;

HB 4-Grass; **HB 5**-Miscanthus; **FB 1**-Crude olive cake; **FB 2**-Exhausted olive cake; **FB 3**-kernels/stones; **FB 4**-Crude grape cake; **FB 5**-Exhausted grape cake; **FB 6**-Apricot, peach, cherry fruit stone; **FB 7**-Almond, hazelnut, pinenut shells; **FB 8**-palm shell, nut, fibre.

The most relevant methodologies to forecasting ash related problems are described below. However, there are still no tools that provide definitive results capable of accurately predicting and preventing problems related to ash, as the formation of deposits or bed agglomeration depends on several factors such as the characteristics of the fuels, combustion technology, and operational parameters, which are difficult to encompass in a single prediction methodology. Thy *et.al.* (2009) emphasized that, given the heterogeneity and diversity of different types of biomasses, the chemical analysis of these materials, upon which most prediction methods depend, should be conducted on representative samples to avoid drawing incorrect or inconsistent conclusions.

2.2.2. Interpretation of Biomass Composition

To ensure efficient biomass combustion and minimize issues related to deposit formation, it was recommended to maintain the bio-fuel elemental content within specified ranges (Table 2), based on the identified precursors of deposit formation (Obernberger *et al*., 2006).

Table 2. Recommend range of element content in biomass to direct combustion proceed without ash-related problems.

Element	Content (%)
Ca (ash basis)	15-35
K (ash badis)	< 7
S (fuel, dry basis)	< 0.1
Cl (fuel, dry basis)	<0.1

The presented ranges are relatively common for woody biomass. However, for herbaceous and fruit biomass, these levels are rarely achieved without some form of pre-treatment of the biomass.

B Indices Based on the Chemical Composition of Biomass

Several indices have been developed to predict deposit formation or bed material agglomeration, based on the total chemical composition of biomass. Table 3 presents some relevant indexes and critical values. The indices developed by Visser et al., 2004) can be applied to fluidized bed reactors, while the indices suggested by Sommersacher et al. (2012), are primarily applicable to grate combustion systems, as they do not account for possible interactions between the ash and the bed material used in fluidized bed combustion.

Table 3. Indices to predict deposits or bed material agglomeration based on biomass chemical composition

Indices to predict deposits or bed material agglomeration	Critical Value	Observations	Ref.
$\mathrm{I_A = \frac{Na + K}{2S + Cl}}$	>1	Assumes that all Cl and S react with Na and K, facilitating their volatilization, and does not account for the fact that a significant portion of S and Cl may be released as HCl and SO_2, neither consider that other cations might react with Cl and S.	Visser et al (2004)
$\mathrm{I_B = \frac{Na + K + Si}{Ca + P + Mg}}$	>1	Applies to fluidized bed reactors that use SiO_2 as bed material. It is assumed that a formation of a coating composed of refractory elements (Ca, Mg and P) around the SiO_2 particle, should prevents sintering and bed agglomeration.	Visser et al (2004)
$\mathrm{I_X = \frac{Si}{Ca + Mg}}$	>1	Assumes that the presence of Ca and Mg increases the ash fusion temperature due to the formation of calcium or magnesium silicates, which have high melting temperatures.	Sommersacher et al. (2012)
$\mathrm{I_Y = \frac{Si + P + K}{Ca + Mg}}$	>1	This index takes into account the role of K and P in ash fusion. In addition to K, the presence of P in the fuel also lowers the ash fusion temperature due to the formation of potassium phosphates.	Sommersacher et al. (2012)
$\mathrm{I_Z = \frac{Si}{K}}$	>2.5	It assumes that for values higher than 2.5, the K retention in the bed was high, increasing the ash related problems.	Sommersacher et al. (2012)

C Index Based on Ash Fusibility

The application of the Ash Fusibility Index (AFI), originally developed for coal, to biomass combustion appears to be a methodology that can approximately predict the behaviour of biomass during combustion. The fusibility temperatures used are the Initial Deformation Temperature (IDT in °C) and the Hemisphere Temperature (HT in °C).

$$AFI = \frac{4 \times IDT + HT}{5}$$

The tendency for slagging is classified based on the AFI values (Lopez *et al.,* 2003):

- below 1149 °C- Severe
- between 1149 and 1232 °C- High
- between 1232 and 1343 °C- Medium
- above 1343 °C- Low

While the AFI does not explain the phenomena occurring during deposit formation or agglomeration, it is a straightforward methodology that has the advantage of not relying solely on mathematical correlations of independent parameters ignoring possible synergies between them.

Because it is based on the experimental behaviour of the ashes, the AFI accounts for potential synergies between the inorganic elements in the ash, which is reflected in the observed fusibility temperatures. However, it should be noted that the accuracy of this methodology is also affected by inherent differences between ashes produced in the laboratory and in installations like boilers, including temperature gradients, the effect of atmospheric conditions, interactions between ash particles, and ash segregation based on particle size. Wall observed differences in the IDT value obtained from ashes of the same fuel, produced in a muffle furnace or a combustion installation, due to temperature differences associated with ash production (Wall *et al.,* 1999).

D Use of Ternary Phase Diagrams

The use of ternary phase diagrams can be useful in interpreting the behaviour of ashes, as they identify the mineral compounds likely present in the ash based on the relative amounts of each oxide, and cumulatively identify the associated melting temperatures. However, one of the main limitations of using ternary diagrams is that the ashes from the fuel typically consist of several oxides, not just the species represented in each diagram. According to the literature, obtaining accurate information from ternary diagrams is only possible if the sum of the oxides present in the diagram is equal to or greater than 90% (Öhman *et al.,* 2000).

Scala *et. al.* (2008) observed that when the initial composition of biomass ashes is identified in the ternary diagram as being prone to the formation of eutectic points at low temperatures, due to the low Ca content and high Si and K content, ash fusion can occur before the ashes come into contact with the bed material particles. Salour *et. al.* (1993) observed similar results during the assessment of rice straw and wood residue ash compositions. Rice straw showed a high tendency to agglomerate compared to wood residues, likely due to the high Si content and low Ca content in the rice straw ash. The formation of potassium silicates during the combustion of herbaceous biomass has been frequently observed (De Geyter *et al.,* 2007).

E Thermodynamic Modelling Tools

In the last decade, the use of tools based on chemical equilibrium has increased considerably. Advances in thermodynamic studies and viscosity models for oxide systems, along with the development of computational methods and improvements in computer software and hardware, have made it possible to predict equilibrium phases in complex systems with multiple components with a fair degree of accuracy (Hanxu *et al.,* 2006).

In the field of thermochemistry, one of the most widely used software programmes is Factsage™, a modelling tool capable of performing a wide range of equilibrium calculations. This software resulted from the combination of two thermochemical models, namely FACT-Win and

Chemsage, which perform calculations based on the concept of minimizing Gibbs free energy (Teixeira *et al*., 2014). Based on chemical equilibrium, Factsage™ provides information about the physical state of formed compounds, their proportions and compositions, the activity of individual chemical compounds, and thermodynamic properties over a wide range of temperatures and pressures (Doshi *et al*., 2009; Hanxu *et al*., 2006).This tool can be useful for predicting the tendency for fouling by estimating the amount of condensates and the fraction of molten compounds that may form during the thermochemical conversion of fuels. For example, in combustion, as the gaseous compounds cool, some of them may deposit in heat transfer areas of the combustion systems *(e.g.,* the top of the boiler and in gas ducts), leading to the formation of deposits. This software can also be useful for predicting the tendency for slagging or bed agglomeration, particularly through the formation of molten or softened oxides in the heat zone, due to radiation in combustion systems, depending on temperature, pressure, fuel chemical composition, and combustion atmosphere.

F Influence of biomass type in the pollutant's emissions

The inorganic ash components of biomass, as well as elements like nitrogen (N) and chlorine (Cl) play a significant role in the formation of aerosol and gaseous pollutant emissions.
For instance, Verma *et al*. (2012) observed that biomass fuels with higher Si content in the ashes produced the lowest total PM emissions. Carrol *et. al*. (2013) observed that biomass briquettes made from willow and pear trees (woody biomass) emit fewer particles than biomass briquettes made from straw and grass (herbaceous biomass). However, Huang et al (2023) review about pollutant emissions of industrial biomass boilers show that in case of the particulate matter lower than 2.5 µm ($PM_{2.5}$) higher values can be found for wood logs of spruce and willow (>4.5 g/kg), than for grass pellets or maize straw (*ca*. 1-2 g/kg). The use of flue gas technologies, such as electrostatic precipitators, high energy scrubbers and fabric filters is crucial to minimize the healthy and environmental problems provoked by the PM.

The NO_X emissions from the biomass combustion depend upon the amount of nitrogen in the fuels and the temperature of the boilers (Huang, 2023). The NO_x is especially high (>300 mg/m^3) in case of herbaceous biomass (barley straw, rape straw, wheat straw and miscanthus), but lower values are achieved for woody biomass. Orzen et al (2021) recommend that the non-woody biomass combustion should be accompanied by proper abatement measures given the usually high fuel-N content in these biomasses. For instance, Abelha *et al.* (2003) observed that the amounts NO_x and N_2O formed during the combustion of poultry litter (straw based) in a fluidised bed reactor were dependent on the staging of the secondary air and were lower that the permitted emission values with the effective staging of the secondary air.

The VOCs emissions are usually lower for woody biomass than for herbaceous biomass, values lower than 0.25g/kg were found for wood and switch grass, for straw it increases to values among 0.5 and 1g/kg. Wang *et al* (2014) also found a higher VOC content in herbaceous biomass than in woody biomass. However, a higher concentration was achieved for both types of biomasses, *i.e.* 2-7g/kg and < 1g/kg for herbaceous (straws of rice, wheat, bean and rape) and woody biomass, respectively. The differences can be related with the combustion conditions since field and stove burning was assessed. The authors identify some differences in VOC composition during the burning of different biomasses. Oxygenated VOC (o-VOC) were the largest contributors to the mass concentration of measured VOCs from straw burning, with a proportion of 49.4%, followed by alkenes 21.4%, aromatics 13.5%, alkanes 10.6% and halogenated VOC (x-VOC) 5.0%. More aromatics and x-VOC were emitted from wood burning compared with straw burning. Besides, field burning emitted more o-VOC due to more air being supplied during the burning test compared with stove burning, which show the relevance of combustion conditions.

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic compounds comprising two or more aromatic benzene rings that have received much attention due to their toxicity to humans. Colom-Diaz *et al.* (2017) evaluate the emissions of PAHs from the combustion of several biomass residues (furniture residues, grape pomace, kiwi residues, olive residues, wheat straw, rice husk and platanus residues) in a drop tube furnace. The authors observed that PAHs emission have two distinct features as the temperature varies: a decrease of PAHs as the temperature rises (*e.g.* furniture residues and wheat straw) and an emission maximum at 1000 °C (*e.g.* olive residues and rice husk). For all biomass residues the most significant PAHs are naphtalene and phenanthrene, followed by acenaphthylene, fluoranthene and pyrene. The grape pomace, kiwi residues and platanus residues presented the lowest PAHs emissions (< 100 mg/kg), while the highest PAHs emissions were found for the furniture residues (until 1200mg/kg fuel). Gulyurtlu *et al.* (2003) carried out one of the earliest studies to investigate how operating parameters, such as bed temperature, particle size, fuel moisture content, and the proportions of primary and secondary air, affect the formation of polycyclic aromatic hydrocarbons (PAHs) during coconut shell combustion in a small-scale pilot fluidized bed combustor. The authors verify that among the studied parameters, the excess air was the one that more influence the PAH formation, i.e., at 750 ºC, an increase of excess air from 20 to 80% resulted in a twelfth fold reduction of PAH emission. In addition, it was stated that the CO concentration can be employed as an indicator of PAH level in the exhaust gas. Zhang *et al* (2022) also evaluate the parameters that affect the PAHs formation during the biomass combustion. The authors stated that biomass with high volatile matter content can increase the formation of phenyl radicals that increase the PAH emissions, and potassium salts in biomass can act as catalysts for PAH formation. Burning of biomass with a high moisture content causes oxygen deficiency during combustion, which increases PAH formation and leads to a higher health risk. To overcome these issues, the authors suggested to increase the biomass density to reduce the biomass burning rates and decrease incomplete combustion leading to low PAH emissions. In addition, it was recommended to wash the biomass with deionized water and pelletizing, briquetting or carbonizing the biomass after drying the washed biomass.

2.2.3. Design of direct combustion technology

Direct combustion is responsible for more than 97% of global bioenergy production. This technology is the oldest and most common method of converting solid biomass into energy. Due to its simplicity and long-standing use, several commercial technologies have been developed to suit the specific properties of biomass and the scale of energy application. Biomass is the world's fourth largest energy resource, contributing about 14% of total energy supply. It is particularly critical in developing countries, where it accounts for about 35% of their energy consumption. The use of biomass as a fuel source offers significant environmental benefits, especially in terms of managing carbon emissions. Indeed, during its growth, biomass absorbs carbon dioxide (CO_2) from the atmosphere, which is then released during combustion. This cyclical process, in which the amount of CO_2 absorbed is equivalent to the amount of CO_2 emitted, means that the combustion of biomass does not contribute to net greenhouse gas emissions, thus facilitating the recycling of atmospheric CO_2 and mitigating climate change impacts (McGowan, 1991). Bio-fuels can be classified into three main categories: 1) commercially valuable wood and recycled fuels, 2) agricultural by-products of a generally lignocellulosic nature, including pits, shells and hulls; and 2) herbaceous materials, such as straws and grasses. Firewood, a traditional fuel, continues to be widely used, especially in rural areas and developing countries, for domestic heating (Demirbas, 2007). In addition to wood, wood chips, derived from residues of forestry operations or wood processing industries, are widely used in large-scale bioenergy plants and district heating systems due to their low moisture content and ease of handling (Cowie et al., 2021). Another common fuel is wood pellets, made from compressed sawdust and shavings. Pellets are a densified form of biomass that provides higher energy content per unit volume than raw wood, making them a preferred choice in modern combustion systems, including residential stoves and industrial boilers (Thrän et al., 2019). Forest residues, such as tree tops, branches and bark left after logging operations, are also often collected and used as fuel, contributing to renewable energy production in many regions of Europe (Sikkema et al., 2011). Among agricultural residues, one of the most used materials is rice husk, a by-product of rice processing. This fuel is readily available in many rice-producing countries and is commonly used in small boilers and industrial plants due to its high silica content and low energy density (Bhattacharya et al., 1990). Similarly, corn stools, which include stalks and leaves, are often used in direct combustion systems for energy production, especially in rural areas or in bioenergy plants (Graham et al., 2007). Miscanthus, a herbaceous perennial plant known for its high biomass yield, is grown specifically for energy production and has gained popularity in direct combustion applications due to its substantial energy content (Lewandowski et al., 2000). Panicum virgatum (switchgrass) is also a suitable grass for bioenergy production. It thrives in low-quality soils and is ideal for combustion due to its high carbon content and minimal input requirements (McLaughlin and Adams Kszos, 2005). Regardless of the origin of biomass, it has unique characteristics based on composition, moisture content, and inorganic elements, all of which affect combustion behaviour. Organic matter in biomass, produced through photosynthesis and respiration, is composed of cellulose, hemicellulose, lignin, and various carbohydrates, which store most of its energy. The concentration of each class of compound varies according to plant species, tissue type, development stage, and growing conditions. In addition to its organic composition, biomass contains a considerable fraction of inorganic elements such as potassium, sodium, chlorine, sulphur, and silicon. These elements are crucial to understanding ash fouling, slagging, and bed agglomeration in combustion systems. For example, silicon and potassium, common in herbaceous fuels such as straws and grass, are major constituents of ash, along with chlorine. The presence of these elements can increase the problems of promoting corrosion and harmful emissions. Silica and sulphur can react with alkalis to form alkali silicates and alkali sulphates, respectively. These compounds have low melting points and contribute to fouling on combustion chamber heat transfer surfaces (Baxter et al., 1998). As reported above, moisture content is another critical factor in biomass combustion. The amount of water present in the biomass can significantly affect the energy balance and combustion efficiency. Moisture levels are typically expressed on a dry or wet basis, with biomass generally containing up to 25% moisture under normal atmospheric conditions. High moisture content reduces the heating value of the biomass, as energy is consumed to evaporate the water during combustion. This can lead to lower flame temperatures, incomplete combustion, and a decrease in overall system efficiency. In terms of combustion efficiency, biomass is highly oxygenated compared to fossil fuels. On average, dry biomass contains 30-40% oxygen, while the carbon content varies from 30-60%, depending on the specific type of biomass. This higher oxygen content contributes to the lower energy density of biomass compared to fossil fuels but also facilitates combustion. The molar ratios of hydrogen to carbon and oxygen to carbon in biomass are consistent among the various feedstocks, with the general composition being represented by the formula $CH_{1.41}O_{0.64}$. These ratios indicate the presence of complex carbohydrate structures, such as cellulose and lignin, which determine the combustion characteristics of biomass (Jenkins et al., 1998). Furthermore, the combustion process is non-selective, which means that biomass is reduced to carbon dioxide, water, and smaller quantities of other compounds. Unlike biochemical conversion methods that focus on specific components such as sugars or starches, combustion utilizes the entire biomass. This makes it a versatile process, applicable to various biomass types and residues, from woody materials to agricultural by-products. However, the inorganic content, particularly ash-forming elements, must be carefully managed to prevent operational issues in combustion systems. Overall, the type of biomass used in combustion systems plays a significant role in determining the efficiency, emissions, and operational challenges of the system. Biomass with high moisture content, abundant alkali metals, or other problematic inorganics may require pre-treatment, such as drying, to improve combustion performance.

Biomass combustion technologies include traditional and modern power generation systems, from basic applications such as cooking stoves to advanced and highly efficient power plants. Total annual biomass energy use is estimated at 33.5 EJ for traditional uses and 16.6 EJ for modern combustion (Koppejan and van Loo, 2007). The main use of biomass through combustion remains in traditional cooking, heating, and lighting, especially in developing countries. However, emissions from these systems pose significant health risks and contribute to greenhouse gas emissions (Yinping Zhang et al., 2022). Biomass combustors are classified into small-scale systems, mainly for residential or commercial heating, and large-scale systems designed for power and heat generation. At the industrial level, the use of biomass is also expanding, with its co-firing alongside coal and other fuels for energy and heat production. Small-scale biomass combustors are designed primarily for residential heating and cooking. Efforts to modernize these systems have focused on improving efficiency and reducing pollutant emissions, such as carbon monoxide (CO), polycyclic aromatic hydrocarbons (PAHs) and particulate matter (PM). Newer stoves incorporate automatic control and pre-processed fuels such as biomass pellets, which provide better combustion regulation and significantly lower emissions than traditional wood-burning systems. Advanced stoves equipped with catalytic combustors have been proven to further reduce CO and PM emissions by improving combustion efficiency. These catalytic units support reactions at lower temperatures, resulting in cleaner exhaust gases. However, the high cost and ongoing maintenance requirements of the catalyst present a persistent challenge to their widespread adoption (Ghorashi and Khandelwal, 2023). Among additional methods to control emissions from small-scale biomass combustion systems, electrostatic precipitators and baghouses are emerging and becoming increasingly common. Not least, research coordinated by the International Energy Agency (IEA) continues to advance small-scale biomass combustion technologies, focusing on improved designs, emission control, and fuel efficiency (IEA Bioenergy, 2007a). Large-scale plants mainly use the Rankine or steam cycle, in which biomass fuels are burned in a boiler to generate steam. The steam is then directed into one or more turbines that drive an electric generator.

Steam pressure in these plants typically ranges between 6 and 17 MPa, with temperatures up to 540°C (Wiltsee G., 2000). In biomass energy systems up to a few megawatts, reciprocating and screw steam engines are used instead of steam turbines. In these configurations, exhaust steam is condensed, and water is recirculated to the boiler via feed pumps. Combustion products are treated before being released into the atmosphere using cleaning technologies such as wet or dry scrubbers to control sulphur and chlorine, especially in waste-to-energy (WTE) units that burn municipal solid waste (MSW). Additional equipment such as cyclones, high-temperature cloth filters (baghouses), and electrostatic precipitators are used to remove particulate matter (PM). Systems can also include selective catalytic reduction (SCR) or selective non-catalytic reduction (SNCR) to control nitrogen oxide (NOx) emissions, while proper air-fuel ratio management helps keep carbon monoxide and hydrocarbon (HC) emissions low. Organic Rankine Cycles (ORCs), which replace water with organic fluids, are typically used in low-temperature applications such as waste heat recovery and solar thermal systems. Table 4 highlights the main advantages and disadvantages for each type of biomass combustion system (Yin et al., 2008).

Table 4. Type of biomass combustion systems

Combustion type	Advantages	Disadvantages
Grate Furnaces	• Economical in terms of operational costs. • Can handle a wide variation in fuel quality (moisture, particle size).	• Fair dust load in flue-gas Non-homogenous combustion Requires unique designs for mixing fuels like wood and herbaceous fuel. • Efficiency drops with excess oxygen (7-8% by volume).
Suspension Burners	• Very high specific capacity.	• Feedstock moisture must be ≤ 15%. • Requires feedstock drying and size reduction to minimize discharges and unburnt residues.
Underfeed Stokers	• Low investment cost • Simple system with good load control due to continuous fuel feeding.	• Suitable only for feedstock with lower ash content (e.g., woodchips, sawdust). • Limited to small-scale operations (boiler capacity < 6 MWth).
Circulating Fluidized Bed Furnaces	• High turbulence enhances heat transfer. • Suitable for various biomass types with different moisture content. • High efficiency due to very low excess oxygen (1-2% by volume).	• Uneconomical for boiler capacities > 30 MWth. • Prone to bed agglomeration with high-alkaline feedstocks (e.g., straw). • High dust content in flue-gas.
Bubbling Fluidized	• No moving parts in the hot combustion chamber.	• No moving parts in the hot combustion chamber.

Bed Furnaces	• Suitable for a wide range of biomass types with varying moisture content. • Higher efficiency due to lower excess oxygen (3-4% by volume)	• Suitable for a wide range of biomass types with varying moisture content. • Higher efficiency due to lower excess oxygen (3-4% by volume).

The efficiency gap between biomass power plants and their fossil fuel counterparts is certainly a challenge to address. In general, biomass power plants operate at lower efficiencies for several reasons. The higher moisture content in biomass fuel requires more energy to dry the fuel before combustion can take place effectively. This reduces the overall efficiency compared to fossil fuels, which have a lower moisture content. Moreover, in biomass systems, steam temperatures, and pressures are kept lower to mitigate fouling- deposits of ash and other materials on heat transfer surfaces - that can occur instead at higher flue gas temperatures. Such fouling can lead to corrosion, reduced performance and costly maintenance shutdowns. Biomass power plants tend to be smaller in size, which inherently limits their efficiency. Smaller plants require more energy to run internal components such as pumps, fans and conveyors than they produce. However, there is promising research on biomass integrated gasification combined cycles (BIGCC), which are expected to achieve electrical efficiencies of more than 35% (Craig and Mann, 1996). The co-firing of biomass with fossil fuels in larger, more efficient coal-fired plants is another promising strategy, as it allows the greater efficiencies of fossil fuel infrastructures to be utilised while reducing overall carbon emissions. In terms of efficiency, CHP applications stand out as a particularly beneficial use of biomass. These systems can achieve efficiencies of 80% or more, utilizing not only the electricity generated but also the heat that would otherwise be wasted in energy-only plants (Damstedt et al., 2007). This makes CHP an attractive solution for industries and communities seeking to maximize energy efficiency while reducing reliance on fossil fuels. Finally, it’s important to note that the type of combustor used in biomass power plants can impact overall performance. Whether using grate burners, suspension burners, or fluidized bed systems, each has its strengths and limitations. Fluidized beds, for instance, introduce an intervening heat-transfer medium and are particularly well-suited for handling fuels that are prone to fouling, but each technology presents different challenges related to fuel particle velocity, emissions, and operational considerations. Table 5 shows the advantages and disadvantages of biomass combustion (Li et al., 2012).

Table 5. Listed advantages and disadvantages of direct combustion

Advantages	Disadvantages
• Significant net carbon emission reductions compared to fossil fuels, thus contributing to a cleaner development mechanism (CDM) for diminishing greenhouse gas (GHG) emissions.	• High-temperature combustion in fixed-bed systems can lead to issues such as agglomeration, fouling, slagging, and corrosion, particularly from the by-product ash due to the coalescence of molten particles.
• Transformation of waste wood materials, such as sawdust or wood chips, into pellets that can be utilized as a biomass energy source to generate electricity.	• Biomass fuel supply is often limited to economically feasible sources, such as waste wood products or by-products from agro-processing operations.
• Co-firing, such as using straw with coal, is another efficient option for larger power plants, producing lower emissions of CO_2, SOx, and NOx.	• Harvesting whole trees for biomass may not be the most effective way to ensure low-carbon electricity production.

However, while the efficiencies of biomass power plants are generally lower than those of fossil-fuel plants, innovations such as BIGCCs, co-firing, and CHP applications offer promising pathways to close the gap. Biomass plays a critical role in diversifying our energy mix and reducing our carbon footprint, and with ongoing research and technological improvements, it is possible to enhance its efficiency and overall viability. Biomass combustion technologies continue to evolve, with significant advancements in both small-scale and large-scale systems. Efforts to reduce emissions and improve efficiency are driving innovation in stove design, power plant operation, and fuel utilization. While challenges remain, particularly in controlling emissions, fouling, and efficiency, biomass combustion remains a key component of global energy strategies, particularly for achieving renewable energy goals and reducing greenhouse gas emissions.

2.2.4. The technology status of combustion technology design

Biomass direct combustion technology is a well-established method for converting biomass into heat and power. The Technology Readiness Levels (TRLs) for biomass direct combustion typically range from TRL 7 to TRL 9, indicating that these technologies are in the demonstration to full commercial application stages (Liao, W., 2024).

2.2.5. Advantages and disadvantages of combustion technology design

Key Points about Biomass Direct Combustion are:

Feedstock Suitability: Waste biomass combustion is a highly versatile process, capable of utilizing a broad spectrum of feedstocks, including woody biomass, herbaceous biomass, fruit biomass as well as a category known as "blends and mixtures." This adaptability allows for the effective conversion of various organic materials into energy, making waste biomass an attractive renewable resource.

Advantages: One of the standout benefits of waste biomass combustion is its high efficiency in transforming biomass into heat and power. The technology is well established, with mature processes that are well understood and have been extensively optimized over time. Additionally, existing coal-fired power plants can often integrate waste biomass combustion systems with minimal modifications, facilitating a smoother transition toward more sustainable energy production (Chen, S. et al., 2020).

Disadvantages: However, biomass combustion does come with certain challenges. Emissions control is critical to minimize pollutants, which is a significant concern in maintaining environmental standards. Furthermore, a consistent supply of biomass feedstock is essential for reliable operation, necessitating effective management of supply chains. The disposal of ash generated during combustion can also pose logistical challenges that must be addressed to ensure efficient operation.

Operating Conditions: Biomass combustion systems typically operate at atmospheric pressure, although some advanced systems may employ pressurized combustion to enhance efficiency. This adaptation can lead to improved performance and higher energy output, further maximizing the potential of biomass as an energy source.

Conversion Efficiency: Modern waste biomass combustion systems are capable of achieving efficiencies of over 90% under optimized conditions (IEA Bioenergy, 2023). This high conversion efficiency highlights biomass as a promising and viable renewable energy option, capable of contributing significantly to sustainable energy solutions.

2.3. Pyrolysis

2.3.1. General review and evaluation of Biomass types for Pyrolysis conversion technology

Pyrolysis is a foundational thermochemical process and the precursor to both gasification and combustion of waste biomass (Bhaskar et al., 2013). It involves the thermal decomposition of materials under high temperatures in an oxygen-free environment. During pyrolysis, complex organic compounds break down into simpler molecules, resulting in the formation of gases, liquids (such as bio-oil), and a solid char residue. This process not only releases energy but also generates valuable intermediate products, which can be further utilized in bio-fuel production, chemical synthesis, and other applications.

Pyrolysis is a thermochemical process that converts biomass into valuable products such as bio-char, bio-oil, and syngas. The efficiency and product distribution of pyrolysis depend significantly on the type of waste biomass used. This review evaluates various waste biomass types suitable for pyrolysis conversion technology, highlighting their characteristics, advantages, and challenges.

Agricultural Residues, including straw, husks, and stalks, are characterized by high cellulose and hemicellulose content, with moderate ash levels. They are abundant and inexpensive feedstock, making them an attractive option for pyrolysis. However, there are several issues and challenges (e.g. high ash content) associated with their use, as well as necessary pretreatments to optimize the conversion process.

Agro-industrial biomass, such as fruit peels, vegetable and fruit pomace, shells, fruit kernels/stones/pits etc, are generally suitable for pyrolysis technologies. Nevertheless, this kind of waste biomass often require pretreatment (e.g. drying, size reduction and cleaning) before pyrolysis to ensure optimal performance and product yield.

Forest/wood biomass, such as forest residues, wood processing industry residues etc, are generally suitable for pyrolysis. Nevertheless, they often require pretreatments to reduce moisture content, size reduction, reducing high ash content, cleaning etc, before they can be used in suitable pyrolysis technologies.

Organic parts of Municipal Solid Waste (MSW), such as food waste, paper and cardboard, yard waste, wood waste etc, are well-suited for pyrolysis, which can convert them into valuable products. Organic parts of MSW presents a heterogeneous composition, often characterized by high moisture and ash content. Utilizing organic parts of MSW can reduce landfill waste and enable energy recovery, but it requires extensive sorting, preprocessing, drying, and size reduction to separate valuable materials and minimize contaminants.

Several factors significantly influence the pyrolysis process. The chemical composition of the biomass, including lignin, cellulose, and hemicellulose content, plays a critical role in determining the yield and quality of pyrolysis products. Additionally, high moisture content can reduce the efficiency of the pyrolysis process and increase energy consumption for drying. Biomass with elevated ash content can also lead to operational challenges, such as slagging and fouling in the reactor. Finally, smaller particle sizes generally enhance heat transfer and reaction rates, leading to more efficient pyrolysis.

Selecting the appropriate waste biomass type is crucial for optimizing pyrolysis conversion technology. Each biomass type presents unique advantages and challenges that must be carefully considered to achieve efficient and sustainable bioenergy production. By understanding the characteristics of various waste biomass sources, researchers and practitioners can improve the overall efficiency and effectiveness of pyrolysis processes, contributing to a more sustainable energy.

In this section, for each different pyrolysis technology, suitable waste biomass and its pretreatment processes are presented.

2.3.2. Design of Pyrolysis technology

Pyrolysis is a thermal decomposition process that occurs in the absence of oxygen, breaking down organic material into gases, liquids (bio-oil), and solid residues (bio-char). The design of pyrolysis technology involves optimizing reactor configurations, feedstock preparation, temperature control, and process parameters to achieve the desired product distribution. This section will explore the key considerations and engineering principles required for efficient pyrolysis system design, focusing on maximizing energy yield and improving overall system performance.

A Slow Pyrolysis (Carbonisation)

Waste biomass suitable for Slow Pyrolysis

Many types of waste biomasses can be used in the slow pyrolysis process to produce bio-char, from forest/woody biomass, agricultural biomass, industrial waste, organic parts of municipal solid waste, and non-traditional biomass (such as algae, sewage sludge, animal manure, etc.). Most of these biomasses, except for dedicated crops or algae, are available in large quantities, some are easily accessible and have low costs. Industrial wastes and agricultural and forestry/woody biomass wastes are easier to convert into bio-char, while municipal solid waste and other non-traditional materials are not easily processed uniformly due to their great variety and heterogeneity (Wang et al., 2023).

Forest biomasses include wood chips, stumps, bark, stems, branches, and leaves, while agricultural biomasses comprise residues from various crops such as husks, stalks, straws, flowers, and grass (Tripathi et al., 2016).

The composition of biomass is a crucial determinant of the properties and yield of bio-char. Some important biomass properties to be considered are cellulose, hemicellulose, and lignin content, physical properties (density, particle size, moisture content), and chemical composition (ash, carbon (C), oxygen (O), hydrogen (H), nitrogen (N), sulfur (S) content).

Biomass properties

The composition of biomass is one of the main aspects to be considered when selecting biomass for the slow pyrolysis process. Forestry/woody and agricultural biomass wastes are the most used biomasses for bio-char production (Sørmo et al., 2020), due to their composition (lignin (10 – 40 wt%), cellulose (25 – 50 wt%), and hemicellulose (15 – 40 wt%), with varying amounts of minerals and other components) (Kan et al., 2016). These biomasses are characterized by high bulk density and calorific value, and low moisture and ash contents. Lignocellulosic biomass has a higher proportion of lignin and is more suitable for bio-char production. The lignin content is directly related to the yield of the bio-char, as the lignin is more resistant to thermal decomposition and properties of the bio-char such as the specific surface area (Al-Rumaihi et al., 2022; Ippolito et al., 2020; Rijo et al., 2022). Both lignin and cellulose have a positive influence on the yield of bio-char, but a higher yield of bio-char is achieved when the biomass contains more lignin than cellulose (Keiluweit et al., 2010; Tripathi et al., 2016). For example, eucalyptus residues that had a higher lignin content (23 %) compared to pine residues led to a higher yield of bio-char, around 42 % (Rijo et al., 2022). Wood-based feedstocks, when pyrolyzed, result in a more robust, coarse bio-char that can be up to 80% carbon (Al-Rumaihi et al., 2022). In addition, bio-char based on woody biomass has a higher specific surface area and total pore volume, probably due to the lower ash content and volatilization of water and volatiles and the loss of organic compounds from macromolecules. The higher surface area and porosity of the bio-char can also be attributed to the preservation of the pore structure by the stability of the lignin during pyrolysis (Ippolito et al., 2020; Leng et al., 2021).

Biomass has a complex chemical composition involving C, O, S, N, ash, and trace amounts of metals. The proportions of C, H, and O in biomass are the primary contributors to the energy content of bio-char. Given the high content of C in forest and agricultural biomass, the corresponding bio-char exhibits a high calorific value. The energy content of bio-char, as measured by its higher heating value (HHV) on a dry basis, is positively correlated with its carbon and hydrogen contents and negatively correlated with its oxygen content (Khan et al., 2009; Tripathi et al., 2016). The presence of N and S in biomass is undesirable, as slow pyrolysis can lead to the formation and release of toxic gases such as SO_x and NO_x. While forest and agricultural biomass wastes have very low levels of these elements, non-traditional biomass (animal residues, sewage sludge, and algae) and industrial and municipal solid wastes contain significant amounts of S and/or N (Tripathi et al., 2016).

Regarding ash content, biomass wastes with a high ash content, such as some agricultural wastes, also produce bio-char with a high ash content, a higher pH and a low micropore surface area. These bio-chars could be interesting for soil improvement, helping to regulate acidic soils and replace or retain minerals and nutrients in the soil (Ippolito et al., 2020; Leng et al., 2021). Additional biomass properties can also serve as indicators of pyrolysis product yields and their characteristics, including moisture content, fixed carbon, and volatile matter. Biomass moisture content impacts heat transfer during pyrolysis, and a higher moisture content results in lower bio-char yields and increased energy consumption, ultimately leading to higher process costs (Monir et al., 2018; Tripathi et al., 2016). High values of fixed carbon enhance bio-char production, whereas syngas and bio-oil yields are favored by high volatile matter content in biomass (Monir et al., 2018).

The properties of biomass, many of which have been discussed, often do not align with the ideal requirements for slow pyrolysis. Therefore, pre-treatments may be necessary.

Feedstock preparation

The biomass pre-treatment process is a fundamental step in increasing pyrolysis efficiency. Biomass can be pre-treated by physical processes (grinding and densification), thermal processes (drying, torrefaction, and steam explosion or treatment with liquid hot water), chemical processes (treatment with bases, acids, and ionic liquids), biological processes (treatment with fungi and microbial consortium) or a combination of these (Kan et al., 2016).

Physical pretreatment

Physical pretreatments include reducing the size of the biomass, which can be done by grinding, and densification, which can be achieved essentially by pelletizing. Grinding biomass makes it easier to feed into reactors and small biomass sizes promote heat and mass transfer, improving the performance of slow pyrolysis (Kan et al., 2016). The reduction of biomass particles allows for an increase in the surface area of the derived bio-char and the enrichment in oxygen-containing functional groups (Kumar et al., 2020). Nevertheless, small biomass particles imply a shorter distance for the heat to travel inside the particles, thus accelerating the rate of heat flow and decreasing the yield of the bio-char (Al-Rumaihi et al., 2022). In addition, reducing the size of the biomass particle increases the cost of the operation. According to Bruna et al. (2022), the raw materials for slow pyrolysis can be between 5-50 mm in size(Rijo et al., 2022). Densification by pelletizing is another physical pre-treatment that makes it possible to homogenize the biomass properties, reduce the moisture content, and increase the apparent and energy density of the biomass, while at the same time facilitating the handling and fluidity of the material (Kan et al., 2016; Rezaei et al., 2020). The biomass is pre-treated with physical processes to improve the physicochemical properties of the derived char, along with improving the surface area and pore volume (Ganesapillai et al., 2023).

Thermal pretreatment

The main purpose of thermal pretreatment is to remove water from the biomass and to increase the carbon content of the derived bio-char (Ganesapillai et al., 2023). One of the main thermal methods for pre-treating biomass before slow pyrolysis is drying, which has the advantage of increasing the energy efficiency of the pyrolysis process (Kan et al., 2016). Since the water present in the biomass needs to be vaporized during pyrolysis, reducing the water content by drying will reduce the amount of energy needed in the pyrolysis process to increase the pyrolysis temperature (Hu and Gholizadeh, 2019).

Chemical pretreatment

Chemical pretreatment aims to reduce polymerization, crystallinity, and mineral content while increasing the biodegradability and adsorption capacity of bio-char derived from slow pyrolysis (Ganesapillai et al., 2023). Washing with water or acids is one of the chemical methods used to remove dirt and inorganic minerals on the surface of biomass particles or structural minerals within the biomass matrix (Kan et al., 2016). Pretreatment with hydrochloric acid (HCl) can reduce the ash content in the derived bio-char. Alkaline pretreatment can result in higher total pore volume and specific surface area of the derived bio-char, making the treated biomass suitable to produce bio-char for use as an adsorbent (Ganesapillai et al., 2023).

Biological pretreatment

Biological pretreatments are slower pre-treatments, but they have a better environmental footprint and consume less energy than physical and chemical pre-treatments. These processes use biological microorganisms to improve the properties of the biomass and, consequently, the derived bio-char and improve the efficiency of the slow pyrolysis performance (Kan et al., 2016). As an example, corn straw was pre-treated with white-rot fungi before the slow pyrolysis process. The results showed a reduction of up to 35°C in the initiation temperature of biomass decomposition during pyrolysis, compared to non-retreated biomass. The sulfur content in the biomass was also reduced by 30- 45 %, which contributed to the reduction of sulfur-based toxic emissions during the slow pyrolysis process (Yang et al., 2010).

Description of slow pyrolysis

Slow pyrolysis, or conventional pyrolysis, also known as carbonization, is an ancient pyrolysis technique applied to maximize the yield of the solid product, and therefore to produce charcoal (Kan et al., 2016). It is a process where biomass is thermally decomposed at relatively low temperatures (~300-700 °C), under atmospheric pressure, in an inert atmosphere (usually N_2), with little or no oxygen, for a long residence time and using low heating rates (less than 1 °C/s). These turn out to be the operating conditions that most influence the yield and properties of bio-char. Slow pyrolysis is an endothermic process, and an external energy source usually provides the heat of the process. The relatively low temperature and slowness of the process (high residence time and low heating rate) favor cracking and secondary reactions, which lead to higher bio-char yields. Slow pyrolysis has a bio-char yield of around 35 % by weight, 35 % by weight of gas, and 30 % by bio-oil (Feliz Florian et al., 2024; Kan et al., 2016; Premchand et al., 2023; Rijo et al., 2022; Ronsse et al., 2013).

Influence of the process parameters on the product characteristics

Temperature

During the slow pyrolysis process, being a thermochemical process, temperature is a crucial parameter for the yield of bio-char and its physicochemical properties (Al-Rumaihi et al., 2022). The higher the temperature, the lower the yield of char and the hydrogen and oxygen content in the bio-char. On the other hand, high temperatures promote an increase in carbon content, pH, surface area, and pore diameter (Feliz Florian et al., 2024; Hu and Gholizadeh, 2019). In the study performed by Zhang et al. (2015), it was shown that as the temperature of slow pyrolysis of straw and lignosulfonate increased, the properties of bio-char such as total carbon and ash content, pH, stability, porosity, and aromaticity were improved. On the other hand, the opposite effect was observed for bio-char yield, total hydrogen, oxygen, nitrogen, and sulfur content, and volatile matter (Zhang et al., 2015).

Heating rate

The heating rate is the main parameter that distinguishes slow pyrolysis from other types of pyrolysis (Hu and Gholizadeh, 2019). The heating rate affects the distribution and composition of pyrolytic products, as it has a direct impact on the rates of degradation and devolatilization of biomass in inert atmospheres (Al-Rumaihi et al., 2022; Modak et al., 2024). At constant temperatures, varying heating rates can influence the dynamics of heat and mass transfer within the pyrolysis reactor. A higher heating rate promotes secondary cracking reactions, producing more volatiles (bio-oil) and less bio-char (Hu and Gholizadeh, 2019; Modak et al., 2024). Under these conditions, the bio-char produced has a smaller pore volume and low surface area due to the greater evaporation of volatile matter (Al-Rumaihi et al., 2022). At slower heating rates, secondary slow pyrolysis reactions are favored, and re-polymerization and re-condensation reactions occur leading to the formation of more bio-char (Al-Rumaihi et al., 2022; Modak et al., 2024).

Residence time

When the biomass remains in the reactor for longer period, secondary reactions can occur, producing secondary products such as bio-char. However, excessively long residence times result in an intensified biomass decomposition. Such extended periods are often inefficient, demand excessive energy, and can compromise the quality of the resulting bio-char (Afshar and Mofatteh, 2024). According to Li et al. (2024), temperature and time can be negatively correlated with the mass yield of bio-char. Despite this, variations in residence time seem to have little influence on the heating value of bio-char (Li et al., 2024). Zhang et al. (2015) demonstrated that the residence time during the production of straw and lignosulfonate bio-char had no significant effect on the properties of the bio-char. While residence time by itself doesn't greatly affect bio-char properties, it becomes more important when considered alongside temperature. Therefore, the impact of residence time on bio-char characteristics should not be overlooked (Afshar and Mofatteh, 2024).

Reaction medium

Slow pyrolysis takes place in an inert atmosphere, with N_2 being the most used purge gas due to its availability and cost-effectiveness (Al-Rumaihi et al., 2022; Ganesapillai et al., 2023). Other gases have been used as carriers, such as CO_2, H_2O, CO, CH_4, H_2 and argon (Ganesapillai et al., 2023; Hu and Gholizadeh, 2019). These gases are used to change the mechanism of the pyrolysis reactions, influencing product yields and product properties, such as functional groups distribution and energy content, among others (Hu and Gholizadeh, 2019). Replacing N_2 with a CO_2 atmosphere has several advantages including greater conversion of biomass into pyrolysis products, greater reactivity, and greater overall efficiency. In addition, the CO_2 produced in the pyrolysis gas stream can be recycled to the pyrolizer, which would improve its performance and mitigate greenhouse gas emissions. However, slow pyrolysis in a CO_2 atmosphere produces fewer char compared to other atmospheres. As CO_2 seems to have an affinity for reacting with hydrogenated and oxygenated groups, the bio-char resulting from slow pyrolysis is richer in carbon. Furthermore, the bio-char obtained under a CO_2 atmosphere has a larger surface area and is more porous and recalcitrant than that produced in an N_2 atmosphere (Hu and Gholizadeh, 2019; Lu et al., 2020; Premchand et al., 2023). Other atmospheres, such as water vapor (H_2O), have also been investigated. In the study done by Juncheng Ouyang et al. (2020), pyrolysis was studied in an atmosphere of N_2, CO_2, and H_2O. It was found that CO_2 and H_2O atmospheres resulted in low bio-char yields compared to the N_2 atmosphere. The bio-char yields were 71.4 %, 68.1 %, and 66.1 % for the N_2, CO_2 and H_2O atmospheres, respectively. The atmosphere containing H_2O produced a bio-char with a greater surface area and high pore volume due to the release of volatiles which promote the development of more pores. This leads to a disordered structure, with more active carbon sites and greater reactivity. These characteristics are more evident in an atmosphere containing H_2O than in an atmosphere containing CO_2 (Ouyang et al., 2020).

Pyrolysis Reactor Design

The most common reactors used in slow pyrolysis are electric or muffle furnaces, screw/worm reactors, drums, tubular reactors, and rotary kilns (Ganesapillai et al., 2023; Hu and Gholizadeh, 2019; Lu et al., 2020). Existing reactors can be classified into different types, according to the heating method, or based on how the process works: batch processes (fixed bed reactors), semi-continuous and continuous processes (Nicolae et al., 2019). Commercial applications of slow pyrolysis for bio-char production mainly use continuous processes, such as screw pyrolizers and rotary kilns, due to the higher yield, energy efficiency, and quality of the bio-char produced (Panwar et al., 2019). The description, advantages and disadvantages of the main slow pyrolysis reactors are shown in Table 6.

Table 6. A summary of slow pyrolysis reactor types. Adapted from (Al-Rumaihi et al., 2022; Cai et al., 2021; Ganesapillai et al., 2023; Garcia-Nunez et al., 2017; Nicolae et al., 2019; Wang et al., 2022).

Reactor type	Reactor mechanism	Advantages	Disadvantages
Batch reactor	The feedstock does not move within the reactor, and the bio-char can only be collected once it is cooled	Can cope with a range of feedstocks Straightforward technology, very cheap to construct Low heating rate Low costs	Difficult to feed continuously Low char yields (5–20 wt. %) Require significant time for operation Difficulties in scaling up
Semi-continuous reactor	The feeding of the feedstock and the discharge of the bio-char can be carried out simultaneously	It can be an energy-efficient process since the gas produced is usually burned in a combustion chamber to provide energy for drying or for the pyrolysis stages.	Low bio-char production rate due to not-uniform heat and mass transfer Can have a high operating cost
Continuous reactor **(Screw/Auger reactor)**	It consists of a helical screw that rotates inside a horizontal tubular reactor. The screw moves the feedstock along the axis	Simplicity of construction and operation Ability to handle a wide variety of feedstocks High yields of bio-char	Difficulty in scaling up Issues related to heat transfer to the middle of the feedstock particle

	and ensures uniform mixing of the feedstock	Manageable residence time, controlled by the auger speed	Mechanical wear and tear of the reactor Higher residence times
Continuous reactor **(Rotary kilns/drum)**	The reactor consists of a cylindrical casing that rotates around its axis, and the material is kept inside and mixed gradually. The residence time is controlled by the angle of the drum and the speed of rotation.	Allows uniform mixing of the feedstock and heat transfer through a tumbling motion Easy process control and low energy requirements Flexibility in terms of shapes and sizes of the feedstock (widely used for tires, sewage sludge, MSW, and plastics wastes). Short residence time and better heating efficiency than batch reactors	Slower heating rate Difficulty to seal the rotary kiln Severe wear on the reactor caused by energetic collisions and friction between the feedstock particles and the reactor walls Additional drive to maintain the long-term rotation
Retorts **Lambiotte/Lurgi retorts**	Vertical reactors. The feedstock is fed from the top and slowly flows down the reactor with a counter-current flow of hot inert gas that dries the feedstock and increases the temperature	High level of automation Mature technology with commercial plants in operation for several years It can be an energy-efficient process since the gas produced is usually burned in a combustion chamber to provide energy for drying or for the pyrolysis stages. Higher yields of bio-char and good quality	Sensitivity to feedstock moisture content (should be below 25wt. %) Higher reactor wear caused by friction Long residence time Some corrosion of the reactor may occur due to the production of acetic acid.

Applications

Due to its physicochemical properties, such as its porous structure, specific surface area, surface chemistry, and high content of carbon, oxygen, hydrogen, ash, sulfur and nitrogen, bio-char is known for its versatility of application. Bio-char can be applied in various fields, from environmental and agricultural to industrial and materials, among others (Afshar and Mofatteh, 2024).

Environmental and agricultural applications

In the environmental field, bio-char can be applied in various processes, from soil improvement, adsorption of pollutants, carbon sequestration, and reduction of greenhouse gas emissions (Afshar and Mofatteh, 2024; Ganesapillai et al., 2023; Garcia et al., 2022; Gargiulo et al., 2018; Mcintyre and Li, 2024). The following is a short description of these applications and related studies.

Soil improvement, carbon sequestration, and reduction of greenhouse gas emissions:

The use of bio-char in soil aims to improve soil properties such as nutrient and water retention, cation exchange capacity, electrical conductivity, pH, soil fertility, and productivity. In addition, bio-char can be used to remove contaminants such as heavy metals and organic pollutants from the soil (Afshar and Mofatteh, 2024; Santos et al., 2024). For example, olive stone bio-char with large amounts of phosphorus and nitrogen in its composition had a positive influence when applied to tomato seedling crops, helping growth and increasing the crop's resistance to pests and diseases (Karakaş et al., 2017). Adding bio-char made from chicken manure and rapeseed straw to soil polluted with heavy metals was found to significantly improve soil quality by increasing its pH, ability to hold nutrients (cation exchange capacity), and organic matter content. It could therefore serve as an alternative in situ material to remediate soils contaminated with heavy metals (Zhao et al., 2016). Hydrological characteristics can also be improved by adding bio-char to the soil. For example, soil moisture can be increased by between 15 % and 30 %, which would reduce the need for irrigation during periods of drought and increase water use efficiency (Mcintyre and Li, 2024). The addition of bio-char to the soil allows carbon to be fixed in stable aromatic bonds, which reduces the immediate release of labile carbon into the atmosphere and contributes to the reduction of greenhouse gas emissions (Garcia et al., 2022). Bio-char in the soil can adsorb NH_4^+ and NO_3^-, preventing their leaching and making them less available for denitrification processes, thus reducing N_2O emissions (Mcintyre and Li, 2024).

Pollutant adsorption:

Bio-char can also be used to remove pollutants from liquid and gaseous effluents in the environment. Bio-char is commonly used as an adsorbent in wastewater treatment plants to remove pharmaceuticals and heavy metals. Pine biomass bio-char was applied as a low-cost sorbent to remove heavy metals from rainwater, and the results indicated high removal efficiencies for Pb, Cr and Cu (Esfandiar et al., 2022). Pollutants such as mercury (Hg) present in the combustion gases were removed by the bio-char, achieving a removal efficiency of 65.9 % when the bio-char is activated. This Hg removal efficiency is comparable to that of commercial activated carbon. Being a cheaper material than commercial activated carbon, bio-char proves to be an economical adsorbent for removing contaminants (Santos et al., 2024). Bio-char can be also exploited as solid sorbents in post-combustion CO2 capture process. Bio-char prepared from wood was also used to separate CO_2/N_2 and CO_2 /CH_4 gas mixtures and showed good selectivity for CO_2(Gargiulo et al., 2018).

Industrial and material applications

This field of application includes energy production, use as catalysts, additives in construction materials, and the production of new materials (Afshar and Mofatteh, 2024; Santos et al., 2024).

Energy Production:

Bio-char is used as a solid fuel on its own or mixed with other fuels in processes such as combustion and gasification to produce energy. It can be integrated into the production process of an operating plant with minor adaptations, eliminating the need for a new industrial enterprise (Ganesapillai et al., 2023). The potential for producing bioenergy using bio-char as a feedstock was investigated. Three bio-chars produced from poplar, rice straw, and sweet potato waste were burned, and the results indicated that poplar bio-char had the greatest potential for generating electricity per ton of dry matter, followed by rice straw bio-char, with 3.8 MWh/dry ton and 2.91 MWh/dry ton, respectively. Since poplar is an energy crop and rice straw a waste product, the cost associated with the latter is considerably lower. This indicates that the efficient use of agricultural waste can generate social benefits such as increasing farmers' incomes, producing clean energy, and mitigating climate change (Kung and Zhang, 2015). Bio-char from waste-derived fuels was evaluated as a feedstock for combustion. The results indicated that the bio-char was capable of combustion without any auxiliary fuel. As for gaseous emissions, it was observed that the values for SO_2, CO, HCl, and Hg were below the standardized limit values, suggesting that no additional treatment was required for these emissions. Bio-char can be an alternative raw material to fossil coal in combustion plants for energy production (Guo et al., 2024).

Additive in construction materials:

In the construction industry, bio-char can be added to cement and used as a sustainable replacement for materials like gravel, sand, and other energy-intensive components used to make concrete (Hu et al., 2021). Some studies have also reported it used to be beneficial. For example, 5-15 % bio-char was added to the asphalt sidewalk and the results showed an improvement in resistance to moisture and cracking and a higher viscosity of the product (Garcia et al., 2022). Also, percentages of bio-char between 0.5 % and 40 % were used in building materials, and it was found that in most composites, there was an improvement in the properties of the building material and durability, strength increased, thermal conductivity, and apparent density of fresh mortars reduced. It also highlighted the importance of finding a balance between the dosage of bio-char and the desirable final properties of the building (Legan et al., 2022).

Advantages and disadvantages

Overall, the production and use of bio-char are in line with sustainable development goals for CO_2 reduction and climate change mitigation, so this is a great advantage for slow pyrolysis as a bio-char production technology. Another positive point is the fact that slow pyrolysis is flexible in accepting different types of raw materials, which makes it possible to use various types of wastes, contributes to more sustainable waste management, and can result in economic benefits due to the production of a value-added product. In addition, the flexibility of using different raw materials combined with the possibility of applying different operating conditions means that it is possible to produce end products with almost the desired characteristics (Al-Rumaihi et al., 2022; Elkhalifa et al., 2019; Jonsson, 2016). As a highly automated, relatively simple and robust process, with a relatively low operating cost (as it takes place at relatively low temperatures), slow pyrolysis turns out to be highly applicable on a small scale. It therefore has the advantage of being able to be applied as a decentralized technology on farms for processing agricultural materials, for example (Afshar and Mofatteh, 2024; Jonsson, 2016.). Also, because it is an old technology, and solidly established on a pilot scale (TRL 4-6) with many plants operating commercially, it ends up being the preferred technology for bio-char production (Al-Rumaihi et al., 2022).

Despite all the positive points pointed out, including the flexibility towards the feedstocks, slow pyrolysis faces the challenge of being able to ensure the quality of bio-char from any combination of feedstock, essentially non-lignocellulosic ones (Al-Rumaihi et al., 2022). Another limitation of slow pyrolysis may be the need to pre-treat the feedstock, including reducing the particle size if it is not within the recommended range (5-50 mm in size) (Rijo et al., 2022) or drying it if the moisture content is too high.

The advantages and disadvantages, conversion efficiency, capital, and operational cost of the slow pyrolysis process are listed in Table 7.

Table 7. The advantages and disadvantages of the slow pyrolysis process. Adapted from: (Afshar and Mofatteh, 2024; Feliz Florian et al., 2024; Mcintyre and Li, 2024; Rijo et al., 2022; Wang et al., 2023).

Type of pyrolysis	Technical condition	Key products	Advantage	Disadvanatge	Conversion efficiency	Capital cost	Operational cost
Sow pyrolysis	Suitable feedstock: forest residues, agricultural residues, industrial wastes, algae, sewage sludge, animal manure, tires, MSW; Feedstock size: 5-50 mm; Temperature: 300-700 °C; Residence time: minutes to hours; Heating rate: <1 °C/s; Pressure:1 bar.	Bio-char	Relatively simple and robust process; Ability to handle a wide variety of feedstocks; Well-established technology.	Need to pre-treat the feedstock (size and moisture restriction); The challenge of standardizing the quality of bio-char derived from diverse biomass sources.	Moderate to high	Moderate	Moderate

B Intermediate Pyrolysis

Waste biomass suitable for Intermediate Pyrolysis

Intermediate pyrolysis allows the utilization of a wide range of biogenic and industrial residues beyond wood residues. Intermediate pyrolysis is suitable for processing materials with a moisture content of up to 40%, anyway it is important that the carbon content of the dried feed material is above 50% (Amenaghawon et al., 2021; Hornung et al. 2011; Jäger et al. 2017; Kazawadi et al 2021).

Waste biomass materials such as tires, plastic or electronic scrap, animal bedding, manure, digestate, municipal solid wastes, paper sludge, sewage sludge and municipal solid waste, forest wastes (bark, sawdust, wood chips), woody biomass, algae, grass, agro-industrial residues (shells, kernels, husks, straws), and oilseeds (rapeseed, neem) have been successfully used as feedstocks for laboratory and larger scale intermediate pyrolysis processes (de Jesus et al., 2019; Funke et al. 2017; Kebelmann et al., 2013; Mahmood et al., 2013; Martinez et al. 2020; Morgano et al., 2018; . Okokpujie et al., 2023; Tinwala et al., 2015; Yang et al.; 2014).

Feedstock preparation

A variety of particle sizes can be used in intermediate pyrolysis as opposed to fast pyrolysis where finely ground particles are required. Overall, intermediate pyrolysis can feed larger feed pieces due to the lower heat transfer rates of the process and the use of screw reactors. Intermediate pyrolysis can be applied to material sizes up to about 20 mm, such as pellets and wood chips, but for process optimization, dimensions in the range of 1 to 5 mm are more recommended (de Jesus et al., 2019). Therefore, the classical mechanical methods to reduce the size of the feedstock (milling and grinding) and to homogenize its dimensions (sieving) are usually applied.

The moisture content of the feedstock can be more than three times higher than that allowed in fast pyrolysis, anyway, for feedstocks with high water content (sludge (including sewage sludge), biogas digestate, manure and olive mill waste) a drying process, which can be mechanical and/or thermal, must be performed (Zimmer et al., 2022).

Thermal and mechanical drying pre-treatments:

Before the biomass can be fed into the pyrolysis process, the feedstock is mechanically dewatered using equipment such as screw separators, drum filters, centrifugal decanters or vibrating screens. After mechanical dewatering, the water content can be further reduced by thermal or solar drying processes. In conventional thermal drying processes, water is removed via convection by circulating warm air over the material, anyway, systems such as belt dryers, drum dryers, or disk dryers can be used for this purpose (Zimmer et al., 2022).

Description of Intermediate Pyrolysis

The intermediate pyrolysis process is characterized by moderate heating rates and long residence times. Typical process temperatures for intermediate pyrolysis are between those of slow pyrolysis and fast pyrolysis. Thus, intermediate pyrolysis aims to achieve a balanced ratio between solid and liquid product yields. The temperature range of intermediate pyrolysis is 300-600°C, the heating rate range is 0.1°C/min-10°C/min and the residence time is 20-600 s (Amenaghawon et al., 2021; Hornung et al. 2011; Jäger et al. 2017; Kazawadi et al 2021).

The typical intermediate pyrolysis conditions result in a different product distribution compared to fast and slow pyrolysis. Typical yields obtained from intermediate pyrolysis are 15%–25% (bio-char), 40%–60% (bio-oil), and 20%–30% (gas).

A comparison of process conditions and product distribution for the same feedstock among the three types of pyrolysis processes is shown in Table 8.

Table 8. Pyrolysis typical operating conditions and product distribution

Process	Temperature [°C]	Heating rate [°C/s]	Residence time [s]	Liquid yield [%]	Solid yield [%]	Gas yield [%]
Slow pyrolysis	300-700	0.1-1	hours	25	50	25
Intermediate pyrolysis	300-600	1-100	20-600	50	20	30
Fast pyrolysis	600-1000	100-500	<2	70	15	15

In terms of the properties of the liquid fraction, less tar can accumulate in it, the viscosity is lower than that of comparable oils from fast pyrolysis, and easier separation of the organic and aqueous phases under gravity can be achieved. Intermediate pyrolysis oil contains a high amount of carbon and hydrogen, and a lower amount of oxygen compared to that obtained by fast pyrolysis, making it superior to fast pyrolysis oils and therefore a candidate of choice for blending with fossil fuel in engines (Kazawadi et al., 2021).

Intermediate pyrolysis also typically produces a valuable char product. Such a solid can be used as charcoal for combustion or bio-char as a soil amendment. If the char is produced from a feedstock with a high moisture content, the char can acquire the characteristics of activated carbon due to activation promoted by interaction with steam.

A high quality fuel gas containing more than 50% combustible gases (H_2, CH_4 and CO) with the remainder being CO_2 is also obtained by intermediate pyrolysis. Such a gas stream can be used to energetically support the process.

Intermediate Pyrolysis Reactors

Different types of reactors have been implemented for intermediate pyrolysis processes.

Fixed bed reactor:

Tinwala et al. explored the possibility of utilizing a fixed bed reactor (stainless-steel reactor of 100 g of capacity, 70 mm ID and 78 mm OD and 165 mm length) for the intermediate pyrolysis of woody biomass, agro-residues and seeds at 500 ± 10°C applying a heating rate (HR) of 10°C/min. The yields were the following: Bio-oil from 20.5% to 47.5%, bio-char from 27.5% to 40% and pyrolysis gas from 24.5% to 40.5%. The highest liquid yield (47.5%) was achieved with neem seed, the highest bio-char yield (40%) was achieved from straws and highest gas yield of 40.5% from Soyabean Straw (Tinwala et al., 2015).

Mamoohd used a bench scale batch fixed bed pyrolysis reactor (cylindrical quartz tube 400 mm L × 215 mm ID immersed in an externally heated electrical furnace) to pyrolyse small samples of brewers spent grain under a range of conditions to simulate continuous intermediate pyrolysis (different values of heating rate and temperature were chosen). A small catalytic steam reformer was added downstream of the reactor to further crack and reform the pyrolysis vapours (Mamoohd et al., 2013). Initial pyrolysis experiments without a catalyst were carried out at 450°C at low and high heating rates to analyze the effects on product yield and composition changes. Catalytic reforming experiments were performed at 500°C, 750°C and 850°C with and without the addition of steam. Catalytic reforming of the pyrolysis vapours, as expected, produced a significant increase in permanent gases mainly (H_2 and CO) with H_2 content exceeding 50 vol% at higher reforming temperatures. Bio-oil yield decreased significantly as reforming temperature increased with char remaining the same as pyrolysis condition remained unchanged (Mamoohd et al., 2013).

Pyroformer and Thermo-Catalytic Reforming reactor:

The Pyroformer technology is widely described in the literature (Hornung et al., 2011; Schmitt et al., 2019; Jager et al., 2017). The Pyroformer is made up by a twin horizontal rotary coaxial screw reactor with internal char recycling and a gas-tight reaction chamber suitable for up to 1 MPa. The partial recycling of the char within the reactor promotes better heat transfer and improves the quality of the products. During reactor operation, the inner screw conveys a mixture of fresh feedstock and recycled char product forward through the reactor, and the outer screw returns a portion of the char product backwards for recycle to achieve internal char recycling (Figure 5).

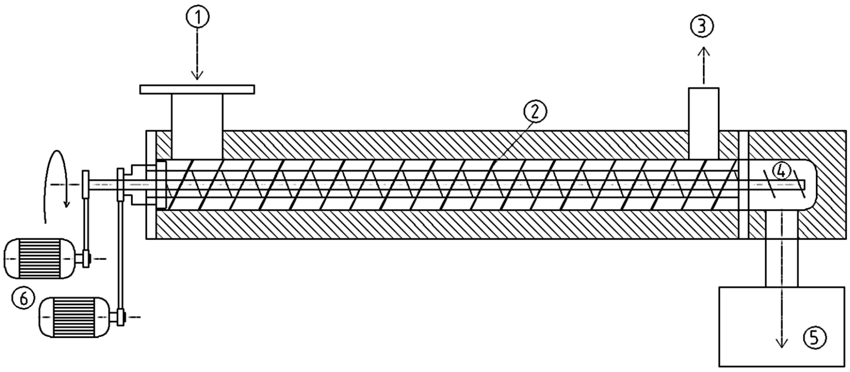


Figure 5. Pyroformer scheme (Schimtt et al., 2019)

Hot recycled char can act both as the heat carrier and as the catalytic cracking medium (due to the presence of ash in the char) thereby enhancing the secondary cracking reactions for pyrolysis vapours. This results in the production of a greater fraction of permanent gases and lower molecular weight condensable organic components and less heavy tars. The robustness of the process permits the utilization of various biogenic feedstocks (Hornung et al., 2011; Schmitt et al., 2019; Jager et al., 2017).

Yang and his collaborators (2014) used a co-axial dual (inner screw and outer) screw pyrolysis reactor, operating between 450-550°C and a long residence time (2–10 min) for intermediate pyrolysis tests and obtained, depending on the type of feedstock and processing conditions, the following product yields: 10–30% liquid (pyrolysis oil and water), 15–20% gas and 50–75% char (Yang et al., 2014).

Mahmood and his colleagues used a pilot scale carbon-steel made pyroformer (1.8 m in length and 0.2 m of diameter) for pyrolysing samples of brewers spent grain (BSG) (residence time between 1 and 4 min, temperature between 300-450°C). The yield of products (mass%) obtained at the final temperature of 450°C were: char 29%, total liquid fraction 52% and gas (by difference) 19%. The condensate bio-oil was found to have an organic and an aqueous phase that could be separated using a gravimetric settler. The aqueous phase was approximately 20% higher than what was reported in literature for liquids produced with intermediate pyrolysis (Mamoohd et al., 2013).

The group of Hornung at Fraunhofer Institute have developed the use of a pyroformer for an intermediate pyrolysis combined with a unique integrated catalytic reforming step (Thermo-Catalytic Reforming (TCR®)). The TCR® process combines an intermediate pyrolysis and additional catalytic cracking/reforming of products. The residence time of biomass is up to 10 min, and gases leave the reactor after 2–10 s. The main core of the TCR® reactor is a multi-zone auger reactor.

The reformer temperature has the biggest influence on the product yields, composition, and quality of the oils and gases. At higher reforming temperatures the gas yield increases (Schmitt et al., 2019; Jager et al., 2017).

TCR® process is a proven opportunity to convert biological wastes and residues into hydrogen-rich syngas, high-quality oil, and char without volatiles. Bio-oil produced from TCR® has a high carbon content, low water content, low oxygen content, and a high heating value; it is therefore directly applicable as feed in boilers or as blend in dual fuel engines. Various feedstocks have been already tested in TCR® plants and reports on them have been published. They include digestate, paper sludge, sewage sludge, wood chips, preconditioned agriculture olive residues, evergreen oak and vine shoots, or even de-inking sludge and municipal solid waste (Schmitt et al., 2019; Jager et al., 2017).

Auger reactor:

Morgano and his collaborators (2015) proposed the use of a bench-scale auger reactor with integrated hot gas filtration for the generation of particle-free vapours and condensates. The screw reactor used had the following dimensions: a heated length of 2 m and a diameter of 0.15 m. By varying the reactor temperature, initial flow rate, heating rate, and solids residence time, the effect on product yields and properties was evaluated. Increasing the temperature was effective in increasing the heating value of all products. The increase in calorific value of the pyrolysis condensate was also achieved by increasing the residence time. The heating rate between 100°C/min and 210°C/min has no significant effect on the properties of the char (Morgano et al., 2015). In the 2018 work, the same authors operated the same reactor for the combined production of pyrolysis char and heat and power using an externally fired micro gas turbine, demonstrating the feasibility of the proposed approach (Moreno et al, 2018).

Funke and colleagues (2017) performed an intermediate pyrolysis process at a bench scale in an auger reactor with a single screw without adding heat carrier. The reactor had a feed capacity of 10 kg h−1 and adopted a 2 m long single screw in a U-shaped vessel to allow the integration of ceramic filters within it along the screw axis. The used feedstocks were beech and poplar wood and white straw and blend of them. The comparison of the yields and the composition of the products obtained by the different feedstocks allowed to highlight the effect of ashes (Funke et al., 2017).

Martinez and his colleagues proposed the valorization of waste tires by intermediate pyrolysis (Martinez et al., 2020). The core of the used pyrolysis plant was a continuous twin-auger reactor with a nominal capacity of 1 kg/h. The proposed configuration led to a high mixing effectiveness of the feedstock, while controlling the residence time inside the reactor. The results collected indicated that the twin-auger pyrolyzer can successfully transform WT into oil (45 wt%), char (40 wt%) and gas (15 wt%) when operated at 475°C, with a feeding rate of 1.16 kg/h, a residence time 3.5 min and N_2 flow rate of 300 mL/min (Martinez et al., 2020).

Applications of Intermediate Pyrolysis Products

Combined Heat and Power:

The most known application of intermediate pyrolysis oils is in combined heat and power (CHP) plants. Pyrolysis oil has a high calorific value and only a low water content, it is non-polar and with a low acidity, so that it can be mixed with vegetable and mineral oils and used directly in engines. Indeed, intermediate pyrolysis oils can be utilized in small and medium scale CHP engines, as well as in diesel and gasoline automobile engines after hydro-treatment (Jager et al., 2017; Schimitt et al., 2019).

Intermediate pyrolysis oil can be treated via hydrodeoxygenation, emulsification, hydrocracking or catalytic esterification to obtain transportation fuel Schimitt et al., 2019). Other studies have investigated steam reforming of bio-oil (in particular the water fraction) to produce hydrogen by the use of catalytic hydro-treatment and catalytic cracking. Moreover, it is possible to extract valuable chemicals from the organic phase which could be used as flavoring additives or preservatives (Kazawadi et al., 2021).

Char from intermediate pyrolysis is suitable as a long-term fertilizer and soil amendment. It can be used as CO_2 storage in the soil, which on the one hand increases the fertility of the soil and on the other hand reduces the emissions of greenhouse gases. In the form of briquettes, char can also be used as a storable fuel and replace fossil coal. Char, especially after activation, finds also applications in adsorption-based technologies as activated carbon (e.g. removal of water pollutants) (Kazawadi et al., 2021). Another option is to use the char as feedstock for gasification to obtain a hydrogen-containing gas (Zimmer et al., 2022).

The permanent gases from intermediate pyrolysis can be used to produce electricity and heat or to undergo further separation and upgrading steps to obtain hydrogen or methanol (Kazawadi et al., 2021, Schmitt et al., 2019).

Capital and operational cost

Intermediate pyrolysis has a big change to become a viable technology thanks to different points of strength: the possibility to treat a wide variety of feedstocks, including wastes varying for size and moisture content (up to 40%) and the possibility to operate at small and medium scale (the most economical advantage is at small scale) (Kazawadi et al., 2021). Anyway, the drying step can involve substantial amounts of process heat and result in significant costs for the entire process (Zimmer et al., 2022). At the same time, pyro-gas may be recycled for heating to make this process self-sustainable (Moreno et al., 2018).

Yang et al (2017) presented a first comprehensive economic evaluation and life-cycle GHG emission analysis for a demonstration scale Combined Intermediate Pyrolysis and CHP (Pyro-CHP) system. The evaluation was carried out at system capacities of up to 1000 kg/h wood pellets throughput (1.5MW electrical or 3 MW CHP capacity). The energy balance computed from the system performance model indicated that the overall CHP efficiency of the Pyro-CHP system is 42.5%, with an engine subsystem CHP efficiency of 87.5% (1000 kg/h system). The results of the economic evaluation showed that deployment of Pyro-CHP systems is therefore not economically viable under the analyzed estimations, due to the difficulty in scaling up the intermediate pyrolysis reactor in its current arrangement (multiple reactors are required for plants over 200 kg/h). The sensitivity analysis of the LEC indicates that energy efficiency, capital cost and feedstock price have the greatest impact and therefore should be the focus of further work if systems of this type are to be deployed. The use of organic waste instead of wood pellets has the potential to reduce LEC over 50%. The life-cycle GHG emission analysis shows that the proposed system has a strong positive environmental impact. If the char produced in the system can be used for farmland application, the net GHG emissions for producing heat and power can be negative (Yang et al., 2017).

Despite these not exiting economical indications, Intermediate pyrolysis has been successfully commercialized by the company PYREG GmbH, which has installed numerous units for the production of bio-char as fertilizer or activated carbon since 2010 (Zimmer et al., 2022).

Advantages and disadvantages of intermediate pyrolysis

Intermediate Pyrolysis advantages and disadvantages are listed in Table 9.

Table 9. The advantages and disadvantages of the intermediate pyrolysis process

Feedstock	Technical condition	Key products	Advantage	Disadvanatge	Conversion efficiency	Capital cost	Operational cost
Used for a wide variety of feeds, single or in mixture with different shape and moisture content up to 40 %. Suitable feedstock: forest residues, agricultural residues, industrial waste, algae, sewage sludge, animal manure, tires, MSW.	Feedstock size: 1-50 mm; Temperature: 300-600 °C; Residence time: 20–600 s; Heating rate: 0.1 °C/min–10 °C/min; Pressure:1 bar.	Bio-oil	- The bio-oil produced from intermediate pyrolysis contains low amounts of tars and low viscosity, low acidity unlike that obtained from fast pyrolysis; - The moisture content of biomass is not the limiting factor; - Relatively simple and robust process; - Ability to handle a wide variety of feedstock; - High quality products; - Well-established technology; - Used to run in pyroforming mode; - Used to produce PAH free bio-char, - Scaled in a wide range and appropriate to small and medium scale; - Combined with filtration, gasification, BAF and CHP	Bio-oil yield is lower compared to fast pyrolysis; Need to pre-treat the feedstock (drying processes); Difficulties in scaling up the process.	Moderate to high	Moderate	Moderate

C Fast Pyrolysis

Waste biomass suitable for Slow Pyrolysis

Several types of waste biomass can be efficiently used for fast pyrolysis process, from organic fractions of municipal solid waste (MSW), due to agricultural residues, industrial biomass waste, forestry residues and even dried manure: animal manure (Pandey et al., 2019, Yanik et al., 2007, Gerdes et al., 2001).

Feedstock preparation

Fast pyrolysis has been studied for more than 40 years and it has been proven to be suitable for a variety of biomass feedstocks, to produce bio-oils and char (Bridgwater and Peacocke, 2000). Biomass feedstocks range from agricultural biomass wastes such as straw, olive pits, and nut shells, forest/wood waste biomass, to solid wastes such as sewage sludge and organic waste from the food industry and municipal solid waste (Hubbard, 2020, Mohan et al., 2006, Silos-Llamas et al., 2023, Yanik et al., 2007, Oasmaa et al., 2019, Park et al., 2010, Gu et al., 2020).

Particle size and bulk density of biomass are closely related properties that have a substantial impact on the pyrolysis process. The size of the biomass particles affects the heat transfer rate and the uniformity of the fast pyrolysis process (Tumuluru J.S. et al., 2018). Higher bulk can improve thermal conductivity within the pyrolysis reactor.

Biomass composition can be comprehensively assessed through biochemical, proximate, and ultimate analyses. Biochemical analysis focuses on identifying key biopolymers such as cellulose, hemicellulose, and lignin, which play crucial roles in determining the behaviour of biomass during conversion processes (Tumuluru J.S. et al., 2018). Proximate analysis quantifies the moisture content, volatile matter, fixed carbon, and ash content of the biomass, providing insights into its thermal stability and combustion characteristics. Meanwhile, ultimate analysis determines the elemental composition—specifically carbon (C), hydrogen (H), nitrogen (N), oxygen (O), and sulphur (S)—and calculates important stoichiometric ratios like H/C and O/C, which are critical for understanding the energy potential and combustion efficiency of the biomass.

The H/C and O/C ratios are particularly significant for fast pyrolysis, as high H/C and low O/C ratios typically indicate a higher energy content and greater feedstock quality (Tumuluru J.S. et al., 2018, Trninić, 2015).

Moisture content is another crucial factor, as it directly affects the efficiency of fast pyrolysis; most fast pyrolysis processes require moisture levels to be below 10% by weight to optimize the yield of bio-oil (Tumuluru J.S. et al., 2018).

Mineral content, particularly the presence of alkali and alkaline earth metals (AAEMs), can significantly influence the pyrolysis process. The AAEMs can catalyse char formation reactions, thereby reducing the yield of bio-oil (Hu and Gholizadeh, 2019). The AAEMs not only affect the pyrolysis process but also pose challenges during subsequent stages. Their presence in bio-oil accelerates the aging process, leading to increased water content, higher viscosity, and potential phase separation over time.

Additionally, the differing polymer structures of cellulose and lignin lead to distinct thermal decomposition pathways, affecting the distribution and composition of the fast pyrolysis products. Cellulose typically produces a higher yield of volatiles and bio-oil, while lignin tends to generate more char and lower yields of bio-oil due to its complex aromatic structure. Understanding these differences is crucial for optimizing fast pyrolysis processes and tailoring them to specific biomass feedstocks for improved efficiency and product quality.

To enhance the fast pyrolysis efficiency, the biomass needs to be pretreated, depending on characteristic of the chosen waste biomass.

Physical pretreatment

Size Reduction:

Size reduction is a common preprocessing method used to decrease the particle size of waste biomass, making it suitable for use as a feedstock in fast pyrolysis. The particle size of waste biomass can have a strong effect on devolatilization timing and influence the yields of bio-oil. The waste biomass needs to be ground to around 1-2 mm in the case of fluid bed reactors to ensure sufficiently small particles for rapid reaction (Bridgewater, 2004, Mašek, 2016). Small particles have higher mass transfer and heat transfer characteristics because of the higher surface area to mass ratio.

Densification:

The density of the biomass can influence the yield of bio-oil and its compositions (Hu and Gholizadeh, 2019). In literature can be found analysis of influence of palletized waste biomass (agricultural and wood residues) (Ndiema et al., 2002, Li and Liu, 2000, Mani et al., 2006). Results confirmed that higher bio-oil yield can be achieved by compacting biomass (Hu and Gholizadeh, 2019). Densified biomass, with its uniformity and reduced moisture content, enhances the efficiency of fast pyrolysis. It leads to higher and more consistent bio-oil yields by providing a homogeneous and drier feedstock.

Chemical pretreatment

Chemical retreatment of inorganic minerals in waste biomass is an important step before fast pyrolysis, as it can significantly impact the efficiency, yield, and quality of the final products. These effects can be mitigated through different chemical pretreatments.

Washing and leaching are chemical pretreatment methods used to prepare waste biomass for fast pyrolysis processes by removing inorganic minerals. Washing involves the quick dissolution of the inorganic materials and the immediate removal of the resulting solution from the biomass. In contrast, leaching is a process that takes a time to dissolve inorganic materials and/or extract the desired product from the biomass (Karnofsky, 2005). The most of soluble inorganic mineral materials can be effectively removed from biomass through washing and leaching processes using water, diluted acids before subjecting it to fast pyrolysis (Tumuluru J.S. et al., 2018).

Water is commonly used for leaching alkali sulphates, carbonates, and chlorides (Dai et al., 2008). The leachates from water leaching are easier to manage and can be repurposed, as they often contain valuable recyclable nutrients like potassium and phosphorus (Wang L. and Skreiberg O., 2023). Consequently, water leaching is increasingly favoured over acid leaching due to its operational ease and lower associated costs.

A common method to remove inorganic minerals from biomass before pyrolysis is acid treatment. This involves using diluted acids, such as sulfuric or hydrochloric acid. Diluted hydrochloric acid (HCl) is particularly effective for dissolving carbonates and sulphates of AAEMs, while mild bases, such as ammonia, are preferred for removing magnesium, calcium, potassium, and sodium (Tumuluru J.S. et al., 2018)(Dai et al., 2008). Acid treatment can significantly increase the bio-oil yield, boosting it from 19% to 27% wt (Hu and Gholizadeh, 2019). However, acid-washed biomass materials are unsuitable for direct use in fast pyrolysis process unless they are neutralized to prevent corrosion of processing equipment and to address health and safety concerns for operators (Wang L. and Skreiberg O., 2023).

Hydrothermal pretreatment

Steam explosion can significantly enhance the fast pyrolysis process by improving the physical and chemical properties of lignocellulosic biomass. This method involves permeating the biomass with saturated steam at moderate temperatures (app. 180–240°C) and high pressures (up to 7 MPa), enhancing its accessibility and reactivity (Tumuluru J.S. et al., 2018). During the steam explosion process, lignin is broken down into smaller polymer fragments (Tumuluru J.S. et al., 2018). In contrast, hemicellulose, which is more prone to degradation, is converted into predominantly water-soluble oligomeric saccharides that are subsequently washed away (Tumuluru J.S. et al., 2018). As a result, steam explosion facilitates more uniform heating and more efficient thermal degradation during fast pyrolysis, leading to higher yields and improved quality of bio-oil.

Liquid Hot Water (LHW) pretreatment is an effective process that avoids the use of added chemicals while utilizing high temperatures and pressures to enhance the treatment of biomass. This method relies on superheated water, typically in the range of 150°C to 260°C, which remains in a liquid state under the elevated pressures applied (Chen et al., 2022, Ashokkumar et al., 2022, Gottumukkala L. et al., 2024). The resulting biomass has reduced hemicellulose content and a modified lignin structure, which facilitates more efficient thermal degradation during fast pyrolysis. Consequently, LHW pretreatment can lead to higher yields and improved quality of bio-oil by enhancing the conversion process and reducing the formation of unwanted by-products.

Thermal pretreatment

Drying:

The moisture content of biomass is crucial in the fast pyrolysis process, impacting both efficiency and yield. High moisture increases the energy needed to vaporize water, reducing overall efficiency as more energy is used to remove moisture rather than convert biomass into bio-oil. This can lead to lower bio-oil yields and affect its quality by reducing heating value, stability, and viscosity. To optimize the fast pyrolysis process, biomass is often dried to reduce its moisture content to an ideal level, typically below 10% wt. before fast pyrolysis (Bridgewater, 2004).

Torrefaction:

Torrefaction as a pretreatment can significantly improve the efficiency of the fast pyrolysis process. By thermally conditioning the biomass, torrefaction reduces its moisture content and increases its brittleness, which, in turn, lowers the energy required for grinding the biomass into smaller particles (Chen et al., 2021). This not only enhanced the processability of the feedstock but also optimized the fast pyrolysis reaction. Furthermore, torrefaction improves the chemical properties of the resulting bio-oil, increasing its energy density (Louwes et al., 2017). This results in high-quality bio-oil that is more suitable for upgrading and refining into advanced bio-fuels.

Description of Fast Pyrolysis

Fast pyrolysis is a high-temperature process, typically in the range of 400 to 600^{o}C, where biomass is rapidly heated (>1000 ^{o}C/min) in the absence of oxygen (Mašek, 2016). To minimize secondary reactions, that could decrease the bio-oil yield and increase the gas yield, short residence times of the biomass particles and pyrolysis vapours are also kept in very short periods (0.5- 2s) (Mašek, 2016, Bridgwater, 2012). Rapid removal of product char is crucial to prevent vapor cracking (Bridgwater, 2012). Rapid cooling of the pyrolysis vapours is crucial to minimize secondary reactions and to condense vapours into the bio-oil (Bridgewater, 2004). In Figure 6, it is presented a simplified scheme of fast pyrolysis.

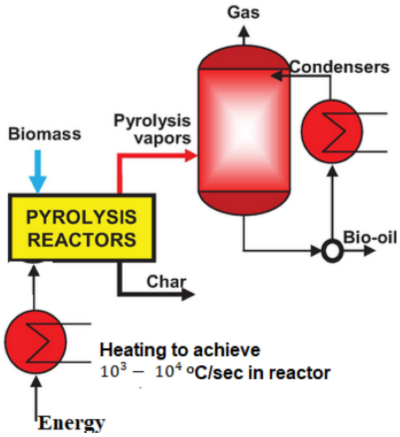


Figure 6. Simplified scheme of fast pyrolysis (Ighalo et al., 2022)

During fast pyrolysis, biomass decomposes rapidly to generate primarily bio-oil (60%–75% wt), along with some char (15%–25% wt) and gases (10%–20% wt) consisting mainly of CO_2 and CO, with small amounts of CH_4 and H_2, and other gases, depending on the operational conditions waste biomass used (Jahirul et al., 2012, Bridgwater, 2012, Kumar Mishra et al., 2023, Figueirêdo et al., 2022). The most straightforward application for gases and char is combustion, which can be used within the process to meet the necessary heat requirements (Bridgwater, 2012, Figueirêdo et al., 2022). Instead of producing heat through combustion, char can be converted into hydrogen or syngas through gasification and subsequent upgrading processes (Figueirêdo et al., 2022). Furthermore, char can be transformed into activated carbon through physical and chemical activation processes (Figueirêdo et al., 2022), unlocking a diverse array of applications, including filtration, adsorption etc. Bio-oil can be directly combusted in industrial boilers to produce heat, offering a renewable alternative to traditional fuels (Czernik and Bridgwater, 2004). In combined heat and power (CHP) systems, bio-oil is used to simultaneously generate heat and electricity. The bio-oil is burned in a boiler to produce steam, which drives a turbine connected to a generator, thus producing electricity. Furthermore, bio-oil can be blended with fossil fuels for co-firing in power plants, where it can be used to produce heat or power engines and turbines for electricity generation. These applications not only diversify energy sources but also significantly reduces the carbon emissions associated with energy production (Figueirêdo et al., 2022, IEA Bioenergy, 2007b). This dual approach of upgrading and co-firing makes bio-oil a versatile and impactful component in the transition to cleaner energy systems. Figure 7 summarizes the possibilities.

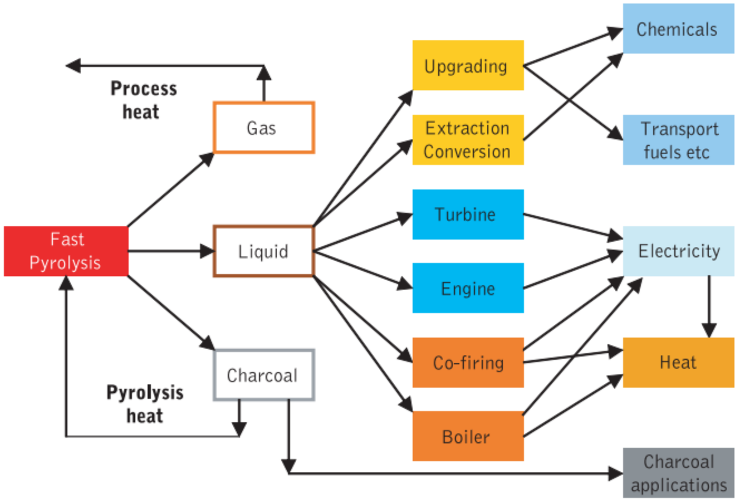


Figure 7. Applications for products of fast pyrolysis (IEA Bioenergy, 2007b)

Influence of the process parameters on the product characteristics

Fast pyrolysis agent:

Pyrolysis of biomass is always carried out in an inert atmosphere. In literature (Zhang et al., 2011), it can be found analysis of the use of nitrogen, hydrogen, carbon monoxide, carbon dioxide, methane and steam. The use of steam has advantages. It can increase the yield of bio-oil through decreasing the secondary cracking reactions' rates (Hu and Gholizadeh, 2019). Fast pyrolysis in atmosphere of CH_4 leads to higher bio-oil yield, while in CO atmosphere led to lower bio-oil yields.

Temperature:

Higher temperatures generally increase the reaction rate, accelerating the conversion of biomass into fast pyrolysis products. This is because elevated temperatures provide more energy for the chemical reactions to proceed. Higher temperatures generally result in a higher yield of gaseous products and a lower yield of bio-oil, due to the gas phase cracking of the hydrocarbons (Karkach et al., 2023). Further increase of temperature resulted in more acidic bio-oil with a higher ash content (Hu and Gholizadeh, 2019).

Heating rate:

The heating rate of waste biomass particles is the key parameter for fast pyrolysis. A faster heating rate can lead to a higher reaction rate by rapidly initiating the decomposition processes. Fast pyrolysis requires heating rates higher than 1000 °C/min. Increasing the heating rate promotes the depolymerization of cellulose and hemicellulose, minimizes the residence time of volatiles inside the reactor, and reduces secondary reactions (Hu and Gholizadeh, 2019). Additionally, higher heating rates enhance cracking reactions, resulting in more volatiles (bio-oil) (Bridgwater, 2012).

Vapour residence time:

The products' yields and properties from biomass pyrolysis are significantly affected by the residence times of vapour and solid inside the reactor (Hu and Gholizadeh, 2019). Shorter residence time of vapours (*i.e.* less than 2 seconds) favours bio-oil production and minimizes cracking reactions (Bridgwater, 2012).

Effect of pressure:

Pressure has a notable impact on the yields of products in fast pyrolysis. Specifically, increasing pressure typically leads to higher yields of bio-oil and lower yields of gases and char (Rasaq et al., 2021). This is because higher pressure tends to favour the formation of bio-oil by limiting the extent of gas formation (Mahinpey et al., 2009).

Effect of catalyst:

Catalysts used in fast pyrolysis can be introduced in two primary ways: either mixed directly with the biomass feedstock (*in situ* catalytic fast pyrolysis) or with the pyrolysis vapours only (*ex situ* catalytic fast pyrolysis).

In the *in-situ* catalytic fast pyrolysis process, biomass is rapidly heated within a fluidized bed reactors in the presence of a catalyst, such as zeolites, doped zeolites, or solid acids. The catalyst is crucial for partially deoxygenating and stabilizing the bio-oil vapours generated during pyrolysis. These vapours are subsequently condensed into liquid bio-oil, which then undergoes further upgrading processes.

Ex situ catalytic fast pyrolysis, the catalyst is introduced only to the bio-oil vapours, rather than the biomass feedstock. This means that the biomass undergoes pyrolysis first, and the vapours produced are then exposed to the catalyst in a separate stage or reactor. *Ex Situ* catalytic fast pyrolysis is a method used to upgrade bio-oil produced from fast pyrolysis. This technique of treating the bio-oil vapours with a catalyst after pyrolysis helps to enhance the quality and usability of the bio-oil.

Influence of the feedstock parameters on the product

Influence of Particle Size:

The size of biomass particles plays a crucial role in the efficiency and yield of products in the fast pyrolysis process. Fast pyrolysis is highly dependent on the rapid heating of biomass particles, and smaller particle sizes are generally preferred. Smaller biomass particles have a higher surface area-to-volume ratio, which allows for a faster heating rate and a higher reaction rate. This rapid heating is essential for fast pyrolysis, where the goal is to quickly reach high temperatures in a very short time. Smaller particles facilitate uniform heat distribution, minimizing thermal gradients and ensuring that the entire particle reaches the desired temperature simultaneously. Smaller biomass particles tend to produce a higher yield of bio-oil. The rapid heating and shorter residence time reduce the likelihood of secondary reactions, leads to a higher yield of liquid products. Larger particles may heat more slowly and unevenly, potentially decreasing the reaction rate. As mentioned above, fast pyrolysis is favoured by waste biomass particles size around 1-2 mm (Mašek, 2016).

Density and Porosity:

Biomass with higher bulk density can be more challenging to process due to its lower porosity, which restricts the flow of heat and volatiles. On the other hand, high porosity biomass allows better heat penetration and volatilization, enhancing bio-oil production.

High porosity in biomass refers to the presence of numerous tiny pores or spaces within the material. During the fast pyrolysis process, these pores play a crucial role in the overall efficiency and product yield. High porosity allows volatile compounds to escape more easily from the biomass structure as it is heated during fast pyrolysis. The pores in high-porosity biomass provide pathways for the volatiles to diffuse out quickly, reducing the likelihood of them being trapped within the biomass. This diffusion is important because trapped volatiles could further decompose into unwanted byproducts, such as char. Since the volatiles can escape more freely, they are more likely to condense into bio-oil, which is the desired product of fast pyrolysis. This leads to a higher yield of bio-oil, as more of the biomass is converted into volatiles that can be collected and condensed. Therefore, high porosity directly contributes to increased bio-oil production. Thus, biomass with high porosity not only enhances bio-oil yield but also minimizes char formation, improving the overall efficiency of the fast pyrolysis process.

Ash Content:

Waste biomass usually contains highly active catalysts, primarily alkali metals such as potassium and sodium. Alkali metals in biomass can act as catalysts for char formation and secondary reactions, decreasing bio-oil yield and altering its composition.

Managing ash content can be partially achieved by selecting specific crops and harvesting times, but it cannot be eliminated from growing biomass. Ash can be reduced through washing with water or dilute acid. The more extreme the washing conditions—higher temperatures or stronger acid concentrations—the more effective is the ash removal (Bridgwater, 2012). However, such conditions also lead to the loss of hemicellulose and cellulose through hydrolysis, which in turn reduces liquid yield and quality. Additionally, washed biomass needs thorough acid removal, and the resulting wet biomass must be dried. Due to these challenges, washing is not commonly considered a viable solution unless there are specific circumstances, such as the need to remove contaminants (Bridgwater, 2012).

Moisture Content:

The moisture content of biomass is a critical factor in the efficiency and yield of the fast pyrolysis process. High moisture content in biomass increases the energy required to vaporize the water during fast pyrolysis, which can slow down the overall reaction rate. This can reduce the overall energy efficiency of the process since a significant portion of the input energy is used to remove moisture rather than convert waste biomass into bio-oil and other products. Moisture lowers the effective temperature inside the pyrolysis reactor, which can affect the thermal cracking of biomass and both the yield and quality of bio-oil. Biomass with high moisture content requires additional energy for drying, which can reduce the heating rate and increase the energy input required for the process. Lower moisture content (generally less than 10%) is preferred to enhance the heating rate and improve the yield and quality of bio-oil.

The volatile matter content in biomass plays a crucial role in determining the efficiency and outcomes of the fast pyrolysis process. Volatiles from biomass include water, acetic acid, methanol, and other organic compounds that contribute to the bio-oil yield. Biomass with high volatile matter content is more reactive and produces higher yields of gases and bio-oil. Understanding the volatile matter content of biomass is essential for optimizing fast pyrolysis conditions, such as temperature and heating rate. For instance, biomass with high volatile content might benefit from lower fast pyrolysis temperatures to enhance bio-oil yield, while biomass with low volatile content may require higher temperatures to achieve efficient conversion.

Cellulose, Hemicellulose, and Lignin:

The primary components of lignocellulosic waste biomass include cellulose, hemicellulose, and lignin. Under non-catalytic conditions Hemicellulose and cellulose decompose at relatively lower temperatures (200°C–300°C), producing volatiles that contribute to bio-oil (Chua et al., 2021). Lignin, being more complex and stable, decomposes over a wide range of temperatures (160°C–900°C), contributing to the char and gas yield (Chua et al., 2021). Biomass with a higher lignin content tends to produce more char and less bio-oil.

Fast Pyrolysis Reactors

A reactor is a crucial component of any pyrolysis process, with the heating system being a vital part of the process facilities. To optimize the pyrolysis process, various reactor designs have been developed over the past decades, each tailored to different heating methods, feedstock characteristics and operational requirements.

Bubbling Fluidized Bed Reactors:

Bubbling fluidized beds (BFB) are a well-established technology, known for their simplicity in construction and operation, effective temperature control, and efficient heat transfer to biomass particles due to the high solid's density (Bridgwater, 2012). High heat transfer rates are achieved, as the bed usually contains small sand particles, generally about 250 µm (Venderbosch and Prins, 2010). The heat required is generated by combustion of the pyrolysis gases, and/or char, and is eventually transferred to the fluid bed by heating coils (Venderbosch and Prins, 2010). Biomass particles are suspended in an upward flow of hot gas, ensuring efficient heat transfer. Typically, these reactors achieve bio-oil yields of 70% to 75% wt from biomass on a dry feed basis (Bridgwater, 2012). For optimal performance, the biomass particle size should be less than 2–3 mm to ensure high heating rates. In fluidized bed reactors, the heating rate of the particles is usually the limiting factor. The fluidizing gas flow rate controls the residence time of solids and vapours, with char generally having a longer residence time than vapours. Post-pyrolysis, the char must be separated from the bio-oil as it acts as an effective vapour cracking catalyst, achieved through an ejection and entrainment system followed by separation in cyclones (Hu and Gholizadeh, 2019). The high inert gas flow needed for fluidization results in low partial pressures for condensable vapours, necessitating efficient heat exchange and collection systems, and increasing equipment size and cost (Bridgwater, 2012). Byproduct char, about 15 wt.% of the products and 25% of the biomass feed's energy, can be used for process heat or exported, though it is pyrophoric and requires careful handling and storage.

Electrostatic precipitators are used for the coalescence and collection of aerosols, which are partially depolymerized lignin fragments with significant molecular weight. These precipitators accumulate liquid, which runs down the plates and collects in the bio-oil product (Bridgwater, 2012). The scheme of this reactor is presented in Figure 8.

The advantages of these reactors include their suitability for continuous operation and their ability to provide uniform heating. However, they require careful control of bed conditions and may encounter issues with reactor scaling.

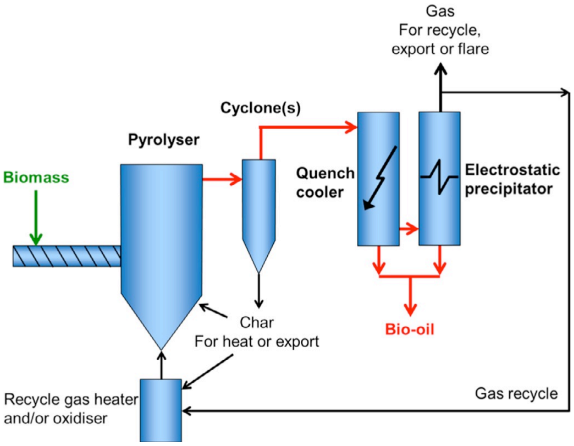


Figure 8. Bubbling fluid bed reactor with electrostatic precipitator (Bridgwater, 2012, Hu and Gholizadeh, 2019)

Circulating Fluidized Bed Reactors:

Circulating fluid bed (CFB) and transported bed reactor systems share many features with bubbling beds, but the residence time of char is nearly the same as that of vapours and gas, leading to higher char content in the collected bio-oil unless extensive char removal is implemented (Bridgwater, 2012). An advantage of CFBs is their suitability for larger throughputs, despite more complex hydrodynamics, as this technology is widely used at high throughputs in the petroleum and petrochemical industry (Bridgwater, 2012, Hu and Gholizadeh, 2019). The heat for CFBs is supplied by recirculating heated sand from a secondary char combustor (Hu and Gholizadeh, 2019). Biomass could be converted to bio-oil at yields of over 70 % wt. (Venderbosch and Prins, 2010). The scheme of this reactor is presented in Figure 9.

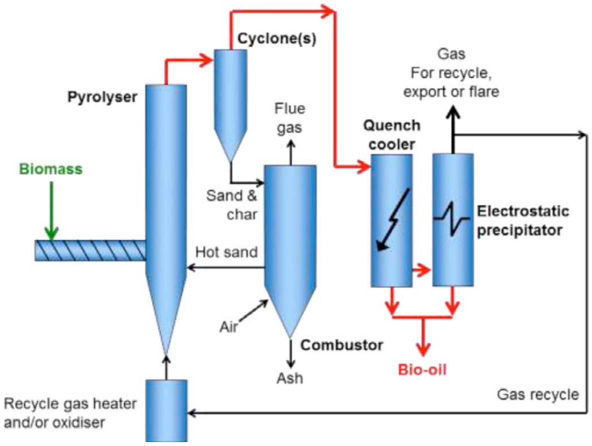


Figure 9. A common schematic of circulating fluidized bed reactor (Bridgwater, 2012, Hu and Gholizadeh, 2019)

Ablative Reactors:

Ablative pyrolysis is a distinctive method compared to other fast pyrolysis techniques. The surface, heated by hot flue gas, is rotating, and biomass is pressed onto the hot surface (approx. 600°C) (Venderbosch and Prins, 2010). Traditional pyrolysis processes are constrained by slow reaction rates due to inefficient heat transfer through small biomass particles. Ablative pyrolysis addresses this limitation by using a hot reactor wall to directly transfer heat to the biomass, facilitating a more efficient reaction under pressure (Bridgwater, 2012). In this method, biomass particles are pushed against the reactor wall, where the intense heat rapidly heats and decomposes the outer layer into vapour, which condenses into bio-oil. This approach requires high pressure to be exerted on the particles against the wall, significant relative motion between the biomass and the reactor wall, and a reactor wall temperature kept below 600°C to ensure effective conversion and maximize bio-oil yield (Bridgwater, 2012). Unlike other methods, ablative pyrolysis does not require inert gas, resulting in smaller, more efficient equipment and better vapour collection due to high partial pressures (Bridgwater, 2012, Hu and Gholizadeh, 2019). The scheme of this reactor is presented in Figure 10.

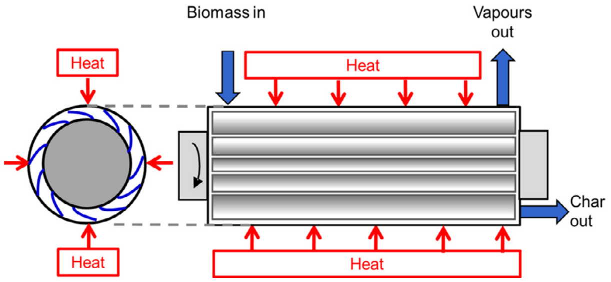


Figure 10. A schematic of ablative reactor (Bridgwater, 2012, Hu and Gholizadeh, 2019)

Advantages of ablative reactors include their simple design and high heat transfer rates. They are capable of processing larger particles and offer system simplicity. However, they also have the disadvantage of experiencing high wear and tear on the reactor surface.

Rotary Cone Reactors:

As the biomass moves away from the heated surface in the rotary cone reactor, a molten layer forms and vaporizes. This initiates a pyrolysis front that progresses unidirectionally through the biomass particles. The residual oil film generated during this process lubricates the particles, ensuring smoother movement and rapid evaporation, effectively converting the biomass into pyrolysis vapours. (Bridgwater, 2012, Hu and Gholizadeh, 2019). High particle pressure on the hot reactor wall ensures better contact and heat transfer, while the relative motion between biomass and the reactor surface facilitates consistent heating. Maintaining reactor wall temperatures below 600°C is crucial to optimize the reaction rate, ensuring efficient thermal decomposition of the biomass. (Bridgwater, 2012). Larger particles can be processed since reaction rates are not limited by heat transfer through the biomass particles. The absence of inert gas results in smaller, more intensive processing equipment and increased partial pressure of condensable vapours, leading to efficient collection and smaller equipment (Bridgwater, 2012, Hu and Gholizadeh, 2019). The char produced is a fine powder separable by cyclones and hot vapor filters, as in fluid bed systems. The scheme of this reactor is presented in Figure 11.

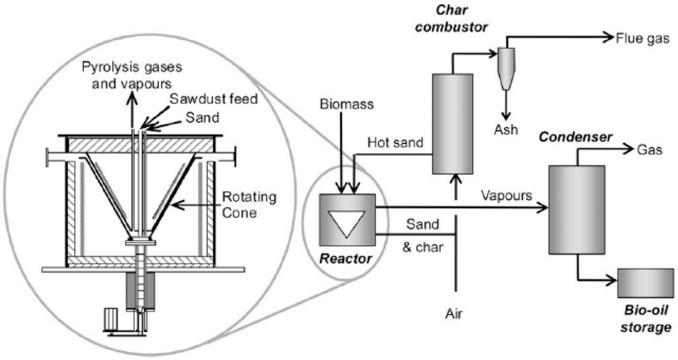


Figure 11. A schematic of rotating cone reactor (Bridgwater, 2012, Hu and Gholizadeh, 2019)

Advantages of rotating cone reactor include its ability to handle various feedstock types and suitability for continuous operation. However, the process is surface-area-controlled, which makes scaling less effective and the reactor more mechanically complex, leading to higher capital costs and increased complexity.

Auger Reactor:

An auger reactor consists of an oxygen-free cylindrical heated tube in which augers move the biomass through (Hu and Gholizadeh, 2019). The temperature inside the tube is raised to the pyrolysis temperature, allowing the biomass to decompose. A condenser is used to liquefy the volatiles produced during pyrolysis. The bio-oil and char yields from auger reactors are comparable to those from fluidised bed reactors (Hu and Gholizadeh, 2019). Unlike fluidised beds, it is difficult to achieve very short residence times with these reactors, with hot vapour residence times ranging from 5 to 30 seconds (Bridgwater, 2012). A schematic layout of an auger reactor is shown in Figure 12.

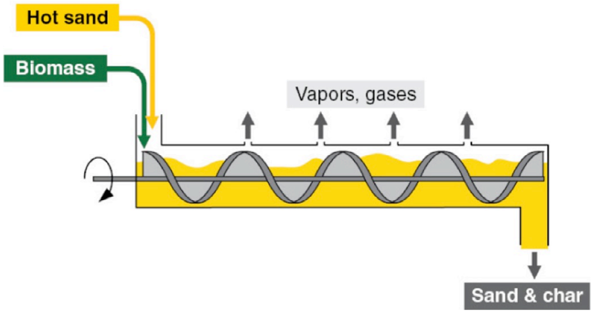


Figure 12. Auger reactor (Hu and Gholizadeh, 2019)

Vacuum Pyrolysis Reactors:

Vacuum pyrolysis includes a combination of slow and fast pyrolysis conditions (Venderbosch and Prins, 2010). Biomass feedstocks are heated relatively slowly while the gas is removed from the hot temperature zone relatively quickly by applying a reduced pressure (Venderbosch and Prins, 2010). The process operates at 450°C and 100 kPa, typically yielding 35–50% bio-oil on a dry feed basis with higher char yields compared to other pyrolysis systems (Bridgwater, 2010). The rapid removal of vapours minimizes secondary reactions, resulting in higher bio-oil yields (Bridgwater, 2010, Bridgwater, 2012, Bridgwater and Peacocke, 2000). Despite its complexity and cost, driven by the need for large vessels and piping to maintain high vacuum, vacuum pyrolysis offers advantages such as the ability to process larger particles, reduced char content in the liquid product due to lower gas velocities, and the elimination of the need for carrier gas.

Entrained Flow Reactors:

Early attempts of fast pyrolysis have been carried out in entrained flow reactors, where biomass particles (1 to 5 mm) were fed to a hot, down-flow reactor (Venderbosch and Prins, 2010). The reaction is completed within a residence time <1 s, if the reactor tube is held at temperatures in between 700 and 800°C (Venderbosch and Prins, 2010). Entrained flow fast pyrolysis is theoretically simple but has faced challenges due to poor heat transfer between hot gas and solid particles (Bridgwater, 2012). High gas flows needed for sufficient heat transfer result in large plant sizes and low vapour partial pressure, making bio-oil collection more complex. Consequently, bio-oil yields are generally lower (50–55 % wt.) (Bridgwater, 2012).

Fixed Bed Reactors:

Fixed-bed reactors are primarily suitable for laboratory-scale experiments due to their simplicity and ease of control (Bridgwater, 2017, Ly et al., 2016, Moralı and Şensöz, 2015, Onay et al., 2001, Adam et al., 2006). In laboratory experiments, fixed bed reactors are used to investigate the kinetics of biomass conversion and to evaluate the fast pyrolysis parameters that affect the distribution and properties of the resulting products (Adhikari et al., 2018). At the laboratory scale, the core component of the process is a tube reaction typically constructed from quartz or stainless steel (Wu and Williams, 2013, Lewandowski et al., 2019). This tube is heated externally by an electric furnace, which maintains precise control over the pyrolysis temperature (Wu and Williams, 2013). This temperature is closely monitored using a thermocouple connected to a temperature controller. Typically, a few grammes of small sized (1-2 mm) waste biomass are placed into the reactor with or without catalysts (*e.g.* HZSM-5). The reactor operates at high temperatures, usually between 450°C and 600°C (Lewandowski et al., 2019, Moralı and Şensöz, 2015). During laboratory-scale experiments, an inert gas, such as nitrogen, is used as a carrier to transport the volatile products generated during fast pyrolysis away from the reaction site. The vapours formed are directed through downstream processing systems to condensation units, where they are treated and analysed to ensure efficient conversion and collection of the pyrolysis products. Most often fixed bed reactors used are of vertical type, as illustrated in Figure 13.

Fixed bed fast pyrolysis is challenging to scale beyond laboratory or bench levels while meeting the basic requirements of fast pyrolysis (Bridgwater, 2017).

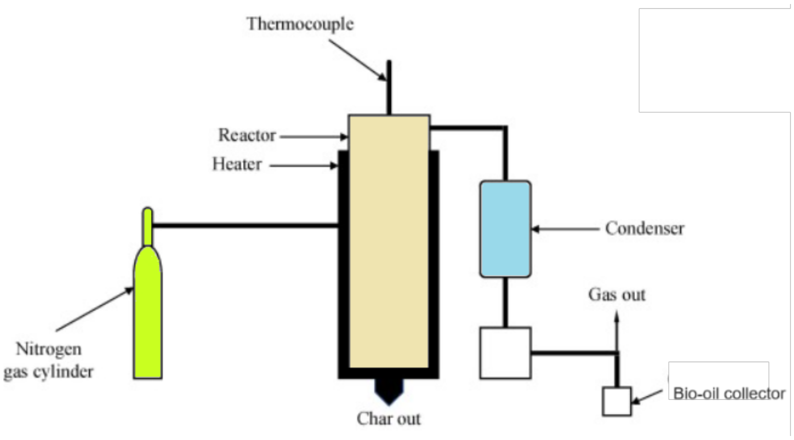


Figure 13. A typical laboratory setup for a fixed-bed reactor in fast pyrolysis (Jahirul et al., 2022)

Bio-oil characteristics

Bio-oil, the target product from fast pyrolysis, is a dark brown homogeneous, free-flowing liquid with a higher heating value (HHV) ranging from 16–21 MJ/kg (Dabros et al., 2018). Bio-oil contains a high water content (15-30 % wt, sometimes up to 60 % wt) and numerous organic components, including acids, alcohols, ketones, furans, phenols, ethers, esters, sugars, aldehydes, alkenes, and various nitrogen and oxygen compounds (Hu and Gholizadeh, 2019, Dabros et al., 2018).

Water content (moisture) in bio-oil primarily arises from the inherent moisture in the biomass feedstock and the water generated during the pyrolysis process (Bridgwater, 2017). Moisture content in bio-oil reduces viscosity, improving flow properties, but it also lowers the heating value (Adeoye et al., 2024).

Moisture removal from bio-oil is particularly difficult because of the solubilizing effects of certain molecules, such as acids, alcohols, and ketones, which tend to bind water within the mixture (Adeoye et al., 2024). These compounds create a stable emulsion, making it challenging to separate water from the bio-oil without affecting its composition and quality.

The high oxygen content in bio-oil is primarily due to its significant moisture levels and the abundance of oxygenated compounds present in the mixture. Due to its high oxygen content (35–50 % wt), bio-oil contains reactive functional groups that make it unstable and prone to polymerization during storage (Dabros et al., 2018). This polymerization increases the molecular weight, subsequently raising the viscosity and density of the bio-oil (Dabros et al., 2018). Over time, the water content in bio-oil increases, potentially leading to phase separation.

Bio-oil contains many reactive molecules and oligomeric species, contributing to its instability, even at room temperature (Hu and Gholizadeh, 2019). Oligomers form aerosols, leading to the aging of bio-oil, which results in increased water content, higher viscosity, and phase separation (Hu and Gholizadeh, 2019). Bio-oil contains small amounts of char, wax-derived compounds, and heavy molecules (Dabros et al., 2018). Waxy compounds crystallize in the upper layer or on cold surfaces, while heavy compounds form networks in the bottom layer, and water droplets can develop over time (Dabros et al., 2018). These factors contribute to phase separation during storage. Chlorine, sulphur, nitrogen, and alkali metals in the bio-oil can also poison catalysts used for upgrading (Dabros et al., 2018).

The pH of crude bio-oil typically ranges between 2 and 3 (Adeoye et al., 2024). Its corrosive nature restricts its use not only as a direct engine fuel but also poses challenges for storage and transport, as it can cause significant damage to oil tanks, pipes, and other components, necessitating the use of more resistant materials.

Density and viscosity are key properties of bio-oil that influence its handling, storage, and application. Both density and viscosity are influenced by factors like the feedstock used, the pyrolysis process conditions, and the amount of water and oxygenated compounds in the bio-oil. Bio-oil typically has a density ranging from 1.1 to 1.2 g/cm^3 at room temperature (Adeoye et al., 2024). This density is higher than that of conventional fossil fuels, which can affect its combustion characteristics and the design of storage and transportation systems. Bio-oil can have a viscosity similar to that of heavy fuel oil, but it tends to increase over time due to aging and polymerization reactions. The viscosity generally ranges from 35 to 1000 cP at 40°C, though it can be significantly higher at lower temperatures or after extended storage (Adeoye et al., 2024).

Therefore, bio-oil is not chemically stable. However, the oil can be stabilized by catalytic (hydrogen) treatment, addition of solvent, and esterification.

Bio-oil upgrading

Utilizing bio-oil presents several challenges that need to be addressed to make it a viable alternative to conventional fossil fuels and chemicals. The chemical instability and high-water content of bio-oil lead to issues with polymerization, phase separation, and reduced calorific value, complicating storage and combustion applications. Its corrosiveness, due to organic acids, leads to the need to use specific, more expensive materials for storage and handling, while the high oxygen content reduces energy density and demands extensive upgrading processes to produce suitable hydrocarbons. Additionally, bio-oil's variable viscosity and tendency for phase separation pose challenges in pumping, atomization, and direct use. Bio-oil needs to be upgraded before its final use.

Physical upgrading of bio-oil:

The most important properties that may adversely affect bio-oil fuel quality are incompatibility with conventional fuels from the high oxygen content of the bio-oil, high solids content, high viscosity, and chemical instability (Bridgwater, 2012). Bio-oil upgrading involves transforming the raw bio-oil obtained from biomass pyrolysis into a more valuable or usable form. This process can be approached through several methods, broadly categorized into physical, chemical, and catalytic techniques (Bridgwater, 2012).

Filtration process removes particulates and ash from bio-oil, improving its quality. Hot-vapour filtration can significantly reduce ash and alkali content, leading to a cleaner product with higher quality. Hot-vapour filtration reduces ash content to <0.01% and alkali to <10 ppm, enhancing product quality by lowering char content, but the catalytic activity of char can decrease yield by up to 20% and reduce viscosity (Bridgwater, 2012).

Solvent addition involves blending bio-oil with solvents (like methanol) to reduce its viscosity and enhance stability of bio-oil (Bridgwater, 2012, Kumar and Strezov, 2021). This helps in making the bio-oil easier to handle and process. Bio-oil can be emulsified with diesel using surfactants, creating stable micro-emulsions with 5-30% bio-oil (Bridgwater, 2012). However, these emulsions can cause increased engine corrosion and erosion, and the cost of surfactants and energy for emulsification is high.

Emulsification combines bio-oil with hydrocarbons (*e.g.* diesel) using surfactants to create stable emulsions, with 5-30% bio-oil (Bridgwater, 2012, Kumar and Strezov, 2021). This approach improves compatibility with existing fuel systems but can be costly and may increase engine corrosion and erosion.

Chemical and Catalytic Upgrading:

Hydrotreating involves reacting bio-oil with hydrogen under high pressure (up to 20 MPa) and moderate temperature (up to 400 °C) to remove oxygen and improve stability (Bridgwater, 2012, Kumar and Strezov, 2021). This process can produce a petroleum like product, which then requires further refining to make conventional fuels.

Hydrodeoxygenation (HDO) is employed as a methodology to improve the properties of bio-oil as engine fuel (Hu and Gholizadeh, 2019). HDO is a catalytic (*e.g.* Ru, Pt , Pd, Ni, Cu, and phosphides) process conducted under generally high pressure (5-20 MPa) and high reaction temperature (200-450°C) to reduce the oxygen content in bio-oil, transforming bio-oil into hydrocarbons suitable for use as transportation fuels (De Miguel Mercader et al., 2011, Ansari et al., 2022). The reduction in oxygen content significantly improves bio-oil by addressing its instability and other associated issues. Consequently, the upgraded oil becomes much less acidic, exhibits a noticeably higher heating value (HHV), and has a greatly reduced viscosity (Ansari et al., 2022). In other words, HDO enhances bio-oil stability, increases its energy density, and improves its compatibility with existing fuel infrastructure.

Catalytic cracking of bio-oils, conducted using porous solid catalysts like zeolites (*e.g.* HZSM-5, Zn/HZSM-5, Hβ) at ambient pressure, is an effective method for upgrading bio-oil, particularly when hydrogen gas is not required. (Chaihad et al., 2022). During catalytic cracking of bio-oil, larger molecules are broken down into simpler, more valuable components, making the bio-oil suitable for use as fuels or chemicals. The primary challenge in catalytic upgrading of bio-oil is catalyst deactivation due to coking, where heating the bio-oil leads to the formation of solid carbonaceous material, needing frequent catalyst regeneration.

Fluid catalytic cracking (FCC) is a refining process primarily used in the petroleum industry to convert heavy crude oil fractions into lighter products such as liquefied petroleum gas (LPG), gasoline and diesel (Wikberg E., 2019). In the context of bio-oil upgrading, FCC reactors break down complex bio-oil molecules into simpler, more valuable hydrocarbons. This process enhances the bio-oil's quality and suitability for use as a transportation fuel. FCC utilizes a fluidized bed of solid catalysts (*e.g.* Zeolite Y, ZSM-5) and operates at high temperatures (above 500°C) and moderate pressures to facilitate the cracking reaction (Wikberg E., 2019, Lappas et al., 2009).

Esterification converts bio-oil into esters by reacting it with alcohols (*e.g*. methanol) in presence of catalysts (K_2CO_3/Al_2O_3–NaOH, Amberlyst 70) (Hu, 2020). Esterification is a reaction between an alcohol and a carboxylic acid, converting the carboxylic acids in bio-oil into neutral esters. This process effectively reduces the acidity and corrosiveness of bio-oil. However, coking remains a significant challenge in bio-oil esterification (Hu, 2020).

Steam reforming (SR) is a process where hydrocarbons react with steam at high temperature (around 550 °C) and in the presence of a catalyst (typically Ni, Co, Fe, Pt, Ir, Rh, or Ru) (Chen et al., 2017, Pafili et al., 2021). This process yields H_2, which is the main aim of the process, and CO. SR is often coupled with water-gas shift and methanation reactions (Trane et al., 2012) increasing the yield of hydrogen or generating biomethane.

Other methods for chemical upgrading of bio-oil:

Integrated catalytic pyrolysis is a process that combines catalytic pyrolysis and fast pyrolysis techniques to improve the efficiency and quality of bio-oil production (Bridgwater, 2012). This method integrates a catalyst within the pyrolysis system to enhance the breakdown of biomass and optimize the formation of desirable products. A catalyst is included in the pyrolysis process, either by incorporating it directly into the reactor or by using a catalytic bed that interacts with the bio-oil vapours. This catalyst helps to lower the activation energy required for the pyrolysis reactions, leading to more efficient breakdown of biomass and improved yields of target products. Integrating catalysis with pyrolysis requires a consistent temperature and robust catalysts capable of withstanding high temperatures and mechanical stresses, which limits operational flexibility and demands sophisticated systems (Bridgwater, 2012).

Gasification converts bio-oil into syngas (a mixture of hydrogen and carbon monoxide) through high-temperature reactions. The syngas can then be synthesized into various hydrocarbons or alcohols, providing flexible options for fuel production.

Supercritical fluids (SCFs) like ethanol, methanol, and water enhance bio-oil upgrading due to their unique properties, including high solubility, gas-like diffusivity, and efficient mass and heat transfer (Panwar and Paul, 2021). These fluids are employed in upgrading processes, often in the presence of catalysts (*e.g.* Ru/C, Pd/C, Pt/C, Ru/HZSM-5, Pd/HZSM-5, Pt/HZSM-5) (Omar et al., 2021). SCFs can improve bio-oil's heating value and reduce viscosity (Panwar and Paul, 2021).

Each method has its advantages and challenges, often requiring integration into existing refining processes or the development of new technologies to optimize bio-oil upgrading.

Applications of Bio-oil

The bio-oil produced from agricultural waste, forest residues, and urban organic waste has a wide range of applications, which include bio-fuels, chemicals, and heat and power generation. However, before utilizing bio-oil for energy-related purposes, it is essential to remove its moisture content.

Use of bio-oil for heat and power:

Heat, power, and other energy sources can be generated by burning bio-oil in gas turbines, Stirling engines, diesel engines, furnaces, and boilers (Mishra et al., 2024). Bio-oil combustion offers lower emissions like CO_2, and SO_x emissions, reducing air pollution and potentially eliminating the need for additional emission reduction processes (Hu and Gholizadeh, 2019). Studies performed by Hu and Gholizadeh (2019) demonstrated that co-feeding 2.5% wt. bio-oil with heavy fuel oil reduced NO and SO_2 emissions by approximately 2.6% and 7.9%, respectively. This is attributed to the lower nitrogen and sulphur content in the bio-oil compared to fossil fuels (Hu and Gholizadeh, 2019). However, since bio-oil has different combustion characteristics, including significant differences in ignition, viscosity, energy content, stability, pH, high-water content (20–30%) and lower heating value compared to heavy fossil fuels, require modifications to conventional burner systems (Basu and Kaushal, 2024b). These modifications included recalculating the air-to-fuel ratio (in between 5-7 for combustion, which is half of the standard fuel oil) using corrosion-resistant materials, and implementing filtration systems to manage ash and solid particles (Hu and Gholizadeh, 2019, Panwar and Paul, 2021, Pafili et al., 2021).. Instead of burning directly bio oil, co-firing with fossil fuel reduces nozzle blockages and improves engine efficiency. This reduces costs associated with burner and engine modifications (Hu and Gholizadeh, 2019). Co-feeding bio-oil (< 5 % wt.) with conventional fossil fuels is more practical than direct bio-oil combustion, though it may require slight modifications to the burner system and sprayer (Hu and Gholizadeh, 2019).

Bio-oil to bio-fuel:

Given that biomass is the only renewable source of fixed carbon, there is significant interest in producing bio-fuels (hydrogen, methane and other biomass-based fuels).

Bio-diesel and bio-gasoline:

Bio-oil may be treated with hydrotreating and hydrocracking processes to generate bio-diesel and bio-gasoline. To stabilize bio-oil, a dual-stage hydrotreating process is employed (Jones et al., 2009). The resulting product is a mixture of hydrocarbons with a low oxygen content (~2%). The stabilized oil is separated into light and heavy fractions, with the heavy fraction—boiling above 350°C—being sent to a hydrocracker for complete conversion into gasoline and diesel blend components (Jones et al., 2009). The gasoline and diesel blend are then separated through distillation. Biodiesel is suitable for blending with petroleum diesel (Basu and Kaushal, 2024b). Figure 14 includes gasification of solid biomass as well as bio-oil from fast pyrolysis for production of transportation bio-fuels.

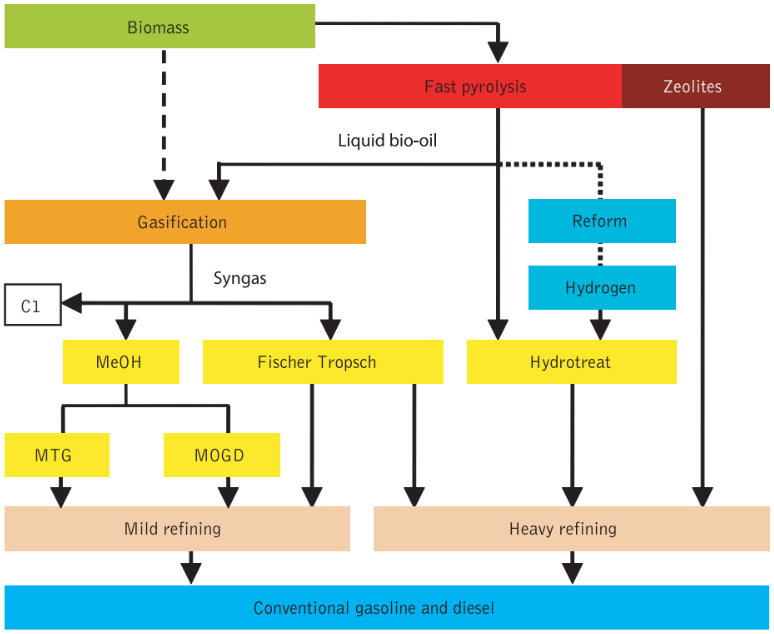


Figure 14. Transport fuels via bio-oil and biomass gasification (MTG-Methanol To Gasoline; MOGD-Methanol to Olefins, Gasoline and Diesel) (IEA Bioenergy, 2007b)

Hydrogen:

The process generates a relatively small amount of gaseous products, which results in limited hydrogen recovery and may render the separation of hydrogen from the gas fraction economically unfeasible (Ahlström, 2021, Parthasarathy and Narayanan, 2014).

Steam reforming is used to convert bio-oil into syngas (a mixture of hydrogen and carbon monoxide), as mentioned above, which can then be further processed into hydrogen, through the water-gas shift (WGS) reaction (Soria et al., 2019).

Gasification can also convert bio-oils into a uniform, syngas intermediate for further conversion to hydrogen (Zheng et al., 2019). Hydrogen, with a high energy content of 120.7 MJ/kg (Mohanty et al., 2012), is a highly attractive fuel and energy carrier.

Methane:

Methane can be derived from bio-oil through a multi-step process that transforms its components into methane. The process includes hydrotreatment, steam reforming, and methanation. The methane produced is then purified to remove any residual carbon dioxide, water vapor, and other trace gases. The resulting product is methane, which can be used as a renewable natural gas substitute or compressed for use as fuel in vehicles.

Bio-oil to chemical feedstocks:

Bio-oil, a hydrocarbon similar to petrocrude but with higher oxygen content, can produce many of the same chemicals derived from petroleum, including resins, food flavourings, agro-chemicals, fertilizers, levoglucosan, adhesives, preservatives, acetic acid, and hydroxyacetaldehyde (Basu and Kaushal, 2024b).

Bio-oil contains a variety of organic compounds, such as phenols, acids, and aldehydes, which can be extracted and used as raw materials in the chemical industry. These compounds can be converted into valuable products such as plastics, bio-based resins, coatings, pharmaceuticals, and specialty chemicals which are utilized in various industrial applications.

Biorefinery concept:

A biorefinery is an overall concept of processing biomass feedstocks into various valuable products. According to IEA Bioenergy "A biorefinery processes and upgrades a renewable raw material (i.e. biomass) into several marketable products, emphasising fuels and chemicals." (IEA Bioenergy, 2007b).

A key advantage of producing bio-oil from biomass is that its production can be de-coupled in time, scale, and place from the final application (Venderbosch and Prins, 2010). Examples of a biorefinery utilizing fast pyrolysis include the use of bio-oil for co-firing in power stations and the production of hydrogen through steam reforming. This concept is presented in Figure 15, including primary, secondary, and tertiary processing of bio-oil. The primary goal is to achieve optimal utilization of products, by-products, and waste.

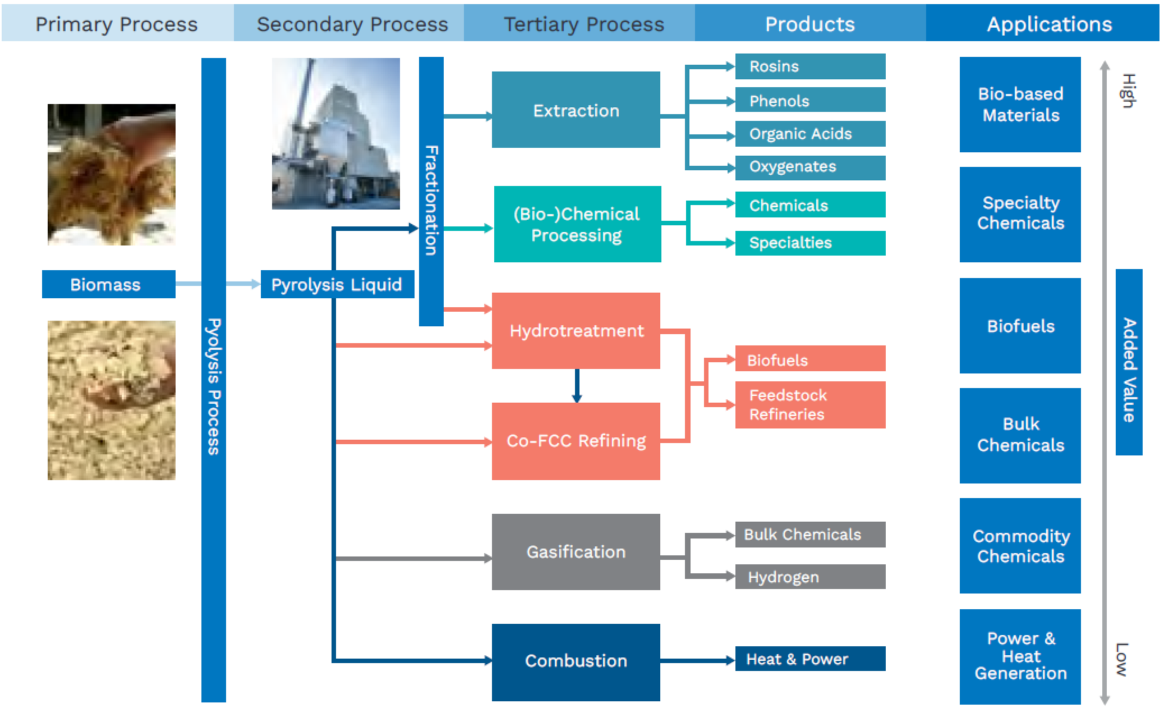


Figure 15. Biorefinery concept (Muggen, 2019).

Advantages and disadvantages of fast pyrolysis

Fast pyrolysis presents several advantages, including high liquid yield, as it produces a substantial amount of bio-oil compared to other methods. It is also versatile in terms of feedstocks, able to process various materials such as agricultural residues, wood residues, solid wastes such as sewage sludge and organic waste from the food industry, municipal solid waste, etc. Additionally, the process can run continuously, making it suitable for industrial applications, and some systems can recover and utilize energy from byproducts like gases and char.

However, there are notable disadvantages. Bio-oil often contains high levels of water, acids, and other oxygenated compounds, which require further upgrading for use in conventional engines or as a chemical feedstock. The process is also complex and costly due to the need for specialized equipment and precise control of operating conditions. Moreover, the generation of char and particulates requires handling and removal.

The capital cost for fast pyrolysis technology is high, driven by the expense of reactors, heat exchangers, and other specialized equipment, with the cost varying based on the scale of operation and system sophistication.

Operational costs include feedstock preparation, energy for heating, equipment maintenance, and byproduct handling. While fast pyrolysis can be cost-effective in terms of bio-oil yield, ongoing maintenance and energy requirements contribute to substantial operational expenses. Overall, fast pyrolysis is a promising technology for producing bio-oil from biomass, offering high yields and flexibility, but it faces challenges related to oil quality, system complexity, and cost.

Advantages and disadvantages for certain technical conditions of the fast pyrolysis process are presented in Table 10.

Table 10. The advantages and disadvantages of fast pyrolysis process

Feedstock	Technical conditions	Key Product	Advantage	Disadvantage	Level of Conversion Efficiency	Level of Capital Cost	Level of Operational Cost
Suitable feedstock: agricultural field residues, agricultural process residues, forest residues, wood from trees outside the forest, wood processing industry residue, sludge, livestock manure. *Feedstock size*: Less than 1 mm	*Temperature*: 500-1200°C *Residence time*: 10s *Heating rate:* very fast (10–100 °C/s) *Pressure:* vacuum – 1bar	Bio-oil	More suitable technology for bio-oil production. Simple and fast process. Scale-up is economically feasible. Efficient energy conversion. Bio-oil can be upgraded to "drop-in" fuel.	Requirement of pre-treatment (size restriction, moisture reduction to below 15%, blending manure or sludge with other biomass types). Requires attention to design and operation. Biomass collection is its main problem of industrialization. Limited commercial experience. The produced bio-oil shows little stability.	Moderate	Moderate to High	Moderate to High

D Flash Pyrolysis

Waste biomass suitable for Flash Pyrolysis

Flash pyrolysis is a rapid thermal decomposition process that effectively converts biomass into valuable products, including bio-oil, syngas, and bio-char. This process, as other pyrolysis processes, can utilize various types of waste biomass, making it versatile for different feedstock sources (agricultural residues, forestry waste, organic parts of MSW, lignocellulosic biomass).

Feedstock preparation

Preparing waste biomass feedstock for flash pyrolysis is a critical process that involves several key steps to optimize conversion efficiency and enhance product quality. Below is an overview of these essential steps:

Size Reduction: The waste biomass must be processed to achieve a uniform particle size, typically less than 2 mm. This reduction is vital for ensuring efficient heat transfer and reaction rates during pyrolysis. Techniques such as milling, grinding, or chipping are commonly employed to achieve the desired particle size.

Drying: Reducing the moisture content of the biomass to below 10% is essential to prevent energy losses and improve bio-oil yield. Various drying methods can be utilized, including air drying, rotary dryers, or other advanced drying technologies, depending on the scale and specific requirements of the operation.

Other pre-treatments: To enhance the properties of the feedstock and improve pyrolysis efficiency, pre-treatment methods may be necessary. Techniques such as torrefaction, steam explosion, or chemical treatments can be applied based on the type of waste biomass, helping to modify its physical and chemical characteristics for optimal conversion.

Homogenization: Achieving a consistent feedstock composition is crucial for stable operation in the pyrolysis reactor. This involves mixing different waste biomass types or batches to ensure uniformity in the feedstock, which helps to minimize variability in the pyrolysis process.

Description of Flash Pyrolysis Process

Flash pyrolysis is characterized by high heating rates, typically exceeding 1000 °C/s, and short residence times, often less than 2 seconds, at temperatures ranging from 400 °C to 650 °C (Giwa et al. 2019; Quan et al. 2023). This process is distinct from other pyrolysis methods such as slow and fast pyrolysis, which operate under different thermal conditions and yield varying proportions of solid, liquid, and gaseous products.

Flash pyrolysis is particularly noted for its ability to produce high yields of bio-oil, which can reach up to 75% of the total product mass, alongside smaller quantities of bio-char and syngas (Aboelela et al. 2023; Amutio et al. 2011). These conditions facilitate the rapid thermal decomposition of biomass, resulting in a high yield of liquid products, primarily bio-oil, along with solid char and gaseous byproducts (Diji 2013; Madhu, Kanagasabapathy, and Manickam 2018).

The products generated through flash pyrolysis are influenced by several operational parameters, including temperature, heating rate, and the nature of the feedstock. The efficiency of flash pyrolysis in producing bio-oil is particularly noteworthy, with reported yields ranging from 60% to 75% of the biomass feedstock (Afrane et al. 2022; Madhu et al. 2018; Ngoc Nguyen 2023). This contrasts with conventional pyrolysis methods, which typically yield lower amounts of liquid products due to longer residence times and lower heating rates (Mujtaba et al. 2021; Patni et al. 2013). The operational parameters of flash pyrolysis, including temperature, heating rate, and feedstock characteristics, play a crucial role in determining the composition and quality of the resulting bio-oil. For instance, higher temperatures generally lead to increased yields of lighter fractions in the bio-oil, while lower temperatures may favour the production of heavier, more viscous oils (Das and Hoque 2014; Demırbas 2004). But, the pyrolysis of biomass at moderate temperatures (around 500 °C) with high heating rates results in an optimal yield of liquid products, primarily bio-oil, while minimizing the formation of bio-char (Amutio et al. 2011, 2012).

The choice of feedstock is also significantly influencing the pyrolysis outcomes; lignocellulosic materials, such as wood and agricultural residues, tend to produce bio-oils with higher energy content compared to other biomass types (Balasundram et al. 2018; Olazar et al. 2000; Strezov et al. 2007). For example, the flash pyrolysis of oleaginous biomass has been shown to yield a diverse range of compounds, including fatty acids and phenolic compounds, which are valuable for bio-fuel production (Papari, Bamdad, and Berruti 2021; Urban et al. 2017).

Technological advancements in flash pyrolysis have focused on optimizing reactor designs and integrating catalytic processes to enhance product yields and quality. Various reactor types, including fluidized bed reactors and conical spouted bed reactors, have been explored to improve heat transfer and biomass conversion efficiency (DeSisto et al. 2010; Saravanakumar and Arunachalam 2021; Williams and Barton 2011). The incorporation of catalysts, such as HZSM-5 zeolite, has also been investigated to facilitate the deoxygenation of bio-oil and improve its stability and energy density (Gayubo et al. 2004; Olazar et al. 2000). These advancements are critical for addressing the challenges associated with bio-oil, such as its high oxygen content and instability, which can hinder its use as a direct substitute for fossil fuels (Xie et al. 2016; Yan, Cheng, and Hu 2010). The introduction of catalysts, such as zeolites, during the pyrolysis process can facilitate the breakdown of complex organic molecules, leading to the formation of lighter hydrocarbons and reducing the oxygen content of the bio-oil (Hakeem, Aberuagba, and Umaru 2018; Imran et al. 2016). This catalytic approach not only improves the energy density of the produced bio-oil but also enhances its compatibility with existing fuel infrastructure (Imran et al. 2016). Moreover, the flash pyrolysis process can be adapted for various feedstocks, including agricultural residues, plastics, and even contaminated biomass. Studies have demonstrated that the pyrolysis of contaminated hardwoods can yield valuable products while simultaneously addressing waste management issues (Stals et al. 2010). The versatility of flash pyrolysis makes it a viable option for the sustainable production of bio-fuels and chemicals from diverse organic materials. Catalytic flash pyrolysis can be considered as a promising approach to enhance the quality and yield of bio-oil.

Environmental considerations are paramount in the assessment of flash pyrolysis as a sustainable energy technology. The process not only provides a means of converting waste biomass into valuable energy products but also contributes to carbon sequestration through the production of bio-char, a stable carbon-rich material that can enhance soil health and mitigate greenhouse gas emissions (Bhupenchandra et al. 2019; Niedziński et al. 2023; Vijay et al. 2021). Furthermore, flash pyrolysis can be integrated into waste management strategies, particularly for the treatment of municipal solid waste and agricultural residues, thereby reducing landfill burden and promoting circular economy principles (Mostakim et al. 2021; Pissot et al. 2019; Williams and Barton 2011).

Despite its advantages, flash pyrolysis faces several challenges that must be addressed to facilitate its widespread adoption. These include the need for further research on the scalability of flash pyrolysis technologies, the optimization of reactor designs for continuous operation, and the development of effective methods for upgrading bio-oil into high-quality fuels (Dayton et al. 2015; Pahnila 2023; Raza et al. 2021). Additionally, the economic feasibility of flash pyrolysis systems must be evaluated in comparison to other biomass conversion technologies, such as gasification and hydrothermal liquefaction (Fendt et al. 2011; Gabhane et al. 2020; Meyer, Glaser, and Quicker 2011).

In conclusion, flash pyrolysis represents a promising technology for the conversion of biomass into renewable energy products. Its ability to produce high yields of bio-oil, coupled with advancements in reactor design and catalytic processes, positions it as a viable alternative to conventional fossil fuel sources. Continued research and development efforts are essential to overcome existing challenges and enhance the economic and environmental viability of flash pyrolysis systems.

Application of Flash Pyrolysis

In Europe, flash pyrolysis technology has potential for the valorisation of biomass resources and renewable energy production, and also it is widely used commercially. As Europe places great emphasis on renewable energy technologies and sustainable waste management, there is considerable interest in advanced conversion methods like flash pyrolysis.

Applications of Flash Pyrolysis in Europe:

Bio-fuel Production:

In Europe, flash pyrolysis is particularly used for bio-fuel production. The bio-oil derived from biomass is a high-energy-density fuel that can be used for both heat and electricity generation. This bio-oil is considered a sustainable alternative to petroleum-based fuels in Europe.

Chemical Production:

The bio-oil produced by flash pyrolysis is used as a raw material for various products in the chemical industry. This method supports the production of bio-based products that can replace fossil-fuel-based chemicals.

Waste Management and Recycling:

Flash pyrolysis also plays an important role in waste management and recycling processes in Europe. The conversion of organic waste (such as agricultural residues, forest products, food waste) into energy enables the transformation of waste into valuable products instead of disposal.

Carbon Sequestration and Bio-char Use:

In Europe, the bio-char resulting from flash pyrolysis is used as a soil amendment and is also considered for carbon sequestration. Bio-char improves soil fertility while removing carbon from the atmosphere, offering environmental benefits.

Leading Countries and Projects:

Flash pyrolysis technology has gained traction across various European countries as a method for converting biomass and waste materials into valuable products such as bio-oil, bio-char, and syngas. Countries such as Germany, the Netherlands, and Finland are at the forefront of implementing flash pyrolysis technology, driven by their commitment to sustainable energy solutions and waste management practices.

Germany has been a leader in the development and application of pyrolysis technologies, including flash pyrolysis. The country hosts several research institutions and companies focused on optimizing pyrolysis processes for biomass and waste materials. For instance, the Fraunhofer Institute for Interfacial Engineering and Biotechnology has conducted extensive research on the pyrolysis of various feedstocks, emphasizing the importance of operational parameters such as temperature and residence time in maximizing bio-oil yield (C. Volpi, 2024). Additionally, Germany's robust regulatory framework supports the integration of pyrolysis technology in waste management and energy production, making it a key player in the European pyrolysis landscape.

The Netherlands is another significant contributor to the advancement of flash pyrolysis technology. The country has established several pilot plants and commercial facilities that utilize flash pyrolysis to convert agricultural residues and organic waste into bio-fuels and chemicals. Research conducted at institutions like Wageningen University has focused on the efficiency of flash pyrolysis in producing high-quality bio-oil from lignocellulosic biomass, highlighting the potential for scaling up these technologies for industrial applications (C. Volpi, 2024). Furthermore, the Dutch government has implemented policies that encourage the adoption of renewable energy technologies, including pyrolysis, to meet its climate goals.

Finland also plays a crucial role in the European pyrolysis sector, particularly in the context of utilizing forest biomass for energy production. Finnish companies have developed innovative flash pyrolysis systems that convert wood residues into bio-oil and bio-char, which can be used for energy generation or as soil amendments. Research initiatives in Finland have demonstrated the feasibility of integrating flash pyrolysis with existing biomass supply chains, thereby enhancing the economic viability of the technology. Other European countries, such as Sweden and Austria, are also exploring flash pyrolysis as a means to enhance their waste management strategies and produce renewable energy. Sweden's focus on sustainability has led to investments in pyrolysis technologies that convert municipal solid waste into valuable fuels. Similarly, Austria has initiated projects aimed at optimizing flash pyrolysis processes for agricultural waste, contributing to the circular economy.

Along with these countries, Turkey also has investments in the field of flash pyrolysis. Turkey has one of the leading facilities in Europe for the pyrolysis of end-of-life waste tires. Erzincan Waste Tire Recycling and Energy Plant (EWTRPP), which produces useful products such as carbon black, pyrolytic oil, pyrolytic gas and electrical energy obtained from pyrolysis technology, is one of the largest facilities in Europe in this field with an installed capacity of approximately 12 MW. Figure 16 shows the schematic layout of EWTRPP (Güngör et al., 2022).

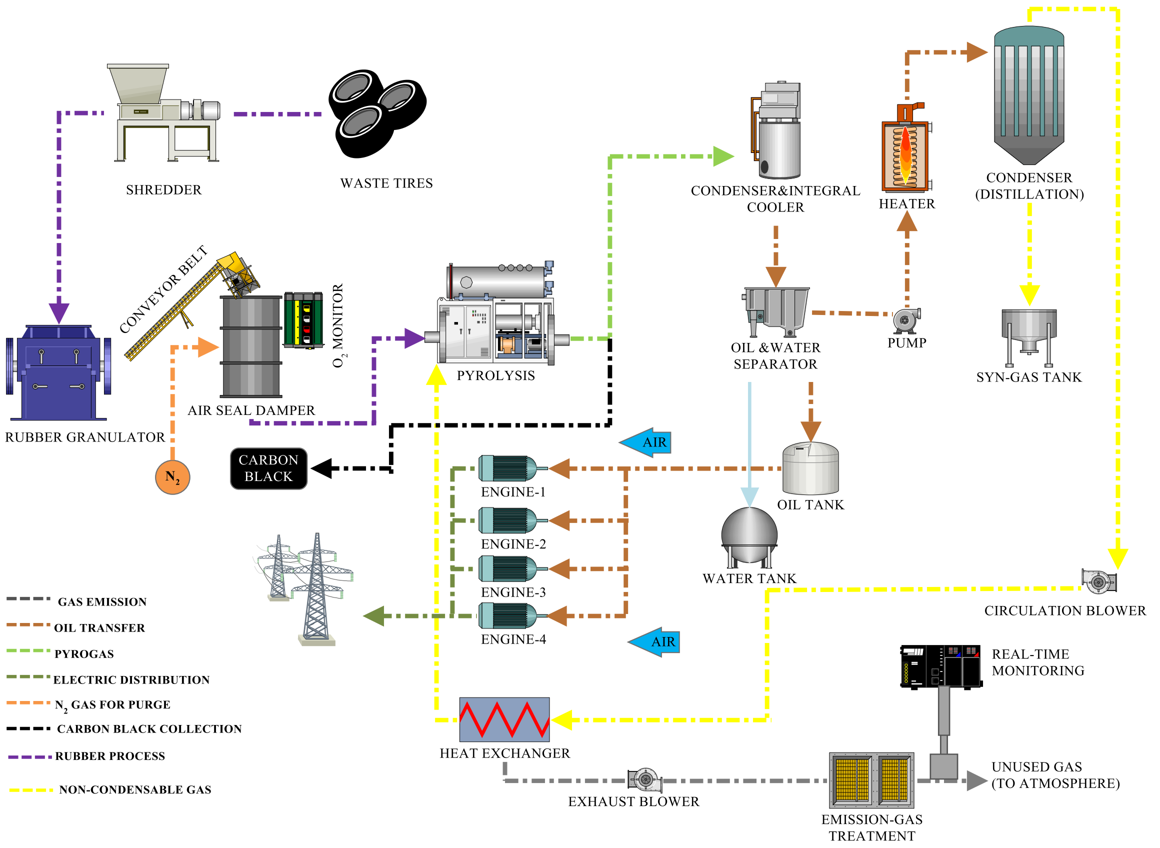


Figure 16. The schematic layout of EWTRPP (Güngör et al., 2022)

Advantages and disadvantages of Flash Pyrolysis

Flash pyrolysis presents several advantages and disadvantages that are crucial to consider when evaluating its potential for biomass conversion (Bridgwater, 2012, Mohan et al, 2006 and Demirbas, 2007):

Advantages

One of the primary benefits of flash pyrolysis is its ability to yield a high quantity of bio-oil. This bio-oil can serve as a renewable fuel or a chemical feedstock, making it a valuable resource in the energy sector. Additionally, the flash pyrolysis process is remarkably rapid, typically taking only a few seconds, which can lead to increased throughput and overall efficiency. The versatility of this technology allows it to process a diverse array of biomass types, including agricultural residues, forestry waste, and municipal solid waste. Furthermore, when integrated with other systems, flash pyrolysis can enhance energy efficiency by utilizing the produced syngas and bio-char. Importantly, it also tends to result in lower emissions of pollutants compared to traditional combustion methods, contributing to environmental sustainability.

Disadvantages

Despite its advantages, flash pyrolysis comes with certain challenges. The feedstock preparation process is extensive, often requiring drying and size reduction, which can add to the overall cost and complexity of the operation. Moreover, the bio-oil produced during flash pyrolysis can be unstable and acidic, necessitating further upgrading or refining before it can be used effectively as a fuel. The capital costs associated with establishing a flash pyrolysis plant can also be significant, posing a financial barrier for some potential operators. Additionally, maintaining the high temperatures and rapid heating rates essential for flash pyrolysis can be technically challenging, requiring advanced technology and expertise. Lastly, managing and effectively utilizing by-products such as bio-char and syngas can introduce complexity to the overall process.

Advantages and disadvantages for certain technical conditions of the fast pyrolysis process are presented in Table 11.

Table 11. The advantages and disadvantages of flash pyrolysis process (Bridgwater, 2012, Mohan et al, 2006, Demirbas, 2007, Giwa et al., 2019 and Quan et al., 2023).

Feedstock	Technical conditions	Key Product	Advantage	Disadvantage	Level of Conversion Efficiency	Level of Capital Cost	Level of Operational Cost
Suitable feedstock: agricultural field residues, agricultural process residues, forest residues, wood from trees outside the forest, wood processing industry residue *Feedstock size*: Less than 2 mm	*Temperature*: 400 °C to 650 °C *Residence time*: 2s *Heating rate:* very fast (1000 °C/s) *Pressure:* 1bar, even at vacuum or higher pressures	Bio-oil	High bio-oil rate, very fast process, energy-efficient process	Requirement of pre-treatment (size restriction, moisture reduction to below 10%). bio-oil produced can be unstable and acidic, requiring further upgrading or refining. Technically challenging process.	High	High	High

2.3.3. The technology status of Pyrolysis

The Technology Readiness Levels (TRLs) for pyrolysis technologies vary depending on the specific type and application.

Slow Pyrolysis is a more mature technology primarily used for producing bio-char. The TRLs for slow pyrolysis are typically around TRL 8-9, indicating commercial availability and widespread deployment.

Torrefaction is mature technology primarily used for producing torrefied biomass. The TRLs for torrefaction are typically around TRL 8-9.

Fast Pyrolysis is used for producing bio-oil and has seen significant development and deployment. The TRLs for fast pyrolysis are generally around TRL 7-8, as it is commercially available but may still be in the process of optimization and scaling up for certain applications.

Intermediate Pyrolysis produces a mix of bio-char, bio-oil, and syngas. The TRLs for intermediate pyrolysis are usually around TRL 6-7, indicating that it is demonstrated in relevant environments but not yet widely commercialized.

Flash Pyrolysis is advanced technology aims to produce high yields of bio-oil with rapid heating rates and short residence times. The TRLs for flash pyrolysis are generally around TRL 5-6, with ongoing research and pilot-scale demonstrations.

In Table 12 is presented TRLs levels of some gasification technologies implemented in Europe.

Table 12. Biomass waste pyrolysis technology readiness levels (TRLs).

Plant Name	Pyrolysis type	Feedstock	Capacity	TRLs	Reference
PYREG Gmb, Germany (50 systems installed worldwide)	Slow pyrolysis (carbonisation)	Wood chips, nutshells, fruit stones	Bio-char (8000t/y)	TRL 9 Commercial	(PYREG Net Zero technology, PYREG)
Twence Hengelo, Netherlands (started 2015)	Fast pyrolysis, Rotating cone reactor	Wood chips, bagasse, empty fruit bunch etc.	Bio-oil (3200 kg/h) Application: Heat and power production, El. power 2200 MWh annually	TRL 9 Commercial	(ETIP Bioenergy Working Group 2 – Conversion Processes and ETIP-B-SABS2 project team, 2020b)
Green Fuel Nordic, Lieksa, Finland (started 2020)	Fast pyrolysis, Rotating Cone	Sawdust and wood residue	Bio-oil 24000 t/y (2000 m^3/y)	TRL 9 Commercial	(ETIP Bioenergy Working Group 2 – Conversion Processes and ETIP-B-SABS2 project team, 2020b, BTG Bioliquids, 2022)
Honeywell UOP and Preem, Sweeden (started 2021)	Fast Pyrolysis	Biomass and biomass coal blends	Bio-oil	TRL 9 Commercial	(BEST - Bioenergy and Sustainable Technologies)
EMPYRO, BTG-BTL Hengelo, Netherlands, (started 2015)	Fast Pyrolysis	Wood pellet processing waste (5,000 kg/h)	Bio-oil (24,000 t/y)	TRL 8 First-of-a-kind commercial	(BEST - Bioenergy and Sustainable Technologies)
Pyrocell facility Gävle, Sweden (started 2021)	Fast Pyrolysis; Co-refining in FCC (fluidized catalytic cracking)	Sawdust	Bio-oil 25 000 ton/year	TRL 7 Demonstration	(IEA Bioenergy, 2021)
Fortum Fortum Joensuu, Finland (started 2013)	Fast pyrolysis, Fluidized bed	Forest residues, sawdust	Bio-oil 6300 kg/h Application: Heat and power production El. power 52 MW, Thermal capacity 180 MW	TRL 6-7 Deployment	(ETIP Bioenergy Working Group 2 – Conversion Processes and ETIP-B-SABS2 project team, 2020b)
To-Syn-Fuel (Fraunhofer Umsicht), Germany, (stated 2021)	Fast Pyrolysis	Sewage sludge, biogenic residues (3,900 t/y)	Bio-oil (450 t/y), solid fuels (2,000 t/y), clean syngas (780 t/y)	TRL 6-7 Demonstration	(BEST - Bioenergy and Sustainable Technologies)
AquaGreen PCE Denmark	Fast Pyrolysis	Organic residues and waste streams (biomasses and sludge)	Syngas and Bio-char	TRL 6-7 Demonstration	(Aqua Green, 2022, BEST - Bioenergy and Sustainable Technologies)

AquaGreen PCE Denmark, (stated 2022)	Fast Pyrolysis	Organic residues and waste streams (biomasses and sludge)	Syngas and Bio-char	TRL 6-7 Demonstration	(Aqua Green, 2022, BEST - Bioenergy and Sustainable Technologies)
Empyro Enschede, BTG-BtL, Netherlands, (started 1998)	Fast Pyrolysis	Biomass (na)	Bio-oil (1,000 t/y)	TRL 4-5 Pilot	(BEST - Bioenergy and Sustainable Technologies)
Green Fuel Nordic, Iisalmi, Finland (started 2011)	Fast Pyrolysis	Wood biomass 350,000 m^3/y	Bio-oil (1 t/y)	TRL 4-5 Pilot	(BEST - Bioenergy and Sustainable Technologies)
SkyClean Stiesdal Sweeden, (started 2022)	Fast Pyrolysis	Organic waste from agriculture and forestry, 40.000 t/y	Syngas and bio-oil	TRL 4-5 Pilot	(Stiesdal, 2023)
RISE ETC, Sweeden	Fast pyrolysis	Lignocellulosics biomass (20 kg/h)	Bio-oil (11 kg/h) for various chemicals	TRL 4-5 Pilot	(BEST - Bioenergy and Sustainable Technologies, Iisa et al., 2019)

2.4. Gasification

2.4.1. General review and evaluation of Biomass types for Gasification Technology

A Evaluation of Biomass types for Gasification Technology

Biomass gasification, a key aspect of thermochemical conversion, is widely regarded as the most attractive method for biomass conversion due to its versatility in treating a variety of biomass and waste-derived feedstocks, such as wood, sludge, crop residues, and agricultural residues (Mohammed Abed Fattah et al., 2017, Guan et al., 2016, Mishra and Upadhyay, 2021).

The performance of gasification technologies and the quality of the resulting products are significantly influenced by the physical and chemical characteristics of the waste biomass. Forest and woody waste biomass, with its relatively low moisture and ash content, is preferred over lower-grade biomass waste such as agricultural, agro-industrial, and other biodegradable materials. These lower-grade biomass wastes often have higher inorganic contents, lower ash melting temperatures, higher moisture content, larger particle sizes or irregular shapes, low bulk density, and unwanted components like heavy metals (Koppejan and Cremers, 2019). The properties of waste biomass that affect the gasification conversion process are presented in Table 13. In Table 14, summarized suitable biomass types for gasification with required pretreatments are presented.

Table 13. Properties of waste biomass that affect the gasification conversion process (based on (Bermudez and Fidalgo, 2016, Gao et al., 2023, Molino et al., 2016, Bermudez Menendez and Fidalgo Fernandez, 2016))

Properties	Influence
Physical properties	
Particle shape and size distribution (biomass as received usually has irregular and asymmetric clumps in size)	Homogenizing the material through size reduction (e.g., palletisation, grinding, chipping) is often necessary. Smaller particles and a uniform size distribution improves heat and mass transfer and a uniform particle temperature profile, enhanced reaction rates and biomass conversion, increase gasification efficiencies resulting in increased syngas yield and H2 yield. Tar and char yields decrease resulting in improved carbon conversion efficiency. Fixed bed gasifiers can handle particle sizes in a range from 0.5 to 10 cm (downdraft 2-10 cm; updraft 0.5-10cm) Entrained flow gasifiers require a particle size not higher than 0.15 mm. Bubbling fluidized bed requires particle size in a range 5-15 cm. Circulating fluidized bed requires particle size less than 2cm.
Porosity	Highly porous biomass promotes uniform temperature distribution and facilitates the easy diffusion of reactants and products, enhancing biomass reactivity.
Density	Low bulk density leads to reduced energy density, impacting both the cost and sizing of the systems.
Thermochemical properties	
Proximate analysis (moisture, volatile matter, ash, and fixed carbon) - wide range of values depending on the biomass feedstock	High moisture content, lowers biomass heating value, reduces process temperature, increase tar content, decreases syngas quality, decreases gasification efficiency and biomass conversion. The moisture content ranging between 10% and 15% is generally required for gasification processes. Plasma gasification is effective for processing high-moisture biomass; however, it involves high installation costs and significant energy demands. Increase in volatile matter has a favourable effect on HHV but has an opposite effect on the H_2/CO ratio. Increasing volatile matter leads to increasing CO and decreasing H_2 decrease High ash content reduces the biomass heating value, complicates the design of gas cleaning systems, and increases operational costs. Moreover, high ash content causes high slag formation in gasifiers.
Ultimate analysis (Elemental C, H, N, S, and O) - wide range of values depending on the biomass feedstock	High H/C and O/C ratios affect the biomass heating value and alter the composition of the produced syngas. High N content leads to the formation of NH_3 and HCN emissions. High S content causes the formation of H_2S and COS emissions, contributes to deposits and corrosion from interactions with alkali metals, and can deactivate downstream catalysts.
Heating value - - wide range of values depending on the biomass feedstock	Low heating value leads to lower energy density, impacting system cost and sizing.
Ash composition (K, Ca, P, Na, Mg, Fe, Al, Si, and other trace elements)	High Na and K content, leads to ash deposition, lower ash melting temperatures, and issues such as deposition, agglomeration, fouling, and corrosion from reactions with Si and S; impacts ash valorisation.

	High Mg, P, Ca content, increases ash melting temperature, affecting ash disposal applications. High heavy metals content, results in increased emissions, higher ash disposal costs, and challenges in ash valorisation. High Cl content lowers the softening temperature of ash. High Cl content results in emissions, deposits, corrosion, and ash sintering due to increased mobility of potassium.

Table 14. Application of different biomass waste for gasification processes (based on (Basu, 2013b, Reed T. B. and Das A., 1988, Tumuluru J.S. et al., 2018, Brown R.C. et al, 2011, Zhu et al., 2023, Maroto et al., 2020, Ferreira et al., 2019, Nowicki et al., 2020, Sánchez-Lozano et al., 2023, Yadav et al., 2023, Fatema et al., 2022, Migliaccio et al., 2021, Carotenuto et al., 2023).

Biomass waste	Required pretreatment
Agricultural biomass	***Drying:*** *Moisture Reduction:* Agricultural residues often have high moisture content which needs to be reduced to 10-20%. ***Size Reduction (Comminution):*** *Chopping/Shredding:* Large residues should be chopped or shredded into smaller, uniform pieces to ensure consistent feeding and gasification. *Grinding:* Further size reduction may be necessary depending on the type of gasifier being used. ***Densification (optional):*** *Pelletizing/Briquetting:* Loose and bulky residues can be compressed into pellets or briquettes to increase energy density, improve handling, and ensure uniform feeding into the gasifier. ***Removing Non-combustible Materials:*** *Screening:* Removing soil, stones, and other non-combustible materials to prevent damage to the gasification equipment. ***Chemical and Thermochemical Treatment (optional):*** *Leaching:* Washing residues to remove unwanted chemicals like chlorine and potassium that can cause fouling and corrosion in the gasifier. *Torrefaction:* Mild pyrolysis (200-300°C) to improve the biomass properties, making it more hydrophobic, increasing its energy density, and reducing its O/C and H/C ratios. ***Storage:*** *Dry Storage:* Ensuring that the pretreated biomass is stored in a dry place to prevent re-absorption of moisture. *Protected Storage:* Keeping the biomass protected from pests and contamination.
Forest/wood biomass	***Sorting and Separation (for Discarded wood products):*** *Material Sorting:* Separating wood materials from non-wood materials like metal, plastic, and rubber. *Contaminant Removal:* Removing nails, screws, and other hardware using magnetic separation or manual sorting. ***Removal of Coatings and Treatments (for Discarded wood products):*** *Stripping:* Removing paint, varnish, or other coatings that may release harmful emissions or create residues during gasification. *Chemical Washing:* Using mild solvents to remove any chemical treatments, although this step should be managed to prevent environmental contamination. ***Drying:*** *Moisture Reduction:* Wood biomass needs to have its moisture content reduced to 10-20% for efficient gasification. ***Size Reduction (Comminution):*** *Chipping/Shredding:* Large wood pieces should be chipped or shredded into smaller, uniform pieces. *Grinding:* Further size reduction may be necessary to meet the particle size requirements of the gasifier.

	Densification (optional): *Pelletizing/Briquetting:* Loose and bulky wood biomass can be compressed into pellets or briquettes to increase energy density, improve handling, and ensure uniform feeding into the gasifier. ***Removal of Impurities:*** *Debarking:* Removing bark from wood logs as it contains high levels of ash and other impurities. *Screening:* Removing soil, stones, and other non-combustible materials. Magnetic Separation: For removing any metal contaminants from the wood chips or sawdust. ***Chemical and Thermochemical Treatment (optional):*** *Leaching:* Washing wood to remove unwanted chemicals like chlorine and potassium that can cause fouling and corrosion in the gasifier. *Torrefaction:* Mild pyrolysis (200-300°C) to improve biomass properties, making it more hydrophobic, increasing energy density, and reducing O/C and H/C ratios. ***Blending (optional):*** *Homogenization:* Mixing different types of wood biomass to achieve a consistent and homogeneous feedstock for gasification. ***Storage:*** *Dry Storage:* Ensuring that the pretreated biomass is stored in a dry place to prevent re-absorption of moisture. *Protected Storage:* Keeping the biomass protected from pests, contamination, and rewetting.
Agro-industrial biomass	(Nutshells and fruit kernels/stones/pits. Vegetable and fruits pomace, Brewers' Spent Grains, Oil cakes) **Removal of Impurities:** Washing or cleaning from dirt. **Drying:** *Moisture Reduction:* Moisture content has to be reduced to 10-20% for efficient gasification. ***Size Reduction (Comminution):*** *Chipping/Shredding:* Large wood pieces should be chipped or shredded into smaller, uniform pieces. *Grinding:* Further size reduction may be necessary to meet the particle size requirements of the gasifier. ***Densification (optional):*** *Pelletizing:* waste biomass compressed into pellets to increase energy density, improve handling, and ensure uniform feeding into the gasifier. ***Storage:*** *Dry Storage:* Ensuring that the pretreated biomass is stored in a dry place to prevent re-absorption of moisture. *Protected Storage:* Keeping the biomass protected from pests, contamination, and rewetting.
Other biodegradable biomass	(Kitchen and food waste, organic fraction of municipal solid waste, sewage sludge) ***Sorting:*** Separation of organic materials from inorganic materials (plastics, metals, glass, etc.). **De-Watering** (for sewage sludge): ***Mechanical Dewatering****:* Using centrifuges, belt presses, or filter presses to reduce the moisture content to 20-30%. ***Drying:***

	Moisture Reduction: Moisture content has to be reduced to 10-20% for efficient gasification. ***Stabilization* (for sewage sludge)**: **Thermal Stabilization**: Heating sludge to high temperatures (around 70°C) to reduce pathogens and stabilize organic matter. **Chemical Stabilization**: Adding chemicals such as lime to enhance stability and reduce odors. ***Size Reduction (Comminution):*** *Chipping/Shredding:* Large wood pieces should be chipped or shredded into smaller, uniform pieces. *Grinding:* Further size reduction may be necessary to meet the particle size requirements of the gasifier. ***Densification (optional):*** *Pelletizing/Briquetting:* Loose and bulky residues can be compressed into pellets or briquettes to increase energy density, improve handling, and ensure uniform feeding into the gasifier. ***Storage:*** *Dry Storage:* Ensuring that the pretreated biomass is stored in a dry place to prevent re-absorption of moisture. *Protected Storage:* Keeping the biomass protected from pests and contamination.

2.4.2. Review of Gasification Technology

Gasification is an endothermic process that converts biomass waste into useful gases and chemicals. To drive the chemical reactions forward, energy is provided by feeding the reactor with a sub-stoichiometric amount of oxygen (Khalil, 2009). The gasification process can utilize mediums such as air, oxygen, steam, carbon dioxide, or a mixture of these, and supercritical water (Mishra and Upadhyay, 2021). The operating temperature for gasification is typically quite high, ranging from 850 to 1500°C (Khalil, 2009), and pressures ranging from 1-30 bar (Papadokonstantakis S., 2019), depending on the technology and biomass used. High temperatures are necessary to drive the main gasification reactions forward. The resultant mixture of gases, known as product gas or syngas, typically contains carbon- monoxide (CO), hydrogen (H_2), carbon- dioxide (CO_2), methane (CH_4), and nitrogen (N_2) as well as light hydrocarbons such as ethane and propane, and heavier hydrocarbons like tars (Molino et al., 2016). Undesirable gases, such as hydrogen sulphide (H_2S) and hydrochloric acid (HCl), or inert gases like nitrogen (N_2), may also be present in the syngas (Molino et al., 2016), as well as char, ash, bed material, depending on technology and biomass used (Rauch et al., 2014) The major obstacle faced in the gasification process is the formation of tar, which is difficult to purify and decreases the yield of H_2 (Mishra and Upadhyay, 2021, Xu et al., 2010). The presence of mentioned impurities depends on the biomass treated and the operational conditions of the gasification process.

Emissions of sulphur and nitrogen compounds (mainly their oxides), particles are significantly reduced by use of gasification process. The lack of oxygen during the gasification process prevents the formation of free chlorine from hydrogen chloride (HCl). This prevents contact of hydrogen chloride gas comes with moisture, and formation of hydrochloric acid, which is a very corrosive substance. Depending on the feedstock characteristics, the gasification technology and the operational conditions low heating value (LHV) ranges from 7 to 18 MJ/Nm^3 and in case of supercritical gasification even above 40 MJ/kg (Gao et al., 2023, Mishra and Upadhyay, 2021).

A Fundamental Concepts in Biomass Gasification

Biomass gasification is a complex process due to the presence of multiple reacting agents, resulting in several simultaneous stages regardless of the technology used. Main gasification stages are oxidation, drying, pyrolysis, reduction and tar decomposition. These stages are presented in Figure 17.

The oxidation stage is exothermic and is necessary to obtain the thermal energy required to sustain the entire gasification process, and to maintain the operative temperature at the required value. The combustion product is a gas mixture of CO, CO_2 and steam. N_2 may be present in this mixture if air is used for the biomass oxidation; otherwise, nitrogen is virtually absent when only oxygen is employed. The main reactions that take place during the oxidation phase are the following (Molino et al., 2016, Gao et al., 2023):

Char combustion: $C + O_2 \rightarrow CO_2$, 406 kJ/mol
Hydrogen combustion: $2H_2 + O_2 \rightarrow H_2O$, 242 kJ/mol
Partial oxidation: $C + \frac{1}{2}O_2 \rightarrow CO$, 111kJ/mol

Drying is the endothermic process of evaporating moisture from the waste biomass feedstock. The heat necessary for pyrolysis is derived from the oxidation stage of the process. The energy required for drying is directly proportional to the moisture content of the feedstock. Drying is generally deemed complete when the biomass reaches a temperature of 150°C (Gao et al., 2023). The drying process can be schematized with the following overall reaction:

$$Wet\ Biomass \rightarrow steam + dry\ Biomass$$

Pyrolysis occurs at temperatures between 250–700°C and is an endothermic process. The heat required for pyrolysis is derived from the oxidation stage of the process. Pyrolysis decompose carbonaceous materials into condensable vapours (heavy hydrocarbons), gas, and char fractions, subsequent thermal cracking of heavy hydrocarbons into gas and char (Khalil, 2009). The pyrolysis process can be schematized with the following overall reaction:

$$Biomass \rightarrow H_2 + CO + CO_2 + CH_4 + steam + tar + char$$

The reduction, endothermic, phase incorporates all the products from the preceding oxidation and pyrolysis stages. During this step, the gas mixture and char react to produce the final syngas (Molino et al., 2016). The reduction temperature critically influences the syngas composition and its properties. Higher temperatures promote char oxidation, reducing the solid residue and decreasing tar formation but can increase the risk of ash sintering and lower the energy content of the syngas (Molino et al., 2016). The key reactions occurring in the reduction phase include (Molino et al., 2016):

Boudouard Reaction: $C + CO_2 \leftrightarrow 2CO$, 172 kJ/mole
Carbon Reforming Reaction: $C + H_2O \leftrightarrow CO + H_2$, 131 kJ/mol
Water Gas Shift Reaction: $CO + H_2O \leftrightarrow CO_2 + H_2$, 41 kJ/mol
Methanation Reaction: $C + 2H_2 \leftrightarrow CH_4$, *75 kJ/mol*

Boudouard and carbon reforming reactions are endothermic, while reactions water gas shift and methanation reactions are exothermic.

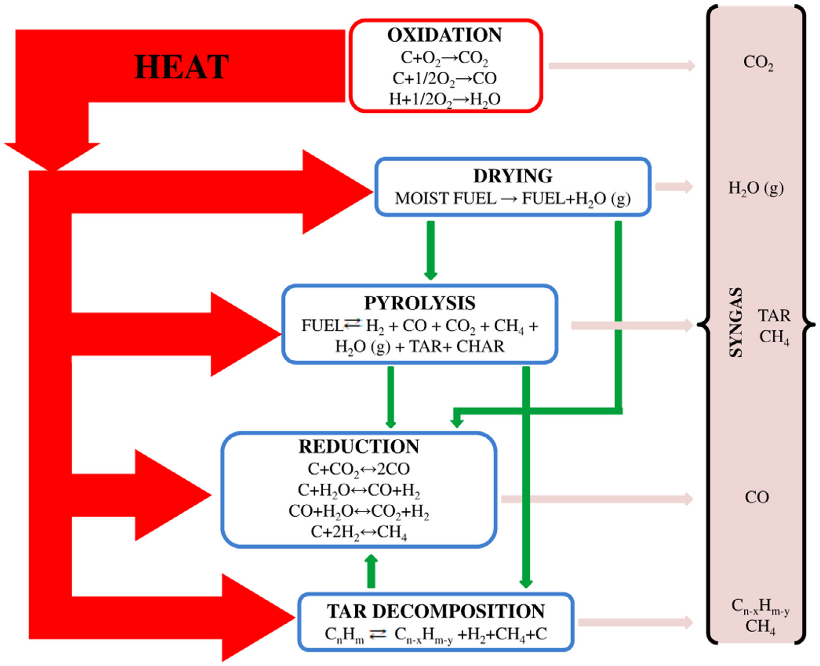


Figure 17. Main stages of the gasification process (Molino et al., 2016)

B Influences of waste biomass properties on syngas quality

Different waste biomass has different moisture, ash, and volatile matter contents and different elemental compositions.

Ash Content

When the ash content and alkali and alkaline earth metals (AAEMs) are high, it results in a lower ash melting point and a high risk of molten slag formation on the exterior of agglomerated particles. This reduces the biomass gasification reaction, lowers syngas production, and influences syngas quality and its high heating value (HHV) (Gao et al., 2023).

According to the literature, biomass with an ash content greater than 10% w/w tends to cause substantial slag formation. To mitigate slagging issues, it is advisable to operate the gasifier either below the ash flow temperature or above its melting point (Molino et al., 2016).

Volatile Content

The effect of volatile content on syngas production is significantly influenced by the gasification temperature. Higher gasification temperatures facilitate the conversion of tar into gas species such as H_2, CO, and CH_4, which leads to a considerable reduction in tar yield and an increase in the overall gas yield (Gao et al., 2023). Additionally, an increase in volatile matter (VM) positively impacts the HHV of the syngas but adversely affects the H_2/CO ratio (Gao et al., 2023).

Moisture Content

One of the crucial elements to consider is the moisture content. When the moisture content in the biomass feedstock is excessive, it substantially lowers the gasification temperature, impairs the overall gasification performance, leads to incomplete reactions, and diminishes both the yield of syngas and the concentration of combustible gases (Gao et al., 2023). With the increase of the moisture content, the percentage of CO_2 increases, while CO decreases (Trninić, 2015). A similar trend is also observed for the H_2 in the fuel gas increases continuously with the moisture content. The heating value of producer gas decreases, because it affects the reactions of steam reforming (of tar), char gasification, water gas, and water gas conversion (Trninić, 2015, Gao et al., 2023). The moisture content should be below 20%, ideally ranging between 10% and 15%. It is recommended to dry the biomass if the moisture content exceeds 20% (Trninić, 2015).

Particle size

The particle size of biomass feedstock significantly impacts the efficiency and effectiveness of the gasification process.

Smaller particles provide a larger surface area for interaction with gasifying agents, which can enhance the solubility of the biomass and improve reaction rates (Mishra and Upadhyay, 2021). This increased surface area facilitates better heat and mass transfer, leading to improved product yields. The decrease in particle size improves the H_2/CO ratio (Mishra and Upadhyay, 2021, Hernández et al., 2010). Conversely, with larger particle sizes, the reactions are primarily controlled by the gas diffusion process (Feng et al., 2011). Larger particles have reduced surface area relative to their volume, which can slow down the diffusion of gases and hinder the overall gasification process (Feng et al., 2011).

Particle size requirements for biomass vary depending on the type of gasification reactor. Fixed bed gasifiers can process particles ranging from 0.5 to 10 cm (2-10 cm for downdraft and 0.5-10 cm for updraft), whereas entrained flow gasifiers require particles no larger than 0.15 mm (Bermudez and Fidalgo, 2016). Bubbling fluidized bed gasifiers need particles between 5 and 15 cm, while circulating fluidized bed gasifiers require particles smaller than 2 cm (Bermudez and Fidalgo, 2016).

In summary, smaller particle sizes in biomass feedstock enhance surface area, improve heat and mass transfer, and lead to better syngas quality and higher conversion efficiencies. These advantages contribute to more effective gasification and reduced formation of undesirable by-products like char and tar.

C Influences of various operating parameters on syngas quality

The main gasification parameters are temperature, gasifying agent, equivalence ratio.

Temperature

Temperature is a crucial parameter influencing both the quality of the syngas and the efficiency of the gasification process. Higher temperatures enhance the endothermic nature of the gasification process, leading to increased syngas yields (Gao et al., 2023). Simultaneously, elevated temperatures facilitate the tar cracking reaction, which reduces tar content and promotes the formation of gases such as H_2, CO, and CO_2, thereby increasing the overall gas yield (Trninić, 2015, Gao et al., 2023). However, the gasification temperature is influenced by the characteristics of the biomass, such as the amount and composition of ash. For example, agricultural waste biomass often contains a high proportion of low-melting ash. The temperature must be high enough to ensure an efficient gasification process but not so high as to cause problems with ash melting.

Pressure

In gasification processes, both atmospheric and elevated pressures are commonly employed. The choice of pressure largely depends on the intended use of the syngas. For applications such as methanol production or bio-fuels, higher pressures are preferred to enhance process yields and reduce tar content, while for generating combustible gases, atmospheric pressure is typically used (Xiang et al., 2018).

Higher pressure tends to favour the production of hydrogen and methane, but can be less favourable for carbon monoxide generation (Wang et al., 2023b). For supercritical water gasification, pressures are typically above 22.1 MPa (Wang et al., 2023b, Wang et al., 2023a).

Elevated pressure is generally recommended for large-scale gasification operations, whereas atmospheric pressure is more suitable for smaller-scale processes (Xiang et al., 2018).

Residence time

Residence time has a remarkable impact on the composition and produced tars (Mohammed Abed Fattah et al., 2017). Residence time refers to the duration that the biomass remains in the gasifier and interacts with the gasifying agents before being converted into syngas. Extended residence time promotes further reactions, such as the reforming of tars and hydrocarbons, leading to higher concentrations of desirable gases like hydrogen and carbon monoxide. However, too long a residence time might lead to undesirable reactions, such as methanation, which can reduce the concentration of carbon monoxide and hydrogen. The ideal residence time depends on various factors, including the type of biomass, gasifier design, temperature, and the specific goals of the gasification process.

Gasifying agent

Generally, the use of air, oxygen, steam, CO_2 or a mixture these as the gasifying agent results in different heating values of the produced gases.

Air is the most used gasifying agent in gasification processes due to its easy availability and low cost (Meng et al., 2011). However, the higher percentage of nitrogen present in air results in a lower HHV of syngas, 4 -7 MJ/Nm^3 (BEIS, 2021, Molino et al., 2016). Lower HHV is influenced by lower lower concentrations of CO and H_2 in syngas mixture.

Oxygen, when used as a gasifying agent, leads to higher reaction temperatures and faster reaction rates, resulting in the production of higher-quality syngas. (Gao et al., 2023). Syngas has a higher concentration of CO and H_2 and low concentration of tar. Syngas has HHV up to to 28 MJ/Nm^3 (Molino et al., 2016). However, oxygen gasification is an energy-intensive and costly process, primarily due to the separation of oxygen from air, which requires compression and refrigeration (Bhattacharya et al., 2012).

Using steam as a gasifying agent significantly enhances the production of H_2 and CO, resulting in a syngas with a heating value in the range 10–18 MJ/Nm^3 (Couto et al., 2013, Molino et al., 2016, BEIS, 2021).
CO_2 gasification produces a syngas rich in carbon monoxide (CO) and with a high heating value (Molino et al., 2016). This process benefits from enhanced syngas quality but requires an external heat source to sustain the necessary reaction temperatures and drive the conversion effectively (Molino et al., 2016).

Additionally, as a gasifying agent can be used supercritical water (SCW). The primary application of SCW lies in the gasification of waste biomass to produce hydrogen. Heating values of syngas can be up to 41.6–61.6 MJ/kg (Mishra and Upadhyay, 2021, Hantoko et al., 2019). SCW has garnered considerable attention as an ideal medium for biomass gasification due to its safety, non-toxicity, widespread availability, cost-effectiveness, and environmental friendliness (Guo et al., 2010). Despite these advantages, the process requires high temperatures and pressures to achieve the necessary reaction conditions. However, SCW gasification is an energy-intensive and costly process.

Equivalence ratio

The equivalence ratio (ER) is defined as the ratio between the actual air/oxygen supply to the gasifier and amount of air/oxygen theoretically required for a complete combustion of the waste biomass. The ER affects not only the balance between the biomass feed rate and the oxygen supply to the gasifier but also influences the temperature, pressure, heating value, and gas composition within the gasification reactor (Gao et al., 2023). The ER is determined by factors such as the type of gasifier, the gasification agent, and the properties of the waste biomass. As the ER increases, the percentages of H_2 and CO generally decrease, while CO_2 may increase slightly (Trninić, 2015). This shift leads to a reduction in the overall heating value of the syngas. In general, a lower ER results in incomplete gasification, increased char formation, and the production of syngas with a lower heating value. Conversely, a higher ER may shift the process from gasification towards combustion due to the higher oxygen supply (Gao et al., 2023). In practice, maintaining the ER between 0.2 and 0.3 is ideal for achieving optimal gasification performance in both fixed bed and fluidized bed gasifiers while entrained flow gasifiers typically require an ER approximately 20% higher (Molino et al., 2016).

Bed material

The choice of bed material in fluidized gasification is crucial in the design and operation of a gasifier. Bed materials can be categorized as inert or catalytic based on their role and the specific process requirements (Mishra and Upadhyay, 2021). Inert materials, such as silica, dolomite, limestone, olivine, and alkaline metal oxides, are selected for their physical properties, including thermal stability, high heat capacity, and resistance to chemical reactions (Mishra and Upadhyay, 2021). In contrast, catalytic bed materials, such as nickel and potassium-based catalysts, actively enhance the gasification process by facilitating specific chemical reactions. They improve process efficiency, influence operating parameters (e.g., pressure and temperature), and modify the composition of the produced syngas (Mishra and Upadhyay, 2021). For instance, Nickel based catalysts can accelerate the reforming reactions, while Potassium based catalysts can enhance the gasification of char.

Catalyst

Catalytic biomass gasification improves syngas yield compared to noncatalytic biomass gasification. The main objective of catalysts is to reduce the tar production (Faizan and Song, 2023). Compared to non-catalytic gasification methods, catalytic biomass gasification offers several notable advantages. It enhances hydrocarbon conversion and results in a higher catalytic yield, leading to increased syngas production (Faizan and Song, 2023). Various catalysts have been employed in biomass gasification, tailored to the type of biomass feedstock and the design of the gasifier. These include: alkali metals and alkaline earth metals, zeolites and alumina, limestones and dolomites, zinc-based and nickel-based catalysts, even platinum and ruthenium etc. (Faizan and Song, 2023). Each type of catalyst offers specific benefits depending on the application, influencing factors such as syngas composition and overall gasification efficiency

The influence of different gasification technologies on syngas characteristics will be presented in section 2.4.3. Design of Gasification Technology.

D Cleaning and Conditioning of Syngas

Depending on the application, syngas may require cleaning of particulates and other contaminating gases (Basu, 2013b). These pollutants include condensable hydrocarbons (tars), particulate matter (PM) consisting of unconverted char and ash, nitrogen compounds (NH_3, HCN, etc.), sulphur compounds (H_2S, COS, etc.), hydrogen halides (HCl, HF, etc.), alkali metals (primarily potassium and sodium), CO_2 (Woolcock and Brown, 2013, Abdoulmoumine et al., 2015). The presence of these impurities poses significant environmental concerns and technical issues in downstream equipment, such as catalyst poisoning, corrosion, and fouling (Abdoulmoumine et al., 2015).

The tolerance to pollutants and the cleanup methods varies depending on the end-use technology and environmental emission regulations. For instance, for Fischer-Tropsch and methanol applications, the maximum allowable concentrations of sulphur and nitrogen should be less than 1 ppm and 0.1 ppm, respectively (Elsaddik, 2022). Further, for the use of syngas in an internal combustion engine, tar concentration should be less than 100 mg/m^3 whereas for methanol synthesis it is required to be less than 0.1 mg/m^3 (Bermudez and Fidalgo, 2016). Detailed syngas specifications on impurities required for different applications are available in literature (Asadullah, 2014, Ephraim et al., 2020, Spath P. L. and Dayton D.C., 2003, Bermudez and Fidalgo, 2016). The choice of method depends on factors such as syngas composition, operational conditions, and the required purity of the final gas stream.

Tars present a significant challenge in biomass gasification processes due to their detrimental effects on downstream equipment and product quality. Two main approaches are employed: primary measures within the gasifier and secondary treatments after gasification (Bermudez and Fidalgo, 2016).Primary measures focus on optimizing gasifier design, adjusting operational conditions, and incorporating additives to mitigate tar formation (Bermudez and Fidalgo, 2016). Secondary measures are taken after the gasification process, trough hot and cold tar removing routes. In the cold route, methods like wet scrubbing (using water or oils), filtering, cyclones, or electrostatic precipitators are employed to further remove tars, alkali metals, and particulates (Bermudez and Fidalgo, 2016). In the hot route, tars are subjected to thermal or catalytic (Ni-based catalysts, Sn, Co, Rh, Cu) cracking processes. Thermal cracking involves extremely high temperatures, even higher than in gasification process (Bermudez and Fidalgo, 2016). During cracking, tars react with steam, CO_2, O_2, or H_2, altering the syngas composition.

Particulates (unreacted char and ash) are removed by cyclones and filters. Fine particulates can be removed by wet scrubbing.

Carbonyl sulfide (COS) is a challenging compound to remove from syngas due to its low reactivity with many conventional absorbents. A common method for COS removal is hydrolysis. In this process COS is hydrolyzed using steam to produce hydrogen sulfide (H_2S) and carbon dioxide (CO_2). This process is often carried out at elevated temperatures and pressures (Gupta et al., 2023). The resultant H_2S can then be removed using conventional methods for acid removing.

Syngas can contain various metal impurities, including elemental mercury (Hg), iron (Fe), and nickel (Ni). Biomass feedstocks can contain mercury, with concentrations varying between 1 and 40 mass ppb (dry basis) (Gupta et al., 2023). During high-temperature gasification, mercury species are generally converted into elemental mercury (Hg_0). Additionally, synthesis gases can be contaminated with metal carbonyls (M-CO), iron carbonyl ($Fe(CO)_5$) and nickel carbonyl ($Ni(CO)_4$), which are formed when the gas is cooled (Gupta et al., 2023). The most effective technology for mercury removal utilizes guard bed trapping media, where mercury is chemically transformed into a stable, non-hazardous compound through chemisorption and solid bulk phase changes (Chiche et al., 2013). Typically, the trapping media contains sulfur-based compounds that react with mercury to form solid mercuric sulfide (HgS), also known as cinnabar or metacinnabar (Chiche et al., 2013). Alternatively, some sorbents use silver, which forms an amalgam with mercury (Chiche et al., 2013). Once the active phase of the sorbent is exhausted, the spent material must be disposed of at a hazardous waste facility. Metal carbonyls can be removed by reacting them with metal oxides like zinc oxide (ZnO) or copper oxide (CuO) or by use of activated carbon to adsorb metal carbonyls due to its high surface area and adsorption capacity.

Ammonia can be removed by cold and hot route. In the hot conditioning route, ammonia can be removed from syngas by means of catalytic (Ni-based, Ru, Fe-based, limonite or dolomite) or selective oxidation decomposition (Bermudez and Fidalgo, 2016). In catalytic decomposition, ammonia is decomposed into hydrogen and nitrogen, while in oxidation is decomposed into nitrogen and steam. In the cold route ammonia is removed by scrubbing with water or acid aqueous solutions (normally H_2SO_4), or activated carbon (Bermudez and Fidalgo, 2016).

Acid gases (e.g. hydrochloric acid, hydrogen sulfide) can be effectively removed by solvent absorption and adsorption process (Mondal et al., 2011). In the solvent absorption process, the syngas containing acidic gases is brought into contact with a solvent that selectively absorbs these acidic components. This absorption process occurs at relatively lower temperatures and can efficiently capture acids. Common solvents employed in this process include aqueous solutions of sodium hydroxide (NaOH), which reacts with HCl to form sodium chloride (NaCl) and water. Similarly, hydrogen sulfide can react with NaOH to form sodium sulfide (Na_2S) and water. Other solvents such as calcium oxide (CaO), magnesium oxide (MgO), and sodium carbonates (Na_2CO3, $NaHCO_3$) are also utilized depending on specific process requirements (Bermudez and Fidalgo, 2016). The gas stream is typically passed through a scrubber or absorption tower where the solvent is sprayed or circulated counter currently. This allows for efficient contact between the gas and the solvent, facilitating the absorption of acidic gases into the solvent phase. The adsorption method is an effective approach for removing acidic gas components from syngas, particularly at elevated temperatures. This process involves the use of metal oxide adsorbents that react with acidic gases, facilitating their removal from the syngas stream. Common adsorbents used in this process include metal oxides such as zinc oxide (ZnO), copper oxide (CuO), chromium oxide (Cr_2O_3), and aluminum oxide (Al_2O_3) (Mondal et al., 2011).

The syngas typically contains high amounts of carbon monoxide (CO), ranging from 30-60% (Mondal et al., 2011). This CO can be converted into hydrogen (H_2) through the water gas shift reaction (WGSR), which is crucial for increasing H_2 production from syngas. The WGSR involves a catalyzed ($Cu/ZnO/Al_2O_3$, Fe_2O_3–Cr_2O_3, Co–Mo/Al_2O_3) reaction where steam and CO react to produce H_2 and carbon dioxide (CO_2) (Mondal et al., 2011). There are two main types of water gas shift reactions: sweet-gas shift and sour-gas shift. The sweet-gas shift occurs after sulfur removal from syngas and generally involves two high-temperature shift (HTS) stages followed by one low-temperature shift (LTS) stage, with cooling in between (Mondal et al., 2011). It requires less steam, making it more cost-effective and reducing CO from 44.6% to 2.1% in two HTS steps and further to 0.5% in the LTS step (Mondal et al., 2011). Conversely, the sour-gas shift is performed before sulfur removal and usually involves two to three stages with heat exchangers and additional steam. It can lower CO from 44.6% to 1.8% in two steps but requires more steam (Mondal et al., 2011). To achieve CO levels below 1%, extra steam is needed before a third reactor.

E Applications of Syngas

Syngas can be used directly in power plants for combine heat and power production (CHP). After purification, syngas can be utilized in high-efficiency facilities such as gas and steam turbines, internal combustion engines, solid oxide fuel cells (SOFC), and molten carbonate fuel cells (MCFC) (Molino et al., 2016). These systems can achieve greater system efficiencies in the range of 30 to 40% (Ciferno and Marano, 2002). To be considered a viable alternative to conventional fossil fuels and to provide maximum flexibility for industrial or utility applications, syngas must have a heating value exceeding 11 MJ/m³ (Ciferno and Marano, 2002). As mentioned, syngas is an important source of valuable secondary products: methane, hydrogen, diesel or gasoline (synthesized using Fischer-Tropsch synthesis), methanol, fertilizers (produced through ammonia synthesis) (Basu, 2013b). Figure 18, shows possible applications of syngas.

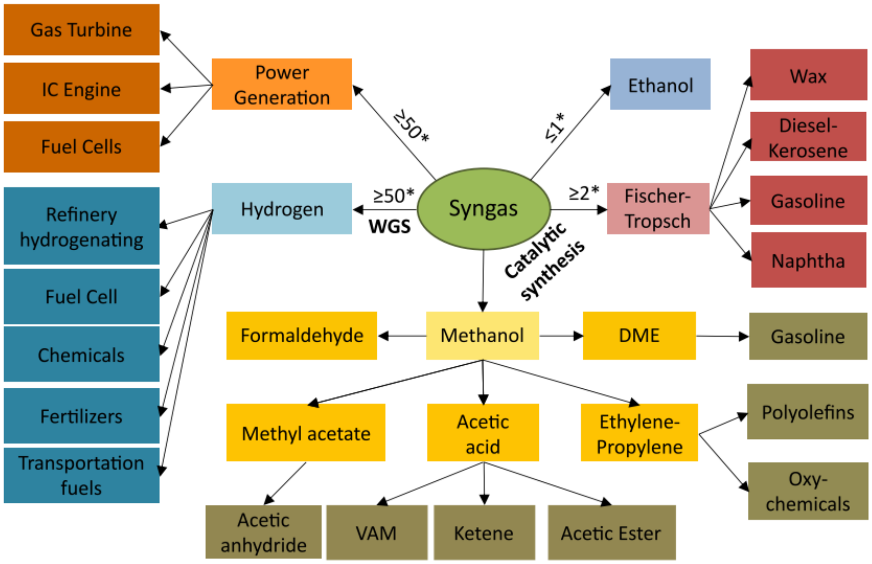


Figure 18. Application of syngas (Elsaddik, 2022).

Hydrogen

Hydrogen is predominantly produced through the steam reforming of hydrocarbons, utilizing a catalyst at approximately elevated temperatures. Steam methane reforming (SMR) based plants are most used to produce a hydrogen. After gasification, the syngas must be purified to remove contaminants such as particles, tar, ammonia, hydrogen sulphide, hydrogen chloride etc. (Brito et al., 2023), since these contaminants can deactivate catalysts. Steam methane reforming (SMR) is an endothermic reaction that is carried out at high pressures (~25–30 bar), high steam-to-carbon (S/C) molar ratios (~2.5–3.0), elevated temperatures (700–1000 °C) and presence of catalyst (Nickel, Palladium, ruthenium, iridium rhodium and platinum) (Brito et al., 2023). During SMR, the methane reacts with steam in the presence of the catalyst to produce hydrogen and carbon oxides through the following reactions (Brito et al., 2023):

Reforming reaction: $CH_4 + H_2O \leftrightarrow CO + 3H_2$, 205.9KJ/mol
Water shift reaction: $CO + H_2O \leftrightarrow CO_2 + H_2$, 41.2 KJ/mol

Methane

Methane production from syngas typically involves a process called methanation, where CO, CO_2 and H_2 from the syngas are converted into methane CH_4 and H_2O (Lisbona et al., 2023). This process occurs in the presence of a catalyst, often nickel-based, and operates under specific conditions of temperature (250°C to 300°C) and pressure (15-25 bar) (Molino et al., 2018). Chemical Reactions (Battulga et al., 2020):

$CO + 3H_2 \rightarrow CH_4 + H_2O$, 206 kJ/mol
$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$, 165 kJ/mol

Methan due to its resemblance to natural gas, methane can be easily integrated into existing infrastructure. Methane can be upgraded to meet natural gas quality standards, allowing it to be directly injected into the natural gas grid. Additionally, it can be utilized as a transportation bio-fuel and for combined heat and power (CHP) applications.

Synthetic Fischer-Tropsch Fuels

Bio-fuels such as gasoline and diesel can be produced from synthesis gas via the Fischer-Tropsch (FT) process (Ciferno and Marano, 2002). FT process converts a mixture of CO and H_2 to a range of hydrocarbons and hydrocracked into mainly diesel or gasoline of excellent quality (Ail and Dasappa, 2016). Before, entering the FT process, syngas after gasification needs to be conditioned to satisfy FT specifications in terms of H_2 to CO ratio and cleaned from impurities such as hydrogen sulphide, carbonyl sulphide, ammonia, etc. (ETIP Bioenergy, 2021). The FT synthesis involves the catalytic reaction (presence of iron and cobalt), typically operating at pressures between 10 and 60 bar and temperatures ranging from 200 to 300°C (Ail and Dasappa, 2016). During the reaction, the reactants CO and H_2 adsorb onto the catalyst surface, where they participate in polymerization to form hydrocarbons. The FT synthesis reaction:

$$(\frac{n}{2}H_2 + m)H_2 + mCO \rightarrow C_mH_n + mH_2O$$

Methanol

Methanol (CH_3OH) is produced through the direct hydrogenation of CO and CO2 in the presence of catalysts (Zn, Cu, Al, and Cr) (Basu, 2013b). The process is conducted under high pressure (typically 50-100 bar) and moderate temperatures (approximately 200-300°C). Methanol is produced through reduction reactions (Ricci and Perego, 2015):

$CO + 2H_2 \leftrightarrow CH_3OH$, 91 kJ/mol

$CO_2 + 3H_2 \leftrightarrow CH_3OH$, 49 kJ/mol

Methanol is an important feedstock to produce transport fuels, in fuel cells for energy storage and conversion and many chemicals (formaldehyde, acetic acid, methyl tertiary-butyl ether (MTBE), methyl methacrylate (MMA), dimethyl terephthalate (DMT), dimethyl carbonate (DMC) and various plastics).

Ammonia

Ammonia (NH_3) production from syngas typically involves a process called Haber Bosch (Flórez-Orrego et al., 2023, Gilbert P. et al., 2009). Before entering the Haber Bosch process, syngas after gasification needs to be conditioned to satisfy process specifications in terms of required content of H_2 (Gilbert P. et al., 2009). To increase the hydrogen content, the syngas is subjected to a water-gas shift reaction, where CO reacts with steam to produce additional hydrogen. Also, it is necessary to add the necessary remaining N_2 to achieve the correct molar ratio and then proceed to the ammonia synthesis step (Gilbert P. et al., 2009). The cleaned and conditioned syngas passes over a bed of catalyst (FeO, Fe_2O_3) at high pressure (60-180 bar) at moderate temperature (Basu, 2013b, Gilbert P. et al., 2009). Reaction of ammonia formation (Ricci and Perego, 2015):

$N_2 + 3H_2 \rightarrow 2NH_3$, 46 KJ/mol

The once-through conversion is low (20–30%), and a substantial part of the unconverted gas is recirculated to enhance the total conversion (Ricci and Perego, 2015). Ammonia is an important chemical used for many applications, including production of fertilizers, disinfectants, nitric acid, and refrigerants.

Urea

Ammonia is predominantly used in the production of fertilizers, particularly urea. Urea is synthesized through a two-step reaction involving carbon dioxide and ammonia: the first step, ammonia and carbon dioxide react to form ammonium carbamate and the second step, ammonium carbamate is dehydrated to produce urea (Ricci and Perego, 2015):

$$2NH_3 + CO_2 \leftrightarrow H_2N - COOO^{-}NH_4$$
$$N - COOO^{-}NH_4 \leftrightarrow H_2NCONH_2 + H_2O$$

2.4.3. Design of Gasification Technology

Gasification technologies are broadly categorized based on the design and configuration of the gasifier, with each type offering specific advantages depending on the feedstock properties, operational conditions, and desired end-use applications. Understanding the distinct features of each technology is essential for selecting the optimal system. This section delves into the critical engineering principles and design considerations necessary for achieving efficient gasification, with a focus on maximizing energy output, enhancing syngas quality, and improving overall system performance.

A Moving bed gasifiers

Moving bed gasifiers, also known as fixed bed gasifiers, are a traditional and widely used type of gasification technology. In these systems, the feedstock moves slowly through the reactor, typically from top to bottom, while the gasifying agent flows in either the same or opposite direction, depending on the specific design.

Updraft Gasification

Waste biomass suitable for Updraft Gasification:

Updraft gasification is a versatile process that can handle a variety of waste biomass types. Some suitable materials include: agricultural residues, forestry residues, organic parts of MSW (paper products, food waste, and garden waste), industrial waste (e.g. de-oiled cakes) (Siddiqui et al., 2022, Zhu et al., 2022, Havilah et al., 2022).

Feedstock preparation:

Updraft gasification is well-suited for a diverse range of waste biomass feedstocks. These include agricultural field residues, agricultural processing by-products, forest residues, wood from non-forest trees, residues from the wood processing industry, and solid wastes like sewage sludge, organic waste from the food industry, and municipal solid waste. This versatility makes updraft gasification an effective solution for converting various types of waste biomass into valuable syngas, regardless of their origin (Seggiani et al., 2012b, Seggiani et al., 2013, Seggiani et al., 2012a, Fatema et al., 2022, Rowland et al., 2009, Taupe et al., 2016, Dogru et al., 2019, Jančauskas et al., 2024, Chen et al., 2013a)

Each type of biomass is defined by unique physical and chemical characteristics, such as moisture content, heating value, bulk density, chemical composition, and levels of ash and volatile matter. These attributes are critical in determining the biomass's effectiveness and efficiency as a fuel source in gasification and other energy conversion processes (Abdollahi-Neisiani et al., 2013). The specific properties of biomass influence its handling, preprocessing requirements, and overall performance.

The composition of biomass significantly affects the updraft gasification process, influencing both efficiency and syngas quality. High moisture content makes biomass hydrophilic and increases energy demand for drying, reducing overall efficiency. Its low bulk density, high porosity, and fibrous nature complicate handling and feeding, often requiring pre-treatment like densification. While high volatile matter boosts syngas production, low fixed carbon limits char formation, affecting the heat balance. Biomass has lower carbon but higher oxygen content than fossil fuels, resulting in a lower heating value. It produces fewer harmful emissions due to lower nitrogen, sulphur, and chlorine levels but its ash, with a low melting point, can cause slagging and fouling. Alkali and alkaline earth metals (AAEMs) in biomass can act as catalysts, enhancing organic breakdown but also causing equipment fouling and corrosion, increasing maintenance costs(Tumuluru J.S. et al., 2018) (Ataie and Riding, 2013).

To enhance updraft gasifier efficiency, the biomass must be pretreated according to the characteristics of the chosen waste biomass.

Physical pretreatment:

Due to the typically low bulk density, irregular shape, and high moisture content of raw biomass, physical pretreatments such as drying, grinding, and palletisation are often essential to ensure efficient operation in updraft gasification systems. These pretreatments help to improve feedstock uniformity, enhance flow characteristics, and facilitate more consistent gasification performance.

Size Reduction:

The particle size of waste biomass should be relatively uniform to ensure consistent feeding and gasification rates. For updraft gasification, the particle size of 5–50 mm is recommended (Bermudez and Fidalgo, 2016). Too large particles can lead to incomplete gasification, while too small particles may cause blockages and excessive tar production.

Drying:

Updraft gasification is well-suited for handling high-moisture-content biomass, thanks to its efficient internal heat exchange mechanism (Bermudez and Fidalgo, 2016). This design allows for higher energy efficiencies by effectively utilizing the heat generated within the system. Waste biomass with moisture content as high as 60 % wt can be processed because the steam released in the drying zone is efficiently removed along with the syngas, preventing it from interfering with the gasification process (Bermudez and Fidalgo, 2016).

Densification:

In updraft gasification, densification significantly enhances both the efficiency and performance of the process. Densification involves compacting raw biomass into denser forms, such as pellets, often after pre-drying to reduce moisture content. This reduction in moisture is particularly beneficial for updraft gasification, as it improves the efficiency of the drying zone and the overall gasification process. By increasing the bulk density of the biomass, densification enhances its energy content per unit volume, making it more suitable for high-efficiency gasification. Additionally, densified biomass with consistent shapes and sizes ensures a uniform feedstock, leading to more stable and predictable gasification performance. The compact nature of densified biomass also improves flow characteristics, facilitating smoother feeding into the gasifier and reducing issues such as clogging or bridging. Overall, these advantages contribute to a more efficient, reliable, and cost-effective biomass-to-energy conversion process in updraft gasification systems.

Chemical pretreatment:

To optimize gasification process, chemical pretreatment of the biomass is often employed. Chemical pretreatment of waste biomass for updraft gasification involves modifying the biomass chemically to improve its properties and enhance the efficiency of the gasification process. This pretreatment is aimed at addressing challenges such as high moisture content, low bulk density, and poor reactivity of raw biomass.

Acid and alkali pretreatment:

In updraft gasification, as in other types of gasification processes, alkali and alkaline earth metals (AAEMs) in biomass can volatilize at high temperatures (Shen, 2024), forming low-melting-point compounds that cause ash fouling, slagging, and equipment damage. However, AAEMs also serve as natural catalysts, accelerating gasification reactions, reducing tar formation, and improving syngas quality (Shen, 2024).

To balance these effects, chemical pretreatment methods are used to manage AAEM levels. Water and acid leaching are common techniques that remove or reduce AAEMs from the biomass before it is gasified. This helps minimize ash-related problems while still benefiting from the catalytic properties of AAEMs. Proper pretreatment is essential for maintaining efficient and reliable updraft gasification, ensuring that the process produces high-quality syngas and operates smoothly over time.

Thermal pretreatment:

Torrefaction

Torrefaction enhances the performance and efficiency of updraft gasification by producing a more uniform, high-energy, and easily handled feedstock. Torrefaction effectively reduces the biomass's moisture content, increasing its energy density, lower O/C and H/C ratios, improved grindability and making it more suitable for gasification. Additionally, torrefaction improves the grindability of the biomass, making it easier to mill and resulting in a more uniform feedstock (Tumuluru J.S. et al., 2018). The use of torrefied feedstock typically led to a fivefold reduction in tar content within the syngas and a 44% increase in the plant's thermal output compared to performance using untreated wood (Cerone et al., 2016). The process also enhances the flow properties of the biomass, reducing issues like clogging and bridging in the gasifier. It can also modify the chemical composition of the biomass, potentially lowering ash fusibility and minimizing ash-related problems during gasification. Overall, torrefaction improves the efficiency and performance of updraft gasification by producing a high-energy, easy-to-handle feedstock.

Description of Updraft Gasification

Updraft gasifiers are among the oldest and simplest types of gasification systems (Abdollahi-Neisiani et al., 2013). It can handle waste biomass with high ash content (up to 25 % wt db). and high moisture content (up to 60 %) (Bermudez and Fidalgo, 2016).

In a typical updraft gasifier, fuel is introduced from the top, while the syngas is also extracted from the top. The gasifying agent, which may be air, oxygen, steam, or a combination of these, is preheated and injected into the gasifier through a grid at the bottom (Basu, 2013a). This counter-current flow facilitates efficient heat transfer and allows for a series of thermochemical processes—drying, pyrolysis, reduction, and oxidation— to occur as the waste biomass travels downward through the reactor (Figure 19).

Oxidation zone: When the gasification agent enters the gasifier, it encounters hot ash and unconverted char. This zone is exothermic, providing the thermal energy necessary to sustain the entire gasification process and maintain the operational temperature. Temperature in this zone is around 1400^{o}C (Quader and Ahmed, 2017). The main reactions that take place during the oxidation phase are char combustion, hydrogen combustion and partial combustion of char. As a result, a very hot gases are produced, consisting mainly of CO, CO_2 and steam (Bermudez and Fidalgo, 2016). N_2 may be present in this mixture if air is used for the biomass oxidation; otherwise, nitrogen is virtually absent when only oxygen is employed. These hot gases move further up into the reduction zone.

Reduction zone: Here endothermic reduction reactions occur at temperature around 900°C (Quader and Ahmed, 2017). Gases from oxidation stage CO_2 and steam are subsequently reduced to CO and H_2 when they interact with the char produced during pyrolysis. The main reactions that take place during the reduction phase are Boudouard reaction, carbon reforming reaction, water gas shift reaction and methanation reaction.

Pyrolysis zone: In this zone endothermic reactions take place at temperatures around 300-500°C (Basu, 2013a). The rising hot gases, from previous zone, preheats the descending biomass, causing it to undergo pyrolysis. This process breaks down the biomass into non-condensable gases, condensable vapours heavy hydrocarbons), and char. These heavy hydrocarbons undergo thermal cracking, resulting in further gas and char production. As the gas stream ascends, it continues to interact with pyrolysis products, facilitating the breakdown and conversion of volatile components into syngas. The resulting volatile vapor comprises hydrogen, carbon monoxide, carbon dioxide, methane, and steam, along with residual tar and char. The syngas rise, while the solid char continues to move downward along with other solids (Basu, 2013a).

Drying zone: In this top zone of the updraft gasifier, the waste biomass is dried as the syngas cools down to approximately 200–400°C (Bermudez and Fidalgo, 2016). This lower temperature is insufficient for many of the cracking and reforming reactions needed to break down tar precursors. **The syngas is a mixture of gasification and pyrolysis products.** As a result, the syngas produced contains a significant amount of tar impurities, ranging from 30- 150 g/Nm^3 (Basu, 2013a).

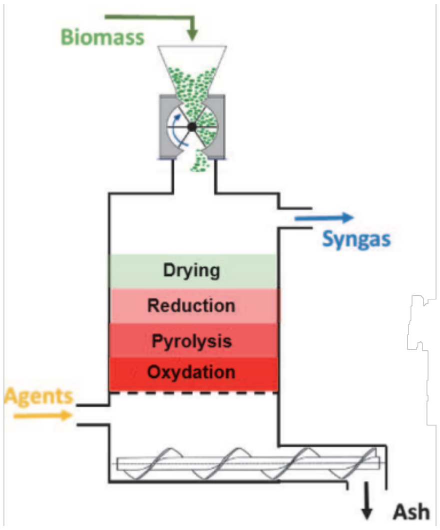


Figure 19. Scheme of a updraft gasifier (Thanh Phong and Dinh Quan, 2020).

Fixed-bed updraft gasifiers, typically capacity of 1MW- 10MW, are suitable for small to medium scale applications such as on-site biomass-to-electricity and heat conversion (Basu and Kaushal, 2024a).

Influence of the process parameters on the product characteristics

Gasification agent:

In updraft gasification, the choice of gasifying medium significantly impacts the efficiency and composition of the produced syngas. The most used agents are:

1. **Air** is often used due to its availability and cost-effectiveness. It provides the oxygen necessary for the oxidation reactions but also introduces nitrogen, which can dilute the syngas and lower its overall energy content. The expected lower heating value of syngas is typically in the range of 3.5-7.8 MJ/kg/Nm³, depending on the characteristics of the biomass and whether the air is preheated before entering the gasifier (Cerone and Zimbardi, 2021, Chopra and Jain, 2007, Chen et al., 2013b).
2. **Oxygen** increases the yields of hydrogen and carbon monoxide depending on the oxygen-to-feed ratio (Chopra and Jain, 2007). This enhancement also boosts cold gas efficiency, resulting in a syngas with a medium heating value in the range of 10-18 MJ/Nm³ (Chopra and Jain, 2007).
3. **Air/Steam Mixture** can moderately enhance the heating value of syngas. Increasing the steam fraction promotes the water-gas shift reaction and steam reforming of tars and hydrocarbons, leading to higher hydrogen yields and lower carbon monoxide yields in the syngas. The expected low heating value of the syngas ranges from 7 to 9 MJ/Nm³, depending on the feedstock characteristics, air/steam ratio, and whether the air/steam mixture is preheated before entering the gasifier (Lucas et al., 2004, Chopra and Jain, 2007). An air/steam mixture lowers the gasification temperature, which helps prevent ash melting and thus avoids agglomeration and clogging in the bed (Chen et al., 2013b). However, a high steam ratio in the gasification mixture tends to lower the overall temperature within the gasifier. Steam absorbs heat, acting as a heat sink, which reduces the temperature at which reactions occur. At these lower temperatures, the thermal decomposition of biomass is less intense, leading to the production of fewer volatile compounds such as tars and light hydrocarbons. Consequently, the reduced temperature results in less energy available for further reactions, leading to the production of more CO_2 (a noncombustible gas) and less CO (a combustible gas) (Chen et al., 2013b).
4. **Oxygen/Steam Mixtures**, more oxygen in the mixture will approach the heating values of pure oxygen gasification, 8-11 MJ/kg (Cerone and Zimbardi, 2021). The oxygen component in the mixture facilitates partial oxidation of the biomass, generating the necessary heat for the endothermic

reactions involved in gasification. This leads to higher concentrations of hydrogen and carbon monoxide in the syngas. The steam component, on the other hand, promotes the water-gas shift reaction, converting carbon monoxide to carbon dioxide while producing additional hydrogen. This process can increase the hydrogen content of the syngas further, making it richer in energy content. This combination of steam and oxygen allows for more controlled gasification with higher hydrogen yields and lower tar content, but careful balancing is required to avoid reducing the gasification temperature too much, which could lead to lower syngas quality due to higher carbon dioxide production.

Temperature:

Temperature plays a critical role in determining the gasification rate and overall performance of a gasifier. At higher temperatures (700-900°C) generally enhance the conversion of biomass into syngas, particularly increasing the production of hydrogen and carbon monoxide. Excessively high temperatures can reduce tar formation and enhance gasification efficiency but also increase the risk of ash melting, leading to operational challenges like slagging and fouling.

Equivalence ratio:

At higher ER, the additional air supplied enhances the combustion of char, resulting in the production of more CO_2 rather than valuable combustible gases such as CO, H_2, and CH_4. For updraft gasification, the ER typically varies from 0.10 to 0.50 (Kumar M. S., 2018). A lower ER typically results in higher concentrations of combustible gases like H_2 and CO but may also increase the production of tar. The impact of ER on gas quality is substantial, with hydrogen production peaking at an ER of 0.35 (Kumar M. S., 2018). Beyond this point, the heating value of the producer gas decreases due to intensified oxidation reactions and increased gas dilution with nitrogen (Kumar M. S., 2018).

Effect of pressure:

Updraft gasifiers usually operate at lower pressures, close to atmospheric pressure or slightly above it. Generally, elevated pressure can enhance the quality of the syngas by increasing the partial pressures of desired gases such as CO and H_2, and reducing the concentrations of CO_2 and CH_4. (Kumar M. S., 2018).

Pressure in updraft gasifiers is atmospheric to slightly above atmospheric pressure (typically 1 to 3 bar). Updraft gasifiers are commonly operated at atmospheric pressure, as they are simpler and designed for lower-capacity applications. Some systems may operate at slightly elevated pressures to enhance syngas quality or for integration with downstream processes like fuel cells, but they generally do not require high pressures due to the lower complexity of the system.

Influence of the gasifier characteristics:

Height-to-Diameter Ratio:

The height-to-diameter ratio affects the residence time of gases and solids. A taller, narrower gasifier allows for longer contact time between the gas and solids, promoting more complete gasification and higher syngas quality. In updraft gasifiers, maintaining an appropriate height-to-diameter ratio is crucial for optimal performance. The ratio is usually greater than 3:1 (Basu and Kaushal, 2024a), which helps ensure efficient gasification and heat distribution. However, when the diameter of the moving bed exceeds 3 to 4 meters, it can cause material flow problems such as channeling or uneven distribution of biomass (Basu and Kaushal, 2024a). These issues can lead to reduced efficiency and operational difficulties, making it essential to carefully design the gasifier dimensions to balance capacity and performance.

Height of biomass bed:

The height of the biomass bed in an updraft gasifier influences the overall performance and efficiency of the gasification process.

A higher biomass bed increases the residence time of both biomass and gas within the gasifier. This allows more time for the biomass to undergo pyrolysis and gasification reactions, leading to higher conversion efficiency and better syngas quality. The height of the biomass bed affects the temperature distribution within the gasifier. A higher biomass bed can lead to more significant thermal gradients, which can impact the efficiency of different reaction zones (pyrolysis, reduction, and oxidation). The height of the biomass bed influences the flow path of the gas. In a higher bed, the gas has to travel a longer distance through the biomass, which can affect the uniformity of gas distribution and the effectiveness of the gas-solid contact.

Influence of the waste biomass parameters on the product:

Influence of Particle Size:

Small particles have higher mass transfer and heat transfer characteristics because of the higher surface area to mass ratio, improve the gas-solid contact, enhancing reaction rates and overall gasification efficiency. Smaller particles improve the gas quality (higher amounts of H_2, CO, CO_2, and CH_4 and lower amounts of char and heavy tars). However, very fine particles can lead to operational issues like clogging and reduced flowability. For updraft gasification, the particle size of 5–50 mm is recommended (Bermudez and Fidalgo, 2016).

Density and Porosity:

Higher bulk density in biomass improves its flow through the gasifier by mitigating issues like bridging and ensuring a more stable bed structure. This stability supports a more uniform and efficient gasification process. Additionally, with increased bulk density, heat transfer within the gasifier is enhanced, leading to more effective thermal management. This helps in maintaining the optimal reaction temperatures required for efficient gasification. The result is a more consistent and reliable conversion of biomass to syngas, improving the overall performance and efficiency of the gasification process.

Porosity in biomass enhances updraft gasification by increasing surface area for better heat transfer and reaction efficiency. It improves gas flow through the bed, reducing pressure drop and aiding in more uniform gasification. However, high porosity can also act as a thermal insulator, affecting temperature distribution.

Ash Content:

High ash content can lead to operational problems like fouling, slagging, and reduced efficiency. The composition of ash (e.g., high AAEMs) affects its behaviour at high temperatures and its impact on gasifier components. High ash content can lead to operational issues such as slagging, fouling, and increased wear on equipment. However, updraft gasification systems are designed to manage higher ash levels (25 % wt db) (Bermudez and Fidalgo, 2016) more effectively than some other types of gasifiers, but managing high ash content still requires careful operational adjustments and maintenance to ensure optimal performance and minimize issues. Effective pre-treatment processes, such as washing or leaching, can help reduce ash content and mitigate its adverse effects on gasification performance.

Moisture Content:

Updraft gasification can effectively handle biomass with moisture content up to 60 wt% (Bermudez and Fidalgo, 2016). This capability is due to the design of updraft gasifiers, which allows for efficient removal of moisture through the gas stream. The high moisture content is evaporated and carried away by the rising syngas, reducing the impact on the overall gasification efficiency and performance.

Cellulose, Hemicellulose, and Lignin:

Lignocellulosic waste biomass is composed of cellulose (approximately 50% on a dry basis), hemicellulose (10–30% in wood biomass and 20–40% in herbaceous biomass), lignin (20–40% in woods and 10–40% in herbaceous materials), along with various extractives. These components significantly influence the distribution of products during conversion processes (Havilah et al., 2022). Cellulose and hemicellulose contribute to the production of non-condensable gases, condensable vapours heavy hydrocarbons), lignin influences the char yield and thermal stability of the gasification process. Balancing the ratios of these components in the feedstock can optimize the performance of updraft gasification systems

Syngas characteristics:

Syngas typically comprises hydrogen, carbon monoxide, carbon dioxide, and methane. The exact composition varies with the biomass type and gasification operating conditions. The lower heating value (LHV) of syngas generally ranges from 4–18 MJ/Nm^3, depending on biomass type and gasification operating conditions (gasification agent etc.) (Cerone and Zimbardi, 2021, Chopra and Jain, 2007, Chen et al., 2013b). The presence of hydrogen and carbon monoxide contributes to higher heating values. The syngas at the exits contains an abundance of tar (30-150 g/Nm^3) since the products of the pyrolysis and drying zone are directly drawn into it without decomposition. The particulates content (unconverted char and ash) in the syngas is reduced primarily due to the low gas velocities within the gasifier, combined with the natural filtering effect of the biomass feedstock as it undergoes drying and pyrolysis, effectively trapping particulates (Chopra and Jain, 2007).

Syngas cleaning and upgrading

Before applications of syngas, syngas must be cooled and cleaned. The raw syngas contains impurities such as solid particulates, inorganic impurities and organic impurities (e.g. tar).
Syngas leaves the gasifier at high temperatures (200–400°C) (Bermudez and Fidalgo, 2016). Syngas needs to be cooled before use. Syngas needs to be cooled before use. Syngas passes through a series of heat exchangers to lower its temperature. The heat extracted can be recovered and used for production of steam which can be used for updraft gasification, or power generation or process heating in the process, improving overall efficiency.

Although the syngas from updraft gasification, generally contains fewer particulates compared to downdraft gasification, removing particulates are needed. For this purpose, cyclones, fabric filters, electrostatic filters and solvent scrubbers can be used (Basu, 2013b).

The primary challenge in updraft gasification is the formation of high amount of tar, which complicates the cleaning and upgrading of the syngas and limits its industrial viability. Tar compounds in the syngas are problematic as they can polymerize into complex structures that cause corrosion, fouling, and clogging in downstream pipelines, heat exchangers, and filters (Cortazar et al., 2023). This results in operational issues and increased maintenance requirements.

For power generation applications like gas turbines, gas engines, fuel cells, and boilers, the tolerance for tar is higher, typically between 1-100 mg/Nm^3 (Cortazar et al., 2023). This difference is due to the varying sensitivity of these systems to tar, where industrial processes and power generation equipment have different thresholds for handling tar impurities. Consequently, managing tar is essential to prevent frequent maintenance issues and operational disruptions, which can otherwise undermine the efficiency and reliability of downstream processing equipment. Proper tar removal or conversion is vital to maintaining system performance and extending the lifespan of gasification infrastructure.

Methods for tar removing can be divided into two primary categories (Cortazar et al., 2023):

1. **Primary methods**, which address tar formation within the gasifier by optimizing operating conditions, utilizing specialized bed materials or catalysts (dolomite, nickel, or alkali metals), or enhancing the gasifier's design; and
2. **Secondary methods**, which focus on reducing tar after the gasification process. Secondary methods are further categorized into physical and mechanical techniques, such as filters, cyclones, and scrubbers, and chemical processes, including thermal and catalytic tar cracking.

Applications of Syngas

Syngas from updraft gasification is a usually implemented in energy production (heat and power) offering significant benefits in terms of efficiency and sustainability.

The syngas after updraft gasification is particularly suited for direct firing applications, where the syngas can be burned directly in a furnace or boiler (Basu and Kaushal, 2024a). In this process, the tar generated during gasification does not require removal, making it a more straightforward and cost-effective option for energy generation.

Syngas for heat and power production:

The syngas after updraft gasification is particularly suited for direct firing applications, where the syngas can be burned directly in a furnace or boiler to produce high-temperature heat and steam(Basu and Kaushal, 2024a). In this process, the tar generated during gasification does not require removal, making it a more straightforward and cost-effective option for energy generation. In the case of heat applications, the produced gas is used into a boiler and most applications are focused on district heating, lime kilns, cement drying and other industrial processes (Huertas B. J. and Dorca D. A., 2008). the case of cement process, the product gas can be used not only for supplying energy but also as raw material. Additionally, lime kilns are used for heating limestone and as in the case of cement, has found an initial niche application.

For syngas intended for turbines or internal combustion engines used in electricity generation or mechanical power, it must undergo extensive filtration and cleaning (Quader and Ahmed, 2017). This process is essential to lower the tar content to permissible levels, thereby preventing damage and ensuring the reliable operation of the machinery. The need for extensive cleaning not only raises investment costs but also diminishes the overall process efficiency, making updraft gasification a less viable option for applications involving internal combustion engines and micro gas turbine (de Mena et al., 2017). This limitation stems from the high tar content in the syngas, which requires substantial treatment to meet the stringent requirements for engine operation.

The syngas for updraft gasification process, can be applied in power generation units that use external combustion chambers, such as Stirling engines, and (Organic Rankine Cycle (ORC) systems (de Mena et al., 2017). In these applications, the syngas, despite being uncleaned, can be utilized effectively. When the producer gas is burned in an external combustion chamber with an excess of air, it reaches high temperatures (above 900–1000 °C) (de Mena et al., 2017). This high-temperature environment leads to the combustion of tars present in the syngas, resulting in a flue gas that is suitable for use in these systems. This approach eliminates the need for intensive gas cleaning, which reduces costs and simplifies the process.

Syngas can be used in applications like a Stirling engine, which has an external combustion chamber. The external combustion chamber allows for the combustion of the producer gas at high temperatures (above 900–1000 °C), where the tars are fully combusted, reducing the need for extensive gas cleaning (Jensen et al., 2002). This syngas is combusted in the external combustion chamber of the Stirling engine, which converts the heat energy from the combustion into mechanical energy. The mechanical energy is then used to generate electricity via a generator connected to the Stirling engine.

The combustion process within the Stirling engine generates a significant amount of heat. This heat is not discarded but is captured and utilized for heating purposes, such as space heating, hot water production, or industrial processes. The heat can be recovered from various parts of the system, including the exhaust gases, the engine's cooling system, and the combustion chamber itself.

According to literature (Cotana et al., 2014), commercially available CHP systems utilizing Stirling engines offer a range of options tailored for various applications. For residential and small commercial use, these systems typically provide electrical outputs between 1 kW and 3 kW, coupled with thermal outputs ranging from 7.5 kW to 30 kW (Cotana et al., 2014). For medium-sized applications, Stirling engines are available with electrical capacities of up to 30 kW and thermal outputs reaching 90 kW (Cotana et al., 2014). For these systems, electrical efficiency varies from 12% to 24%, representing the fraction of fuel energy converted into electrical power, whereas thermal efficiency is significantly higher, ranging from 72% to 77%, reflecting the proportion of energy converted into useful thermal output (Cotana et al., 2014).

When combined with updraft gasification, ORC technology can significantly enhance the efficiency of biomass-based power generation. The integrated system typically consists of several key components: an updraft gasifier reactor, which converts biomass into syngas; a hot gas cyclone to separate particulates from the syngas; a syngas burner to combust the cleaned syngas and generate heat; a thermal oil heater to transfer this heat to the ORC system; and an ORC turbine to convert the thermal energy into electricity, Figure 20. Updraft gasification- ORC plants coupled with CHP systems, can have capacity ranging from 0.2 to 2 MWe (Cotana et al., 2014).

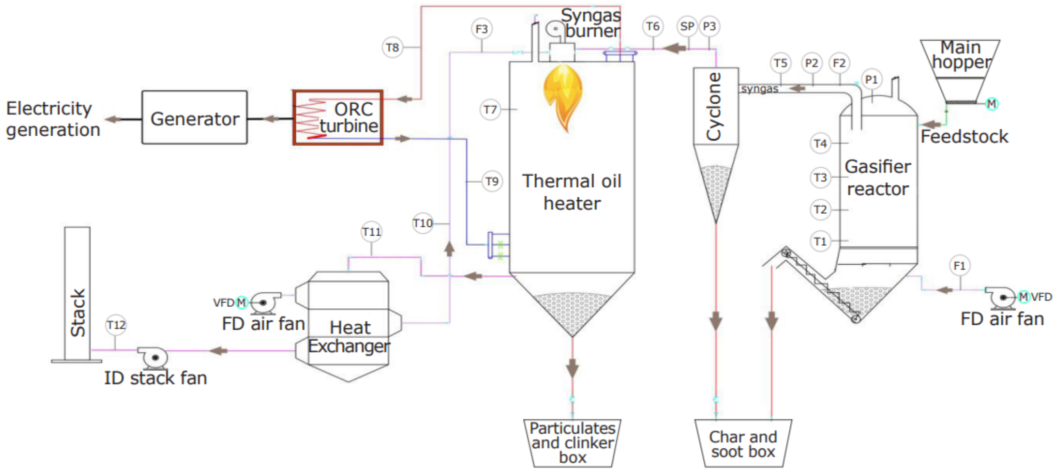


Figure 20. Possible Process flow diagram of the updraft gasification ORC system (thermocouples (Ti), pressure transmitter (Pi), flow meters (Fi), syngas sample collection port (SP)) (Dogru and Erdem, 2020)

Successful application of updraft gasification is its integration with a micro combined cooling, heating, and power (CCHP) plant, which utilizes a spark ignition engine as its core component. This concept has been effectively demonstrated by (Perrone et al., 2023a, Perrone et al., 2023b). A schematic representation of this plant is provided in Figure 21.

The cooled and cleaned syngas enters the spark ignition engine, where it is used to generate electricity. The spark ignition engine develops rated electrical and thermal power of 45 kWel and 95 kWth, respectively (Perrone et al., 2023b). Heat is recovered from the engine cooling system and the hot syngas using two heat exchangers: HEX1 for the engine coolant and HEX2 for the water/syngas. The heated water from these exchangers is directed to the absorption chiller (AC) through HEX6, with its flow rate controlled by a thermo-electric three-way valve (V3) to optimize refrigeration power and efficiency, even at partial loads (Perrone et al., 2023b). The combined flow from HEX1 and HEX2 is then sent to the thermal load. In the engine cooling system, the coolant absorbs heat from the lubricant, engine jacket/head, and exhaust gas. A three-way valve (V1) directs part of the heated coolant to HEX5 within the AC, while the rest is bypassed (Perrone et al., 2023b). After passing through HEX5, the coolant flows are combined and channeled through HEX1 before re-entering the engine cooling circuit. Any excess heat is released into the environment via the dry cooler (DC) (Perrone et al., 2023b).

The cooled and cleaned syngas is fed into a spark ignition engine to generate electricity, while the heated water from the syngas cooling process undergoes further heat recovery in the absorption chiller (Perrone et al., 2023b). On the engine side, the hot coolant—after exchanging heat with the lubricant, engine jacket, head, and exhaust gases—is partially redirected to the absorption chiller for additional heat recovery, maximizing overall efficiency (Perrone et al., 2023b).

Another method is biomass integrated gasification combined cycle (BIGCC). The BIGCC is a power generation process that incorporates a biomass gasification system with a combined cycle power plant. It is an attractive alternative for power generation compared to other CHP processes due to several advantages, such as high thermal efficiency and energy output, reduced production of greenhouse gases, and lower generation of solid wastes (Motta et al., 2018).

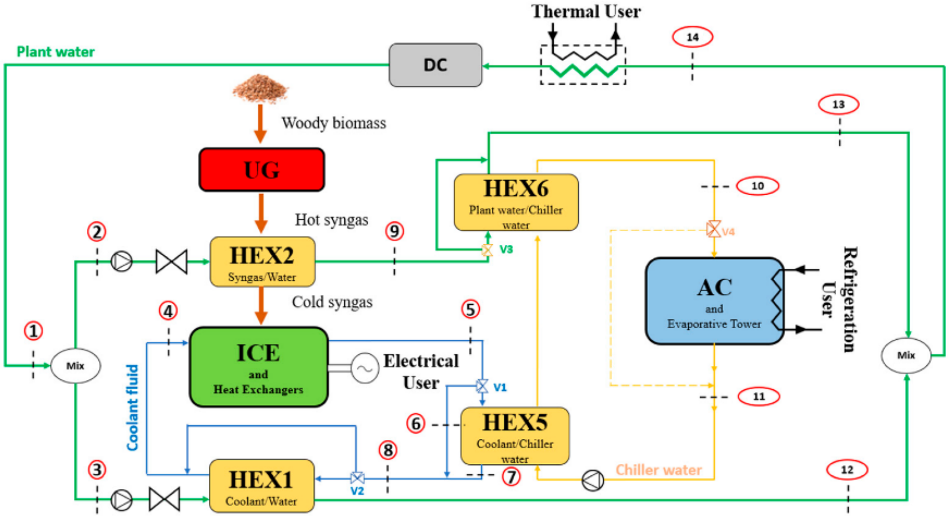


Figure 21. Schematic of Updraft Gasification Integrated with a Micro-CCHP Plant

Advantages and disadvantages of Updraft Gasification

Updraft gasifiers are valued for their simple design and operation, which leads to reduced construction and maintenance costs compared to other gasification technologies. Their effective internal heat exchange enhances energy efficiency, making them a cost-efficient choice for biomass gasification (Basu and Kaushal, 2024a).

One of the significant advantages of updraft gasifiers is their ability to handle a wide range of feedstocks. This setup is particularly adept at processing biomass with high moisture content (up to 60% wt) and significant ash content, efficiently handling up to 25% wt on a dry basis without compromising performance.

The updraft gasifier's design facilitates high thermal efficiency through a counter-current flow of syngas and solid fuel. This arrangement allows for effective heat exchange between the gas and the solid fuel, resulting in better utilization of the energy produced. The updraft configuration ensures that the gasification process benefits from the high temperatures necessary for optimal syngas production, contributing to overall system efficiency.

Updraft gasifiers are adaptable to a range of scales, from small community-based systems to medium-sized industrial applications. Their ability to be scaled up or down based on specific energy needs makes them versatile and suitable for diverse applications. For small to medium-scale plants (1MW- 10MW), updraft gasifiers can be a practical solution, providing a reliable source of syngas for power generation, heating, or combined heat and power (CHP) systems.

One of the primary drawbacks of updraft gasifiers is the high level of tar produced in the syngas (30-150 g/Nm^3). Tar is a sticky, carbon-rich substance that can cause significant operational issues, such as fouling and clogging of engines and downstream equipment. The intensive cleaning process not only increases operational complexity but also raises investment costs, ultimately reducing the overall efficiency of the system. The presence of tar in syngas from updraft gasifiers limits the compatibility with various engines and equipment. This tar contamination poses challenges for effective operation and maintenance, making updraft gasification generally unsuitable for internal combustion engines.

Syngas produced by updraft gasifiers typically has a lower calorific value compared to that from other gasification methods. This lower quality gas contains more impurities and can have a higher proportion of nitrogen and carbon dioxide. The heating value of syngas can be enhanced by using steam, oxygen, or their mixtures as gasification agents. However, this approach may lead to increased operational complexity and cost, as well as potential challenges in managing the by-products and optimizing the gasification process.

The gasification process in updraft gasifiers generates significant amounts of ash and slag, which must be managed and disposed of properly. The accumulation of ash and slag can affect the performance of the gasifier and require regular maintenance and cleaning. Proper management of these byproducts is essential to ensure continuous operation and to prevent potential issues with equipment performance.

The advantages and disadvantages, conversion efficiency, capital and operational cost of updraft gasification process are presented in Table 15.

Table 15. The advantages and disadvantages of downdraft gasification process (modified (Molino et al., 2016) (IEA Bioenergy, 2022))(Donatelli et al., 2018).

Type of gasification	Technical condition	Key Products	Advantage	Disadvantage	Conversion Efficiency	Capital Cost	Operational Cost
Updraft	*Suitable feedstock:* agricultural field residues, agricultural process residues, forest residues, wood from trees outside the forest, wood processing industry residue. *Feedstock size*: 5–50 mm. *Temperature*:500–1200◦C *Residence time*: 900–1800 s. Pressure: atmospheric pressure or slightly above it	Syngas, CHP	Simple and consolidated process Lowe tar product. Long residence time. Uncomplicated reactor. High performance of conversion.	Requirement of pre-treatment (size restriction, moisture reduction). High content of tar requires more extensive and expensive cleaning processes phenomena. High probability of clinkering phenomena	High	Moderate to high	Moderate

Downdraft Gasification

Waste biomass suitable for Downdraft Gasification:

Downdraft gasification, as well as updraft gasification, is well-suited for a variety of waste biomass types. Some commonly used materials include: agricultural residues, forestry residues, industrial waste, organic parts of MSW (Havilah et al., 2022, Keche et al., 2015).

Feedstock preparation:

Downdraft gasification is suitable for a variety of waste biomass feedstocks. These range from agricultural field residues, agricultural process residues, forest residues, wood from trees outside the forest, wood processing industry residue, to solid wastes such as sewage sludge and organic waste from the food industry and municipal solid waste (Midilli et al., 2001, Saravanakumar et al., 2022, Sheth and Babu, 2009, Dogru et al., 2002, Jayah et al., 2003, Jorapur and Rajvanshi, 1995, Kureshi and Kothari, 2021).

The composition of biomass significantly influences the gasification process. Key properties of biomass include high moisture content, which makes it hydrophilic, and low bulk density with high porosity (IEA Bioenergy, 2022). Biomass is fibrous with low friability, high volatile content, and low fixed carbon, and compared to coal, it has lower carbon and higher oxygen content leading to a lower heating value, low nitrogen, sulphur, and chlorine content, lower ash content, but biomass ash has a lower melting point and is very aggressive in its molten state (IEA Bioenergy, 2022). Additionally, biomass contains higher levels of alkaline metals, such as sodium and potassium, which can catalyse decomposition but also cause equipment fouling (Tumuluru J.S. et al., 2018) (Ataie and Riding, 2013). The different polymer structures of cellulose and lignin lead to varied decomposition pathways and product distributions.

To enhance downdraft gasifier efficiency, the biomass must be pretreated according to the characteristics of the chosen waste biomass.

Physical pretreatment:

When designing a material handling system and selecting the appropriate gasifier, it is essential to understand the physical properties of biomass, such as hygroscopicity, particle size distribution, bulk density, particle density and grindability (Tumuluru J.S. et al., 2018). The physical pretreatment such as drying, grinding and palletisation is almost required for the gasification conversion processes, since the raw biomass usually has a poor bulk density, irregular shape and high-water content.

Size Reduction:

The particle size of waste biomass can have a strong effect on devolatilization timing and influence the yields and characteristics of syngas. The waste biomass need to be ground to around 2-10 cm (Bermudez and Fidalgo, 2016). Small particles have higher mass transfer and heat transfer characteristics because of the higher surface area to mass ratio.

Drying:

For downdraft gasification process, ideal moisture percentage of waste biomass feedstock should be between 10% and 15% (Bermudez and Fidalgo, 2016).

Densification:

The density of biomass plays a critical role in downdraft gasification. Low-density biomass often requires pretreatment to increase its bulk density, which helps improve feedstock handling and stability during the gasification process. Higher-density biomass ensures better control over the flow and distribution within the gasifier, contributing to more effective gasification and higher quality syngas production. Densification aims to apply mechanical force to compact selected materials into uniformly shaped and standardized commodities like pellets and briquettes (Tumuluru J.S. et al., 2018). This process offers several benefits, including increased biomass density and uniformity, enhanced handling and storage efficiencies, and improved flow properties (Tumuluru J.S. et al., 2018, Erlich, 2009).

Chemical pretreatment:

To optimize gasification process, chemical pretreatment of the biomass is often employed. This pretreatment alters the biomass's chemical composition by using solvents like hot water, acids, bases, or organic solvents. The main goals are to enhance the biomass’s properties, improve its reactivity, and remove unwanted minerals. Acid washing or leaching is particularly effective in removing most minerals, thereby improving the efficiency and output of the gasification process.

Acid and alkali pretreatment:

In biomass gasification, while inherent alkali and alkaline earth metals (AAEMs) can cause ash-related problems at high temperatures (e.g., 800–1000 °C) due to their partial volatilization and formation of low melting point compounds, they also enhance catalytic gasification, reduce tar production, and improve syngas quality (Shen, 2024). Chemical pretreatment methods, such as water and acid leaching, are commonly used to remove AAEMs from biomass to mitigate problems in gasification processes, as fouling and ash-related issues (Shen, 2024).

Thermal pretreatment:

Torrefaction:

Torrefaction processes yield a product that surpasses raw biomass in several key aspects: increased energy content and density, reduced moisture content, lower O/C and H/C ratios, higher hydrophobicity and better resistance to fungal decay, and improved grindability. In torrefaction, temperature and residence time are crucial parameters influencing the characteristics of the torrefied material (Tumuluru J.S. et al., 2018). Since, waste biomass must be dried and size-reduced before densification, torrefaction is often used in conjunction with densification, as it significantly reduces the energy required for the densification process (Tumuluru J.S. et al., 2018). A torrefaction pre-treatment could enhance the downdraft gasification process to produce syngas by decreasing the required energy for grinding biomass particles and by improving syngas characteristics.

Description of Downdraft Gasification

Fixed-bed gasifiers, where downdraft gasifiers belongs, has been widely used for syngas production due to its advantages such as less maintenance, low production costs, and simple structure and operation (Chopra and Jain, 2007). In a downdraft gasifier, both the feedstock and the oxidant flow downward in a co-current manner. A it is presented in Figure 22, biomass is introduced from the top of the reactor while the oxidizing agent (most commonly air) is directly added into the oxidation zone, producing high-temperature gas with low tar content (Beohar et al., 2012). The gasifier sequentially separates into a drying zone, devolatilization (pyrolysis) zone, oxidation zone, and reduction zone.

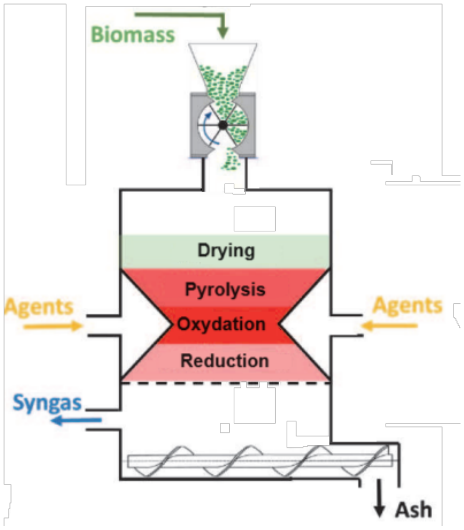


Figure 22. Scheme of a downdraft gasifier modified (Thanh Phong and Dinh Quan, 2020).

Drying zone: temperature in drying zone is about 100–200 °C (Susastriawan et al., 2017). The resulting product from this stage is dried biomass (moisture content reduced to below 5%.) and steam. and dry biomass.

Pyrolysis zone: Dried biomass is heated to temperatures between 250 and 700 °C in a limited oxygen or air environment. This heating causes the volatile components in the biomass to vaporize. The resulting volatile vapor comprises hydrogen, carbon monoxide, carbon dioxide, methane, and water vapor, along with tar and char.

Oxidation zone: Air is supplied through nozzles positioned around the gasifier's perimeter, moving downward and reacting with the pyrolyzed char particles to form a high-temperature combustion zone with temperatures around 1000 ^{o}C (Basu and Kaushal, 2024a). The narrower cross-section promotes turbulence and allows for maintaining a constant high temperature in the oxidation zone. Heat released during oxidation is used for drying, pyrolysis, and other endothermic reactions during reduction (Susastriawan et al., 2017). The oxygen supplied to the gasifier reacts with combustible substances to form carbon dioxide, carbon monoxide and steam. Additionally, the hydrogen in the biomass can be oxidized to generate more steam. The high temperatures in the gasifier also facilitate tar cracking. The heavy organic molecules in the tar gases break down into lighter, non-condensing combustible gases due to the extreme heat. Approximately half of the combustible molecules in syngas are produced through the cracking of tar.

Reduction zone: some carbon dioxide and steam are subsequently reduced to carbon monoxide and hydrogen when they interact with the char produced during pyrolysis. In this step, combustible gases such as hydrogen, carbon monoxide, and methane through a series of reactions are formed.

The syngas exits the reactor below the grate, with temperature around 700 ^{o}C (Basu and Kaushal, 2024a). Unreacted char and ash fall through the grate (Morten, 2002).

This configuration of downdraft gasifier facilitates the thermal degradation of tars into non-condensable gases and water, resulting in a product gas with minimal tar content. Downdraft gasifiers produce syngas with a low tar content (0.015-3 g/Nm^3) in the syngas compared to other types of gasifiers (Basu, 2010a), which reduces the need for extensive gas cleaning and makes the syngas more suitable for use in engines and gas turbines. Fixed-bed downdraft gasifiers, typically capacity of 10 kW–1 MW, are suitable for small-scale applications such as on-site biomass-to-electricity and heat conversion (Vervaeke et al., 2006, Susastriawan et al., 2017, Basu and Kaushal, 2024a).

Influence of the process parameters on the product characteristics

Gasification agent:

In downdraft gasification, the choice of gasifying medium significantly impacts the efficiency and composition of the produced syngas. The most used agents are:

1. **Air** is often used due to its availability and cost-effectiveness. It is straightforward to implement but results in lower heating value gas (4–7 MJ/Nm³) because of the nitrogen dilution (Andriatoavina et al., 2021). Despite this, it is suitable for applications where lower-quality syngas is acceptable, such as in combined heat and power systems.
2. **Steam** increase syngas heating value (10-14 MJ/Nm^3) by increasing H_2 yield and lower tar and particulates (Contec, 2022, Patel, 2017). However, using pure steam requires higher reaction temperatures and can be less efficient in terms of operational cost.
3. **Oxygen/Steam Mixture**, can further enhance the quality of the syngas, increasing heating values (up to 11 MJ/Nm^3) and increased hydrogen content (app. 30 % vol) compared to air gasification (Lv et al., 2007). This mixture allows for more efficient gasification at lower temperatures but incurs higher operational costs due to the need for oxygen.
4. **Air/Steam Mixture** is used to enhance hydrogen production and improve gas quality. It provides increase in heating value (app. 20- 40% higher than in case of air gasification) (Ram et al., 2019, Lawanaskol S. et al., 2016).
5. **Air/Oxygen Mixture** can further enhance the quality of the syngas, by increasing the hydrogen, carbon monoxide and methane yield (Sittisun et al., 2019). As the oxygen enrichment ratio increases from the heating value of the syngas increases due to enhanced tar cracking and water-gas reactions (Cao et al., 2019). This approach, while producing syngas with a medium heating value (9–15 MJ/Nm³), is more expensive due to the cost of oxygen (Niu et al., 2014). It offers a balance between performance and cost but is generally less used due to its higher operational expenses.
6. **Air/Carbon dioxide**, increase yield of hydrogen and carbon monoxide in syngas, and heating value of syngas (Beohar et al., 2012). The addition of CO_2 in the gasifying agent increases carbon monoxide, owing to a greater prevalence of the Boudouard reaction (Pandey et al., 2022). The CO_2 contained in the flue gas produced by the industry can be efficiently utilized in the gasification process and reduce the CO_2 emissions into the environment (Pandey et al., 2022).

Each gasifying medium affects the gasification process differently, influencing factors such as syngas composition, heating value, and overall efficiency. The choice of medium should align with the specific requirements of the gasification system and the intended application of the produced syngas.

Temperature:

Temperature is a crucial factor influencing the gasification rate and overall performance of a gasifier. Higher temperatures accelerate both the oxidation and reduction reactions within the gasifier. Elevated temperatures (700-950°C) improve the rate of biomass conversion, resulting in higher yields of hydrogen and carbon monoxide and reduced tar content. Increased temperatures enhance the cracking of tar, leading to a cleaner syngas with a higher heating value. Elevated temperatures favour the water-gas shift reaction, increasing hydrogen yield in the syngas. Optimal temperatures for downdraft gasification are typically between 800–950°C for the oxidation zone and 650–900°C for the reduction zone, balancing effective gasification with manageable tar levels (Havilah et al., 2022). Although higher temperatures generally enhance gasification efficiency, they also increase the risk of melting ash, which can lead to operational problems. Careful temperature management and ash handling strategies are essential to address these challenges.

Equivalence ratio:

The equivalence ratio (ER) is defined as the ratio between the actual air/oxygen supply to the gasifier and amount of air/oxygen theoretically required for a complete combustion of the waste biomass. ER determine whether the process takes is pyrolysis, gasification or combustion. It also influences the composition of syngas. A higher value of ER will result in low concentration of H_2 and CO, and increased tar production (Kumar et al., 2018). ER ranges between 0.2-0.3 for majority of waste biomass.

Effect of pressure:

Downdraft gasifiers typically operate at or near atmospheric pressure to slightly pressurized (1 to 5 bar), which simplifies the design but can limit efficiency compared to pressurized systems. Downdraft gasifiers are typically designed to operate at atmospheric pressure as well. However, in cases where higher-quality syngas is required (such as for engines or specific industrial applications), moderate pressures up to 5 bar may be used to improve gasification rates and increase energy density in the syngas

Influence of the gasifier characteristics:

Height of reactor:

The height of the reactor directly influences the operational time and gas volume produced, with the combustion zone typically descending at a rate of 1 to 2 cm/min (Kumar et al., 2018). Increasing the reactor height raises airflow resistance, requiring a more robust draft system to ensure efficient operation (Kumar et al., 2018).

Height of biomass bed:

The height of the fuel bed matches the reactor height, and as the bed height increases, resistance to airflow also rises (Kumar et al., 2018). However, a thicker fuel bed extends the biomass residence time, which can reduce tar formation and improve gas yield by promoting more complete combustion and gasification (Kumar et al., 2018).

Influence of the waste biomass parameters on the product:

Influence of Particle Size:

In fixed bed gasifiers, as downdraft gasifiers, there is a limitation in biomass size. Smaller particles typically enhance the gasification process due to increased surface area, which improves heat transfer and reaction rates. This results in more efficient pyrolysis, combustion, and reduction stages, leading to higher syngas quality and lower tar production. However, gasification of small-sized particles can result in significant pressure drops and increased dust content in the produced gas, while also causing issues with forming an effective gasification bed in the reduction zone due to its low density (Susastriawan et al., 2017). Conversely, larger particles may hinder gasification processes, causing incomplete gasification, lower syngas quality, and higher tar and char residues (Susastriawan et al., 2017, Hernández et al., 2010). As mentioned above, downdraft gasification favourites waste biomass particles 2 – 10 cm. Uniform particle size also ensures consistent feeding and stable operation within the gasifier, while irregular sizes can lead to channelling and uneven gas flow, negatively impacting overall efficiency (Belonio, 2005, Susastriawan et al., 2017).

Density and Porosity:

The density and porosity of biomass significantly influence the efficiency of downdraft gasification. Higher density biomass ensures steady feeding and reliable operation, while low-density biomass can cause irregular feeding and process fluctuations. Dense biomass may lead to slower gas flow and reaction rates, whereas very low-density biomass can reduce residence time and cause incomplete gasification. High porosity increases the surface area for reactions, improving contact between biomass and the gasifying agent, enhancing reaction kinetics, and ensuring better heat and mass transfer. Optimal biomass density and porosity balance feeding consistency, gas flow, reaction rates, and heat and mass transfer, ultimately improving syngas quality and quantity.

Ash Content:

Ash content in biomass plays a crucial role in downdraft gasification. High ash content can lead to several operational challenges, such as slagging, fouling, and corrosion of gasification equipment. Ash tends to have a lower melting point, and under high-temperature conditions in the gasifier, it can form sticky residues that obstruct gas flow and reduce efficiency. Additionally, high ash content lowers the overall energy content of the biomass, as ash is an inert material that does not contribute to the gasification reactions. Therefore, biomass with low ash content is preferable for downdraft gasification to minimize operational issues and enhance the quality of the produced syngas. Effective pre-treatment processes, such as washing or leaching, can help reduce ash content and mitigate its adverse effects on gasification performance.

Moisture Content:

Moisture content in biomass significantly impacts downdraft gasification. High moisture levels require additional energy for water evaporation, lowering bed temperatures and reducing overall gasification efficiency. Ideally, moisture content should be below 10-15% to maintain consistent bed temperatures and optimize the gasification process. High moisture content results in lower net calorific value of the produced syngas, increased tar production, and higher CO_2 levels while reducing CO concentrations (Trninić, 2015). Therefore, managing moisture content is crucial for efficient downdraft gasification and high-quality syngas production

Cellulose, Hemicellulose, and Lignin:

Waste biomass contains varying degrees of cellulose (about 50% on a dry basis), hemicellulose (10–30% in woods, 20–40% in herbaceous biomass), lignin (20–40% in woods, 10–40% in herbaceous biomass), and extractives, which influence product distribution (Havilah et al., 2022). The cellulose and lignin contents significantly affect gasification characteristics, with higher cellulose content leading to faster pyrolysis rates and higher cellulose/hemicellulose to lignin ratios resulting in high-quality syngas, while higher lignin content slows pyrolysis and produces more tar (Havilah et al., 2022).

Pretreatment of biomass, including milling, chipping, briquetting, pelleting, and torrefaction, is essential to improve its characteristics for efficient energy use. However, these pretreatment technologies can be costly and may lead to some degradation of vital components.

Downdraft gasification reactors:

There are two main types of downdraft gasifiers: throated and throatless (Basu, 2010a), Figure 23.

Throated Downdraft Gasifier:

A throated (constricted or Imbert gasifier) gasifier features a reduced cross-sectional area at the throat, where the oxidation zone is located. The movement of pyrolysis products through this narrow zone ensures uniform temperature distribution and facilitates efficient tar cracking (Basu, 2010a). The syngas from this type of gasifier has lower tar-oil content (<1%), higher temperature (around 700 ºC), and more particulate matter compared to an updraft gasifier (Chopra and Jain, 2007). The throated gasifier is particularly suited for uniformly sized biomass with moisture content below 20% and ash content below 5% (Chopra and Jain, 2007). Despite its advantages, the gasifier has a lower overall efficiency because a significant amount of heat is carried away by the hot syngas (Reed T. B. and Das A., 1988, Clarke, 1981) Further restrict the capacity of throated downdraft gasifiers to 500 kW (Chopra and Jain, 2007).

Throatless Downdraft Gasifier:

The throatless gasifier (open-top or stratified gasifier), was designed to overcome issues like bridging and channelling found in throated downdraft gasifiers (Chopra and Jain, 2007). The throatless gasifier features vertical walls with no constriction, allowing unrestricted downward movement of biomass (Basu, 2010a). Unlike other downdraft gasifiers, air in a throatless gasifier is drawn from the top by suction created downstream, making it suitable for finer or lighter biomass (Basu, 2010a). The open top ensures uniform air distribution and facilitates easy, even biomass feeding, which helps regulate local temperatures (Chopra and Jain, 2007). In the oxidation zone, the gas moves through a long, evenly arranged bed of hot char, minimizing low-temperature zones and promoting efficient tar cracking, resulting in a low tar content of approximately 0.05 kg tar/kg gas (Chopra and Jain, 2007). The open-top throatless gasifier is particularly effective for processing small-sized biomass with high ash content, up to 20% (Chopra and Jain, 2007). Its design makes it relatively easy to construct and scale up. However, this type of gasifier has several drawbacks: it performs best with pelletized fuel, requires fuel moisture below 20%, produces significant ash and dust, and has lower gasification efficiency due to its high exit temperature (Basu, 2010a).

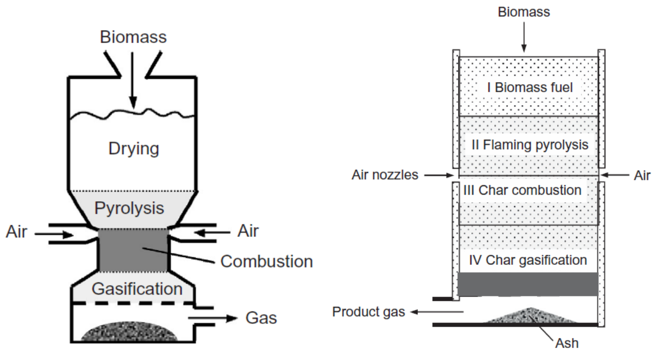


Figure 23. Design of downdraft gasifier (throated and throatless) (Basu, 2010a).

Syngas characteristics:

Syngas typically comprises hydrogen, carbon monoxide, carbon dioxide, and methane. The exact composition varies with the biomass type and gasification operating conditions. The lower heating value

(LHV) of syngas generally ranges from 4–18 MJ/Nm³, depending on biomass type and gasification operating conditions (gasification agent etc.) The presence of hydrogen and carbon monoxide contributes to higher heating values. Downdraft gasification tends to produce syngas with lower tar content (1-5%) compared to other gasification types. This is due to the high temperatures in the reduction zone, which crack most of the tar into lighter gases.

Syngas cleaning and upgrading

Syngas leaves the gasifier at high temperatures; typically 700°C (Basu and Kaushal, 2024a). Syngas needs to be cooled before use. To increase process efficiency, recovering heat from the syngas cooling is crucial. The syngas typically passes through a series of heat exchangers for heat recovery at a lower temperature. In all cases, steam is produced for in-plant power generation or process heating. The design of a syngas cooling and heat recovery system must consider the characteristics of the biomass feed, the syngas produced, and the specific application of the gasification process. For example, the syngas temperature must be below 50 ^{o}C so that it can be used for internal combustion engines (Tri Setioputro et al., 2023).

Regardless of the type of gasification process, the raw syngas typically contains impurities such as tar, particulate matter, and other contaminants that must be removed to make it suitable for synthesis reactions. The raw syngas may contain three principal types of impurities: solid particulates (unconverted char and ash), inorganic impurities (halides, alkali metals, sulphur compounds, and nitrogen compounds), organic impurities (tar, aromatics, and carbon dioxide) (Basu, 2010b). Cleaning has two aspects: removing undesired impurities and conditioning the gas to get the right ratio of H_2 and CO for the intended use. The end-use determines the level of cleaning and conditioning (Basu, 2013b). For example, when a gasification system is used in conjunction with an internal combustion engine or cold gas transfer is used, it is important that the engine is supplied with a gas that is sufficient free from particulates (<50 mg/m³, preferably 5 mg/m³), tars (<500 mg/m³) and acids (50 mg/m³) (UNIDO and NUST, 2016).

To clean the syngas of dust or particulates, four main options are available: cyclones, fabric or other barrier filters, electrostatic filters, and solvent scrubbers (Basu, 2013b).

Among organic impurities, tar is the most problematic and can be removed by scrubbing with an organic liquid such as methyl ester, catalytic cracking using nickel-based catalysts or olivine sand, or high-temperature cracking (Basu, 2013b).

Inorganic impurities should be removed sequentially because some processes produce by-products that also need to be eliminated. The sequence begins with water quenching to remove char and ash particles, followed by hydrolysis to convert COS and HCN into H_2S and NH_3 (Basu, 2013b). Ammonia and halides are then washed with water, and H_2S is adsorbed and removed with the wash water (Basu, 2013b). Finally, carbon dioxide is typically removed using solid or liquid adsorbents.

Applications of Syngas

Syngas from downdraft gasification has various utilization options, primarily due to its composition of H_2, CO, CO_2, and trace amounts of other compounds. Syngas from downdraft gasification is a usually implemented in energy production (heat and power) offering significant benefits in terms of efficiency and sustainability.

Syngas for heat and power production:

The syngas could be directly combusted in a boiler without cleaning to produce high-temperature heat or steam. The most common applications of cooled and cleaned syngas produced from downdraft biomass gasification are in heating and electricity generation, typically utilizing combined heat and power (CHP) systems. The use of CHP systems enhances efficiency by utilizing the waste heat for heating applications. Additionally, gasification-based CCHP (combined cooling, heat, and power) systems have proven to be an effective pathway for converting biomass into electricity, heat, and cooling (Maneerung et al., 2018). Furthermore, biomass integrated gasification combined cycle (BIGCC) systems offer a highly efficient method for producing electricity and heat from biomass, leveraging the syngas in a combined cycle power plant to maximize energy output and minimize emissions.

In CHP plants, gas engines fuelled by clean and cooled syngas can cogenerate electricity and heat on-site. The waste heat produced in a CHP facility is utilized in other industrial processes, used to meet the heat demand of individual buildings, or exported to a district heating system, Figure 24 (Muthu Dinesh Kumar and Anand, 2019).

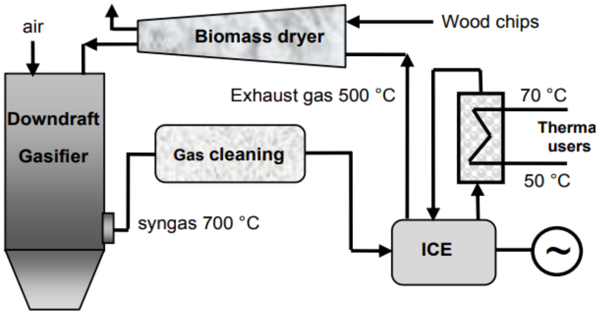


Figure 24. Scheme of a gasification-CHP plant (Frigo et al., 2014).

In the CCHP system cleaned and cooled syngas is sent to gas storage tank, as the fuel of the ICE to generate power (Yang et al., 2017). The waste heat from the ICE is divided into two parts: jacket water, which is used to produce domestic hot water through a heat exchanger, and exhaust gas, which drives an absorption chiller/heater to produce chilled water in summer and heating water in winter (Yang et al., 2017). If the exhaust gas and jacket water are insufficient to meet demand, the syngas from the gas storage tank and the domestic hot water produced by the absorption chiller/heater serve as a supplement (the dashed line in Figure 25).

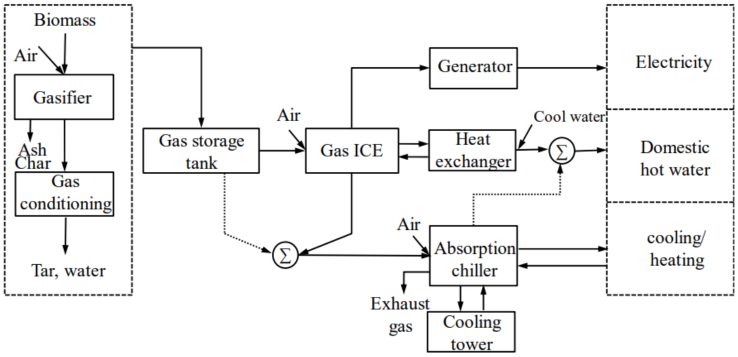


Figure 25. Scheme of CCHP system based on biomass gasification (Yang et al., 2017).

Another method is biomass integrated gasification combined cycle (BIGCC). The BIGCC is a power generation process that incorporates a biomass gasification system with a combined cycle power plant. It is an attractive alternative for power generation compared to other CHP processes due to several advantages, such as high thermal efficiency and energy output, reduced production of greenhouse gases, and lower generation of solid wastes (Motta et al., 2018).

A BIGCC process typically includes four central operating units: an air separation unit (ASU), a gasifier, a syngas cooling and clean-up system, and a combined cycle power plant (Motta et al., 2018). The cleaned syngas is burned with compressed air in the combustion chamber, resulting in hot gases that expand in the gas turbine to generate work. The hot exhaust gases are captured and directed to a heat recovery steam generator (HRSG) to produce steam for the steam turbine (Motta et al., 2018). The BIGCC system typically employs modified gas turbines designed to handle lower calorific value gaseous fuels (Motta et al., 2018). Figure 26 illustrates a simplified scheme of a BIGCC.

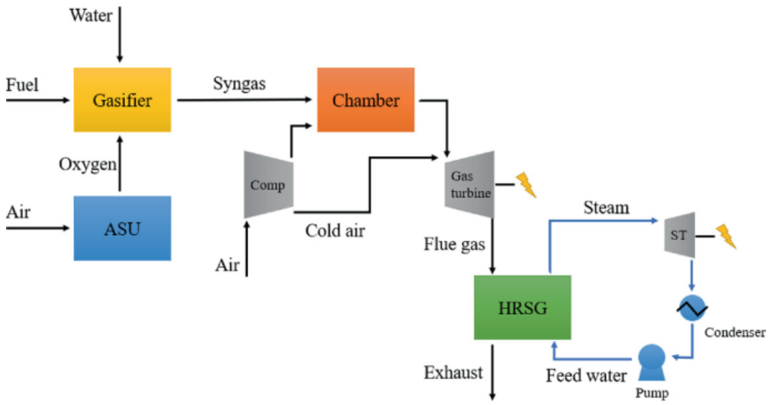


Figure 26. Simplified BIGCC power plant (Xue Sun et al., 2022).

Syngas Utilization in Solid Oxide Fuel Cells (SOFCs):

Solid Oxide Fuel Cells (SOFCs) are high-temperature fuel cells that can efficiently convert the chemical energy in syngas into electricity. Cleaned syngas can be directly used in SOFCs, but it might also undergo internal or external reforming to adjust the H_2 to CO ratio for optimal performance. In the SOFC, hydrogen from the syngas reacts at the anode with oxygen ions from the cathode to produce water, electricity, and heat. CO in syngas can also be utilized, reacting with steam to produce additional H_2 and CO_2 (Yamaguchi et al., 2021). Integrating downdraft gasification with SOFCs presents a promising approach for efficient and sustainable power generation from biomass. While there are technical and economic challenges to address, ongoing research and development aim to optimize these systems for broader commercial deployment.

Advantages and disadvantages of Downdraft Gasification

Downdraft gasification offers several notable advantages, primarily due to its ability to produce high-quality syngas. The process yields syngas with a lower tar content compared to other gasification methods, making it more suitable for downstream applications like power generation and chemical synthesis. This cleaner syngas results in reduced need for extensive tar removal systems, simplifying the overall gas cleanup process.

The design of downdraft gasifiers is typically simpler compared to updraft gasifiers. This simplicity contributes to lower capital and operational costs, making them an economically attractive option. Additionally, downdraft gasifiers generally exhibit high efficiency in converting biomass into syngas, thanks to effective energy utilization and reduced tar production. Overall system efficiency, however, can vary based on factors such as gasifier design, operating conditions, and the quality of downstream syngas processing.

Despite their benefits, downdraft gasification systems have certain limitations. One major disadvantage is the requirement for biomass feedstock to be of a specific size to ensure efficient gasification. Biomass feedstocks must be properly prepared and uniform in size to achieve optimal performance, which can be a logistical challenge.

Although tar production is lower than in some other gasification methods, downdraft gasifiers can still generate tar that may require additional treatment. This is particularly true if the system operates at high temperatures, which can affect material durability and lead to increased operational costs. The need for high operating temperatures may also impact the longevity of components and increase maintenance requirements.

Overall, while downdraft gasification offers high-quality syngas and lower costs due to its simpler technology, challenges related to feedstock preparation, tar management, and operating temperatures must be addressed to optimize its performance and economic viability.

The advantages and disadvantages, conversion efficiency, capital and operational cost of downdraft gasification process are presented in Table 16.

Table 16. The advantages and disadvantages of downdraft gasification process (modified (Molino et al., 2016) (IEA Bioenergy, 2022))(Donatelli et al., 2018).

Type of gasification	Technical condition	Key Products	Advantage	Disadvantage	Conversion Efficiency	Capital Cost	Operational Cost
Downdraft	*Suitable feedstock:* agricultural field residues, agricultural process residues, forest residues, wood from trees outside the forest, wood processing industry residue. *Feedstock size*: 20- 100 mm. *Temperature*:500–1200∘C *Residence time*: 900–1800 s. *Pressure:* atmospheric pressure to slightly pressurized (1 to 5 bar)	Syngas, bio-fuels, CHP	Simple and consolidated process Lowe tar product. Long residence time. Uncomplicated reactor. High performance of conversion.	Requirement of pre-treatment (size restriction, moisture reduction). Although tar production is lower cleaning treatment is required. Difficult to scaling up. High probability of bridging phenomena. High probability of clinkering phenomena	High	Moderate to high	Moderate

Cross-Draft Gasifier

Waste biomass suitable for Cross-draft Gasification:

Cross-draft gasification is another effective method for converting biomass into syngas, characterized by the gas flow being perpendicular to the feedstock. Cross-draft gasifiers are typically suitable for low-ash feedstock, which can limit the types of waste biomass that can be effectively used. Here are some examples of waste biomass that are generally suitable for cross-draft gasification: wood waste, agricultural residues, paper waste, charcoal made from various biomass sources (Siddiqui et al., 2022, Thakkar et al., 2018).

Feedstock preparation:

Preparing feedstock for cross-draft gasification involves several key steps to ensure efficient and effective gasification.

Physical pretreatment:

When designing a material handling system and selecting a suitable cross-draft gasifier, it is vital to consider the physical properties of biomass. To optimize the gasification process, effective physical pretreatment methods—such as drying, grinding, and palletisation—are typically required. Raw biomass often presents challenges such as low bulk density, irregular shapes, and high moisture content, which can negatively impact gasification efficiency. By properly addressing these characteristics through appropriate pretreatment techniques, the biomass can be enhanced for better performance in cross-draft gasifiers.

Size Reduction:

The biomass feedstock needs to be reduced to a uniform size to ensure consistent gasification. This can be achieved through chipping, grinding, or milling. The ideal particle size for cross-draft gasifiers typically ranges from 5 to 10 mm (Bukar et al., 2019). This size range ensures good contact between the biomass and the gasifying agent, promoting efficient gasification.

Drying:

Moisture content in the feedstock should be minimized, ideally below 20%. High moisture content can reduce the efficiency of the gasification process and lead to incomplete combustion (Rajasekhar Reddy and Vinu, 2018)

Description of Cross-draft Gasification

Cross-draft fixed bed gasifiers exhibit many of the operating characteristics of downdraft gasifiers. In cross-draft gasifiers, the waste biomass feedstock is fed from the top the gasifying agent is introduced at high velocity through side nozzles, creating significant circulation as it flows across the biomass and char bed (Mishra and Upadhyay, 2021, Van Holde D. et al., 2002). Unlike updraft and downdraft gasifiers, where the product gas exits from the top or bottom, in cross-draft gasifiers, the product gas is released from the opposite side to where the gasifying agent enters, as shown in Figure 27. The gasifying agent initiates combustion, raising the temperature in the combustion zone to nearly 1500°C (Mishra and Upadhyay, 2021).

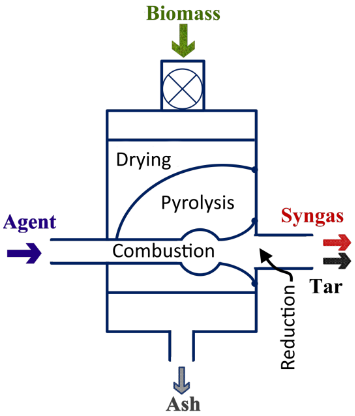


Figure 27. Scheme of a cross-draft gasifier modified (Shahbeig et al., 2022).

As the waste biomass feedstock downward through the gasifier, it undergoes multiple stages: drying, devolatilization, pyrolysis, and finally gasification before leaving the system (Loha et al., 2018). The oxidation zone is located near the gasifying agent's entry, while the gasification zone is near the product gas exit. Above the oxidation/reduction zone lies the pyrolysis zone, with the drying zone at the top (Loha et al., 2018). The syngas temperature in these gasifiers is typically high (800–900°C), necessitating specific material and operational considerations (Loha et al., 2018)

Cross-draft gasifiers have the fastest response time (5-10 min) and the smallest thermal mass among gasifiers due to their minimal inventory of hot char (Reed T. B. and Das A., 1988). While this design facilitates quick gasification, it is less effective at cracking tar, which refers to the thermal decomposition of tar into non-condensable gases (Van Holde D. et al., 2002). Consequently, cross-draft gasifiers tend to produce higher tar levels (0.01–0.1 g/Nm^3) (Loha et al., 2018), although they perform better than updraft gasifiers in this aspect (Van Holde D. et al., 2002).

Cross-draft gasifiers require less extensive cleaning of producer gas compared to updraft gasifiers. Although this design is the simplest and most cost-effective among the three fixed-bed gasifier types, it suffers from several limitations (Van Holde D. et al., 2002). It has the lowest cold gas efficiency and the lowest lower heating value of producer gas, typically ranging 3-4 MJ/Nm^3. Additionally, cross-draft gasifiers exhibit the least tolerance for variations in feedstock moisture content and particle size compared to both updraft and downdraft gasifiers (Van Holde D. et al., 2002). Due to these critical drawbacks, cross-draft gasifiers are infrequently employed in commercial applications.

Influence of process parameters:

The syngas composition in cross-draft gasifiers is influenced by several key parameters. The choice of gasifying agent, such as air, steam, or oxygen, and its flow rate can significantly impact the syngas output. Steam, for instance, increases hydrogen production, while air introduces nitrogen, reducing the syngas's heating value. Using pure oxygen can enhance calorific value but at a higher operational cost (Bukar et al., 2019). The equivalence ratio is crucial for achieving efficient gasification and high-quality syngas. Higher temperatures improve efficiency and reduce tar formation, though extreme heat may degrade materials and raise costs; cross-draft gasifiers typically operate at temperatures up to 1500°C (Mishra & Upadhyay, 2021; Sikarwar et al., 2016). Longer residence times allow for more complete gasification, which enhances syngas yield and quality, while adjusting feed rates and gas flow can help control this process. Though most cross-draft gasifiers operate at atmospheric pressure, higher pressures can boost gasification rates but require more robust equipment, increasing costs (Sikarwar et al., 2016; Jain A.K., 2018).

Influence of the waste biomass parameters on the product:

In cross-draft gasification, several biomass properties critically influence efficiency and syngas production. Smaller particle sizes (5-10 mm) generally enhance gasification by increasing the surface area for reactions, leading to higher syngas yields and improved composition (Jain A.K., 2018). Biomass density and porosity also play key roles; high-density biomass ensures steady feeding but may slow gas flow, while low-density, porous biomass can result in irregular feeding and incomplete gasification. Optimizing the balance between density and porosity improves reaction rates and heat transfer, boosting syngas quality. Ash content is another factor—high ash can cause slagging, fouling, and equipment corrosion, while low-ash biomass is preferable for better efficiency. Pre-treatments like washing can reduce ash and enhance syngas quality. Moisture content should remain below 20%, as higher moisture requires more energy for drying, reducing gasification efficiency. Balancing particle size, density, porosity, ash, and moisture content is essential for optimizing cross-draft gasification performance.

Syngas characteristics:

For cross-draft gasifiers, the composition of syngas generally includes hydrogen, carbon monoxide, carbon dioxide, and methane. The specific proportions of these components depend on the type of biomass used and the operational conditions during gasification. The lower heating value (LHV) of syngas generally ranges around 3-4 MJ/Nm^3, depending on biomass type and gasification operating conditions (gasification agent etc.).

Syngas cleaning and upgrading

Syngas leaves the gasifier at high temperatures; typically, 800–900°C. Syngas must be cooled before it can be utilized. To enhance process efficiency, it is essential to recover heat during the syngas cooling phase. Typically, the syngas flows through a series of heat exchangers, allowing for heat recovery at lower temperatures. In all cases, this process generates steam that can be utilized for in-plant power generation or process heating. After cooling, syngas must be cleaned of dust and particulates using methods such as cyclones, fabric or other barrier filters, electrostatic filters, and solvent scrubbers (Basu, 2013). Among organic impurities, tar is the most problematic contaminant in syngas due to its tendency to condense and form deposits that can hinder downstream processes. Effective removal methods for tar include scrubbing with organic liquids like methyl ester, followed by catalytic cracking and high-temperature cracking. Implementing these techniques is crucial for achieving cleaner syngas, thereby optimizing its use in energy generation and chemical production.

Applications of Syngas

Due to mentioned critical drawbacks, cross-draft gasifiers are infrequently employed in commercial applications. Syngas from cross- draft gasification is a usually implemented in energy production (heat and power).

B Fluidized bed

Waste biomass suitable for Fluidized Bed Gasification:

Fluidized bed gasification, as most of gasification processes, is highly versatile and can handle a wide range of waste biomass types. Some suitable materials include: agricultural residues, forestry residues, industrial waste, organic parts of MSW (Siddiqui et al., 2022, Sumitomo Heavy Industries Ltd., 2023)

Feedstock preparation:

Fluidised beds are comparably flexible regarding feedstock and feedstock quality. In general, a wide variety of water and ash contents can be utilized in fluidized beds. Though, the feedstock has to confirm with certain size restrictions, i.e. feedstock particles generally have to be below 100 mm. Commercially used are woody biomasses but also waste streams and other inhomogeneous feedstocks are especially suitable for fluidized bed applications.

Important to note is that the ash melting point of the feedstock ash has to be above operating temperature to prevent agglomeration of the bed material. Low ash melting point feedstocks are often grasses or, in general, feedstocks with high contents of silicon.

Description of Fluidized Bed Gasification Process:

Fluidised bed reactors consist of a bed material which is held in suspension by the gas stream. The bed material consists of solid particles, typically with a size of 0.5 mm–1 mm, and it can be inert or act as a catalyst (Kaltschmitt, Hartmann, & Hofbauer, 2016). The use of a fluidised bed ensures good gas-solid mixing and a uniform temperature throughout the bed making it possible to use a variety of fuels of different qualities (Basu, 2006) (e.g. possible fuel water contents of 5 m%–60 m% (Kaltschmitt, Hartmann, & Hofbauer, 2016)). Fluidised bed gasification can be performed in bubbling fluidised beds or circulating fluidised beds which vary in the applied gas velocities. A special form of fluidised bed gasifiers are dual fluidised beds (DFBs). DFBs consist of two reactors, with one reactor being dedicated to gasification and the second being dedicated to combustion to supply heat for endothermic gasification reactions.

Fluidized Bed Pyrolysis Reactors:

Bubbling Fluidized Bed Gasifier:

The bubbling fluidized bed (BFB) gasifier, initially developed by Fritz Winkler in 1921, is possibly the oldest commercial application dealing with fluidized beds and has been widely used for coal gasification (Figure 28). In the context of biomass gasification, it is considered one of the most suitable options available.

Countless bubbling fluidized-bed gasifiers with varying designs have been created and are currently in operation ((Lim & Alimuddin, 2008); (Narváez, Orío, Aznar, & Corella, 1996)). Due to their adaptability for medium-sized units (less than 25 MW_{th}), numerous biomass gasifiers are built as BFBs. Depending on operating conditions, BFB gasifiers can be classified as low-temperature or high-temperature types. They can also be operated at atmospheric or elevated pressures.

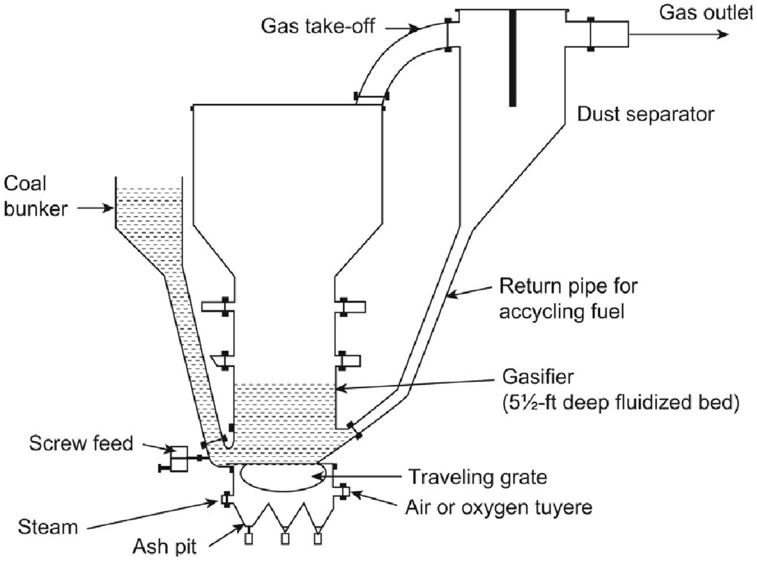


Figure 28. Original design of the Winkler bubbling fluidized bed gasifier (Basu, Chapter 8 - Design of Biomass Gasifiers, 2018).

In BFB gasification, biomass is fed into the hot bed material, which is fluidized by steam, air, or oxygen. Bed temperature is kept below 900 °C to prevent ash fusion and bed agglomeration. The gasifying medium is sometimes supplied in two stages. In the first stage the gasification temperature is maintained, in the second stage unconverted char particles and tars are converted into product gas.

Influence of process parameters on product characteristics:

The choice of gasification agent influences the syngas composition and quality. Steam is commonly used as the primary gasification agent, producing a higher yield of hydrogen-rich syngas. An oxygen-rich air or pure oxygen can also be used to increase the gasification rate and improve the syngas quality. The temperature of the fluidized bed plays a crucial role in the gasification process. Higher temperatures (typically between 700-900°C) promote the conversion of biomass to syngas, while lower temperatures (500-700°C) can lead to the increased production of less desirable tar and char. Proper temperature control is essential to optimize the syngas production and minimize the formation of undesired by-products. The operating pressure of the fluidized bed reactor influences the gasification rate and the syngas production.

Higher pressures favor the gasification process, resulting in higher syngas yields and lower tar formation. However, increasing the pressure also increases the energy consumption and the complexity of the system. The residence time of the biomass particles in the fluidized bed affects the conversion efficiency. Longer residence times allow for better gasification, but excessive residence times can lead to particle attrition, which may cause the loss of feeding material or the blockage of the reactor.

Influence of waste biomass parameters on syngas:

Smaller particle sizes provide a larger surface area for the gasification reactions, leading to higher conversion rates and syngas yields. However, smaller particles may also lead to increased attrition and the requirement for more energy-intensive milling processes. A lower biomass density and higher porosity can enhance the gasification process, allowing for better heat and mass transfer within the fluidized bed. The ash content of the biomass affects the gasification process and the composition of the syngas. High ash content can lead to ash agglomeration, causing reactor fouling and sintering. The ash content also influences the syngas composition, as some elements present in the ash can react with the gasification agents, affecting the syngas quality. The moisture content of the biomass can influence the gasification process, as it affects the available fuel mass and the heat transfer efficiency. High moisture content may lead to incomplete gasification and lower syngas yields. The chemical composition of the biomass affects the syngas production and quality. Lignin, which is rich in carbon and hydrogen, produces a higher yield of syngas compared to cellulose and hemicellulose, which are rich in oxygen. The proportion of these components in the biomass determines the overall syngas composition.

Syngas characteristics:

The syngas produced by BFBG typically consists of hydrogen, carbon monoxide, carbon dioxide, methane, and smaller amounts of other gases, such as ethylene and ethane. The composition of the syngas depends on the biomass type, process parameters, and gasification agents used. The syngas can be characterized by its calorific value, higher heating value (HHV), lower heating value (LHV), and the ratio of H_2 to CO, which determines its suitability for various applications, such as bio-fuel synthesis, CHP, CCHP, or BIGCC.

Syngas cleaning and upgrading

Before the syngas can be used for various applications, it needs to be cleaned and upgraded to remove impurities, such as tar, ammonia, and sulfur compounds. This is typically achieved through a series of processes, including cooling, condensation, scrubbing, absorption, and adsorption. The cleaned and upgraded syngas can then be further processed to meet the specific requirements of the desired application, such as Fischer-Tropsch synthesis for bio-fuels or gas engines for CHP and CCHP.

Advantages and disadvantages of BFB

BFB gasification is another effective technology for converting biomass into syngas. Here are some of its key advantages and disadvantages:

Advantages:

- Fuel Flexibility: BFB gasifiers can handle a wide range of biomass types, including agricultural residues, forestry residues, and industrial waste (Martínez-Lera et al., 2013, Hossain et al., 2022).
- Uniform Temperature: The bubbling action helps maintain a uniform temperature throughout the reactor, which improves the consistency and quality of the syngas produced (Mastellone and Zaccariello, 2015).
- High Heat Transfer The fluidized bed provides excellent heat transfer, which enhances the efficiency of the gasification process (NETL, 2024).
- Scalability: BFB gasifiers are scalable and can be used in both small and large-scale applications (Martínez-Lera et al., 2013).
- Lower Tar Production: Compared to fixed bed gasifiers, BFB gasifiers generally produce lower amounts of tar (Narnaware S.L. et al., 2023).

Disadvantages:

- Complexity: The system is more complex than fixed bed gasifiers, requiring sophisticated control systems and maintenance (Martínez-Lera et al., 2013).
- Higher Costs: Initial capital and operational costs can be higher due to the complexity and additional equipment required (Martínez-Lera et al., 2013).
- Erosion and Corrosion: The bubbling action can lead to increased wear and tear on the equipment, resulting in higher maintenance costs (Mastellone and Zaccariello, 2015).
- Feedstock Preparation: Requires consistent feedstock preparation to ensure uniform particle size and moisture content (Mastellone and Zaccariello, 2015).

Circulating Fluidized Bed Gasifier:

A circulating fluidized-bed (CFB) gasifier is an ideal choice for biomass gasification due to its extended gas residence time, which effectively converts the high levels of volatile components commonly found in biomass. The CFB system consists of a riser, a cyclone, and a solid recycling mechanism (Figure 29). The riser acts as the actual gasifier reactor. Compared to BFB gasifiers CFBs feature higher fluidization velocities and more substantial particle migration. This results in a fast-fluidized bed configuration and the bed material and biomass particles are distributed over the whole length of the gasification reactor. Operating temperatures within the riser typically range from 800 to 1000°C, and the product gas is then led through a cyclone for the separation of solid particles which are returned to the gasification reactor. Several countries have deployed commercial CFB gasifiers, including a 140 MW CFB gasifier in Vaasa, Finland designed for biomass cofiring. This innovative setup allows for the economical supplementation of fuel by gasifying wood, peat, and straw, potentially replacing up to 40% of coal in the process.

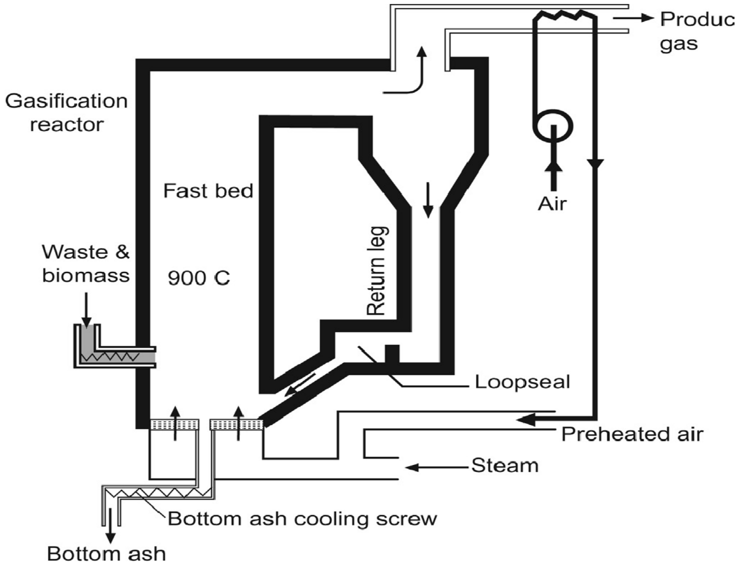


Figure 29. Scheme of a circulating fluidized bed reactor (Basu, 2018).

Influence of process parameters on product characteristics:

The choice of gasification agent (steam or oxygen) affects the syngas composition and quality. Steam gasification produces a higher yield of hydrogen, while oxygen gasification results in a higher carbon monoxide content. The gasification temperature influences the gasification rate and the syngas yield. Higher temperatures improve the conversion efficiency of biomass to syngas but may also lead to the formation of undesirable tar by-products. The operating pressure of the CFBG process affects the syngas production rate and its quality. Higher pressures generally lead to higher syngas yields and improved conversion efficiency.

Influence of waste biomass parameters on syngas:

The size of the biomass particles affects the gasification rate and the syngas yield. Smaller particles have higher surface areas, which allow for more efficient gasification. The density and porosity of the biomass influence the gasification rate and the syngas yield. Biomass with lower density and higher porosity tends to gasify more efficiently. The ash content of the biomass affects the availability of the fuel for gasification and the ash formation during the process. High ash content can lead to ash agglomeration, which may cause operational problems in the CFBR. The moisture content of the biomass affects the gasification efficiency and the syngas yield. High moisture content reduces the availability of fuel for gasification and can also lead to operational problems in the CFBR. The composition of the biomass, particularly the cellulose, hemicellulose, and lignin content, affects the syngas composition. The gasification of these components results in the production of various gaseous products, such as hydrogen, carbon monoxide, and methane.

Syngas characteristics:

The key characteristics of syngas produced from CFBG include its composition, calorific value, and impurities. The syngas typically consists of hydrogen, carbon monoxide, carbon dioxide, methane, and trace amounts of other gases, such as nitrogen and helium. The calorific value of syngas varies depending on its composition and can range from 4 to 13 MJ/Nm^3. The syngas contains impurities, such as tars, particulate matter, and sulfur compounds, which need to be removed before the gas can be used for further processing.

Syngas cleaning and upgrading:

The syngas produced from CFBG requires cleaning and upgrading to remove impurities and improve its quality for use in various applications. The cleaning process typically involves the following steps:

1. Removal of particulate matter using a cyclone or a baghouse filter.
2. Removal of tars using hot gas filtration, adsorption, or condensation.
3. Removal of sulfur compounds using adsorption or scrubbing with a caustic solution.
4. Cooling and compression of the syngas to prepare it for further processing or storage.

Advantages and disadvantages of CFB:

Circulating Fluidized Bed (CFB) gasification is a robust technology with several advantages and disadvantages.

Advantages:

- Fuel Flexibility: CFB gasifiers can handle a wide range of biomass and waste materials, including those with high moisture and ash content (Valmet, 2024).
- High Efficiency: The recirculating loop enhances the efficiency of combustion and gasification processes.
- Low Emissions: CFB gasifiers can achieve lower emissions of pollutants, with reports suggesting up to 95% of pollutants can be absorbed before being emitted.

- Uniform Temperature: The circulating action helps maintain a uniform temperature, improving the quality and consistency of the syngas produced (SFC, 2024).
- Scalability: CFB technology is scalable and can be used in both small and large-scale applications (Valmet, 2024).

Disadvantages

- Complexity: The system is more complex than fixed or bubbling bed gasifiers, requiring sophisticated control systems and maintenance (Valmet, 2024).
- Higher Costs: Initial capital and operational costs can be higher due to the complexity and additional equipment required (Valmet, 2024).
- Erosion and Corrosion: The high velocity of particles can lead to increased wear and tear on the equipment, resulting in higher maintenance costs (SFC, 2024).
- Feedstock Preparation: Requires consistent feedstock preparation to ensure uniform particle size and moisture content (SFC, 2024).

Dual Fluidized Bed Gasifier:

The main challenge in air gasification of coal or biomass is the dilution of the product gas by nitrogen. A twin reactor, like the dual fluidized bed (DFB), addresses this by separating the combustion and gasification reactors, preventing nitrogen from diluting the product gas (Figure 30). However, issues like biomass containing less carbon and the need for external heating to maintain temperature are present.

TU Wien employed a system using a BFB gasifier and a CFB combustor to gasify diverse biomass types. The design was further realized in several commercial plant, e.g Güssing and Oberwart, Austria, Senden, Germany and Sawan, Thailand. The Rentech-SilvaGas process is similar only with both reactors operated as CFBs.

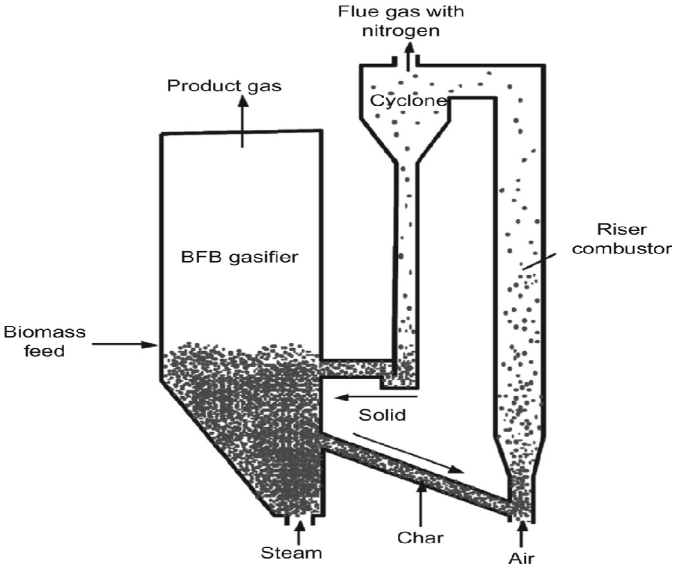


Figure 30. Scheme of a dual fluidized bed (Basu, 2018).

While physically separating the gasification and combustion reactor is often done, it is also possible to realise an internal circulation via separating a reactor in two chambers. Bed material circulation is realized by varying fluidization velocities in the two chambers.

Influence of process parameters on product characteristics:

Typically, steam and/or oxygen are used as gasification agents. Steam gasification produces a higher yield of hydrogen, while the addition of oxygen increases the gasification temperature and enhances the conversion of biomass but can also lead to higher tar content in the syngas. Higher temperatures increase the reaction rate and biomass conversion. However, excessively high temperatures can cause sintering of the fluidized bed materials and increase tar formation. Optimal temperature ranges are typically between 700-900°C for steam-only gasification and 850-950°C for oxygen-blown processes. Increasing the pressure of the gasification process increases the equilibrium conversion of biomass and enhances the yield of hydrogen-rich syngas. However, higher pressures also increase the risk of equipment corrosion and require more robust materials. Typical pressures for DFBG range from 20-30 bar.

Influence of waste biomass parameters on syngas:

Smaller particle sizes have a larger surface area, which can lead to more efficient gasification. However, smaller particles can also cause agglomeration in the fluidized bed. An optimal particle size range of 0.5-2 mm is often used to balance these factors. Lower density and higher porosity particles can lead to more efficient gasification due to increased surface area. However, these properties can also affect the fluid dynamics of the fluidized bed. High ash content can lead to fouling and sintering in the fluidized bed, reducing the efficiency of the gasification process. In some cases, ash can be used as a heat carrier in the combustion bed, but this requires proper bed material and operational conditions. High moisture content can reduce the concentration of volatiles in the biomass, leading to lower yields of syngas. However, it can also play a role in moderating the temperature of the fluidized bed. The main components of biomass have different gasification properties. Cellulose and hemicellulose produce more hydrogen-rich syngas, while lignin leads to the formation of more tar. The proportion of these components in the biomass affects the overall syngas composition.

Syngas characteristics:

DFBG produces a syngas composition that is suitable for various applications. The gas typically contains 15-25% H_2, 25-35% CO, <1% CH_4, <1% CO_2, and traces of other gases like tar, NH_3, and H_2S. The calorific value of syngas is usually around 4-6 MJ/Nm^3.

Syngas cleaning and upgrading:

Before using syngas for various applications, it often needs to be cleaned and upgraded. This can involve removing tar, particulate matter, and other impurities through processes such as filtration, scrubbing, and catalytic tar reforming. Syngas can also be upgraded by increasing its hydrogen-to-carbon monoxide ratio using processes like water-gas shift reaction or pressure swing adsorption.

Sorption Enhanced reforming:

Sorption enhanced reforming aims to create two separate gas streams: one rich in H_2 and the other high in CO_2, allowing CO_2 sequestration and H_2 use for H_2-demanding applications. CaO acts as a CO_2 carrier in two reactors: a gasifier (BFB) and a regenerator (CFB). CO_2 from gasification is captured by CaO, with the product gas also containing CO undergoing a shift reaction to produce more H_2. The removal of CO_2 enhances the water-gas shift reaction and increases H_2 production. Calcium carbonate, formed in the gasifier, is transferred to a regenerator where it is calcined back into CaO and CO_2. The product gas and CO_2 leave the regenerator and gasifier at high temperatures. $CaCO_3$ calcination depends on factors like fluidizing medium, temperature, and residence time, with low conversion when using CO_2 as the medium, but high conversion when using steam.

To achieve the calcination of CaO, the gasification temperature has to be below 720 °C and the regenerator has to be operated above 850 °C (Schweitzer et al., 2016).

Influence of Process Parameters on Product Characteristics:

The choice of gasification agent plays a vital role in the composition and yield of the syngas. Common gasification agents include steam, oxygen, carbon dioxide, and a combination of these. The selection of the agent depends on the desired end product, the type of biomass, and the efficiency of the process. The reaction temperature affects the conversion of biomass into syngas. Higher temperatures promote the breakdown of complex organic compounds, increasing the yield of syngas. However, excessively high temperatures may lead to the formation of unwanted by-products and the degradation of the adsorbent material. The pressure of the gasification process influences the rate of conversion and the composition of the syngas. Higher pressure typically results in higher yields of syngas, but may also increase the risk of side reactions and equipment corrosion.

Influence of Waste Biomass Parameters on Syngas:

Smaller particle sizes have a larger surface area, which can facilitate faster conversion rates and higher syngas yields. However, smaller particles may also be more prone to agglomeration and plugging of the gasifier. The density and porosity of the biomass affect the gasification rate and the accessibility of the reactive gases to the biomass particles. Lower density and higher porosity can be beneficial for improved gasification efficiency. The ash content of the biomass affects the operation of the gasifier and the composition of the syngas. High ash content may lead to ash deposition, which can block the gasifier and reduce its efficiency. Additionally, certain elements present in the ash (such as alkali metals) can cause catalyst deactivation in the downstream reforming process. Moisture in the biomass can act as a heat sink, reducing the gasification efficiency. However, moderate moisture levels can also help maintain the integrity of the adsorbent material, as it can act as a coolant and prevent the adsorbent from overheating. Cellulose, Hemicellulose, and Lignin are the main components of the biomass that are converted into syngas during gasification. The relative proportion of these components in the biomass can affect the composition and yield of the syngas.

Syngas Characteristics:

The composition of the syngas produced by SER depends on the type of biomass and the process parameters. Typical syngas compositions include: CH_4 (10-30%), CO (15-30%), CO_2 (10-20%), H_2 (10-20%),-Other components (e.g., water vapor, nitrogen, sulphur compounds, <5%).

Syngas Cleaning and Upgrading:

After the SER process, the syngas needs to be cleaned and upgraded to meet the specifications required for the desired applications. This may involve:

1. Removal of particulate matter, ash, and other solid impurities.
2. Removal of sulphur compounds (e.g., hydrogen sulphide) to prevent equipment corrosion and downstream catalyst poisoning.
3. Methanation to convert CO and CO_2 into CH_4, increasing the energy content of the syngas.
4. Reforming to increase the H_2 content of the syngas, which is desirable for applications such as bio-fuel synthesis.

Advantages and disadvantages of DBF

DFB gasification is a technology that separates the gasification and combustion processes into two distinct fluidized beds (Table 17).

Advantages:

- High Efficiency: DFB gasifiers can achieve high conversion efficiencies due to the effective separation of gasification and combustion zones (Siedlecki et al., 2011).
- Fuel Flexibility: They can handle a wide range of biomass types, including those with high moisture content (Siedlecki et al., 2011).
- Low Tar Production: The process typically results in lower tar content in the syngas compared to other gasification methods (Siedlecki et al., 2011).
- Better Control: The separation of processes allows for better control over the gasification environment, leading to more consistent syngas quality (Siedlecki et al., 2011).
- CO_2 Reduction: DFB systems can be designed to capture and utilize CO_2, contributing to lower greenhouse gas emissions (Müller et al., 2021).

Disadvantages:

- Complexity: The system is more complex than single fluidized bed gasifiers, requiring more sophisticated control and maintenance (Siedlecki et al., 2011).
- Higher Costs: The initial capital and operational costs can be higher due to the complexity and additional equipment required (Siedlecki et al., 2011).
- Scaling Issues: Scaling up the technology can be challenging, particularly in maintaining uniform fluidization and avoiding channeling (Loha et al., 2018).
- Feedstock Preparation: Requires more stringent feedstock preparation to ensure consistent particle size and moisture content (Loha et al., 2018).

Table 17. The advantages and disadvantages of dual fluidized bed gasification (Basu P., 2006, Basu and Kaushal, 2024a, Kaltschmitt M. et al., 2016, Lim and Alimuddin, 2008, Narváez et al., 1996).

Type of gasification	Technical condition	Key Products	Advantage	Disadvantage	Conversion Efficiency	Capital Cost	Operational Cost
dual fluidized bed	*Suitable feedstock:* *agricultural field residues, agricultural process residues, forest residues, wood from trees outside the forest, wood processing industry residue, livestock manure.* *Feedstock size: up to 100 mm.* *Temperature: 800–1000◦C* *Residence time: sec to min* *Pressure:1 bar*	Syngas, bio-fuels, CHP	Good temperature control. Low level of residues. High carbon conversion. High flexibility of feedstock. no dilution with N_2	Two separate reactors with two gas cleaning lines (product gas and flue gas)	High	High	Moderate to high

Applications of Syngas:

Bio-fuel synthesis: Syngas can be converted into bio-fuels (e.g., Fischer-Tropsch diesel, methanol) through downstream processes such as Fischer-Tropsch synthesis and the Water-Gas Shift reaction.

Combined Heat and Power (CHP): Syngas can be used in combined heat and power plants to generate electricity and useful heat.

Combined Cooling, Heat and Power (CCHP): Syngas can be used in CCHP systems, which can provide electricity, heating, and cooling simultaneously, improving the overall efficiency of energy utilization.

2.4.4. The technology status of Gasification

The technology readiness levels (TRLs) for gasification pathways can vary depending on the specific technology and its application.

Fixed-bed gasifiers are well-established and commonly used for small to medium-scale applications. Their TRLs are generally high, around TRL 8-9, indicating that they are commercially available and widely deployed.

Fluidized-bed gasifiers, also well-established and used for a range of biomass and waste feedstocks. Their TRLs are typically around TRL 8-9, indicating commercial availability and deployment in various applications. Entrained-flow gasifiers are used for larger-scale applications and can handle a wide variety of feedstocks. Their TRLs are generally around TRL 7-8, as they are commercially available but may still be in the process of optimization and scaling up in certain applications.

Plasma gasifiers are more advanced and still in the developmental stage for many applications. Their TRLs are typically lower, around TRL 5-6, as they are demonstrated in relevant environments but not yet widely commercialized.

In Table 18 is presented TRLs levels of some gasification technologies implemented in Europe.

Table 18. Biomass waste gasification technology readiness levels (TRLs).

Plant Name	Gasification type	Feedstock	Capacity	TRLs	Reference
Pelletvergasser AEW Rheinfelden, Switzerland (started in 2018)	Fluidized bed in co-current flow	Wood pellets (110 kg/h)	Power 0,165 Mwel, Thermal 0,26 MWth for district heating	TRL 9 Commercial	(Bioenergy and Sustainable Technologies (BEST), 2023)
Baas Energie BV, Ens, Netherlands (started in 2017)	ReGaWatt updraft gasifier	Wood chips (N/A)	Power 0.5 MWel, Heat 4.5 MWth heat for greenhouse	TRL 9 Commercial	(Bioenergy and Sustainable Technologies (BEST), 2023)
Bioenergie Schnellingen, Germany (started in 2015)	Fluidized bed process in co-current flow	Wood pellets, wood chips (N/A)	Power 0.4 MWel, Heat 0.518 MWth	TRL 9 Commercial	(Bioenergy and Sustainable Technologies (BEST), 2023)
Bio&Watt, Oltrepo Pavese, Italy (started in 2010)	Pyrogasifier	Wood chips (N/A)	Power 0.3 MWel	TRL 9 Commercial	(Bioenergy and Sustainable Technologies (BEST), 2023)
Birmingham Bio-power, United Kingdom (started in 2018)	Nexterra fixed-bed updraft gasification	Waste wood (N/A)	Power 10.3 MWel	TRL 9 Commercial	(Bioenergy and Sustainable Technologies (BEST), 2023)
Buergerenergie St. Peter (started in 2013)	Fluidized bed process in cocurrent flow	Wood pellets, wood chips (N/A)	Power 0.18 MWel, Heat 0.27 MWth	TRL 9 Commercial	(Bioenergy and Sustainable Technologies (BEST), 2023)

Burkhardt Cham, Landkreis Cham, Germany, (started in 2009)	Fluidized bed process in cocurrent flow	Wood pellets, wood chips (N/A)	Power 0.18 MWel, Heat 0.27 MWth	TRL 9 Commercial	(Bioenergy and Sustainable Technologies (BEST), 2023)
Burkhardt Neumarkt, Neumarkt Landkreis , Germany, (started in 2009)	Fluidized bed process in cocurrent flow	Wood pellets, wood chips (N/A)	Power 0.18 MWel, Heat 0.27 MWth	TRL 9 Commercial	(Bioenergy and Sustainable Technologies (BEST), 2023)
Ciamber, Forno di Zoldo, Italy	Downdraft gasification	Lignocellulosic biomass (N/A)	Power 1 MWel, Heat 0.8 MWth	TRL 9 Commercial	(Bioenergy and Sustainable Technologies (BEST), 2023)
Duchi Fratelli Societa Agricola/Agroenergia, Gadesco Pieve Delmona, Italy, (started in 2010)	Downdraft gasification	Wood chips (N/A)	Power 0.96 MWel, Heat 3.2 MWth	TRL 9 Commercial	(Bioenergy and Sustainable Technologies (BEST), 2023)
Comune Quingentole, Italy, (started in 2006)	Downdraft gasification	Wood chips (N/A)	Power 0.07 MWel, Heat 0.14 MWth	TRL 9 Commercial	(Bioenergy and Sustainable Technologies (BEST), 2023)
Burkhardt Nuernberger Land, Landkreis Nürnberger Land, Germany, (started in 2009)	Fluidized bed process in cocurrent flow gasification	Wood pellets, wood chips (N/A)	Power 0.18 MWel, Heat 0.27 MWth	TRL 9 Commercial	(Bioenergy and Sustainable Technologies (BEST), 2023)
Holzgasanlage 1 Kaeser Gasel, Switzerland, (started in 2017)	Downdraft Ligento gasification	Wood chips (133 kg/h)	Power 0.14 MWel, Heat 0.24 MWth	TRL 9 Commercial	(Bioenergy and Sustainable Technologies (BEST), 2023)

Holzgasanlage 2 Kaeser Gasel, Switzerland, (started in 2017)	Downdraft Ligento gasification	Wood chips (133 kg/h)	Power 0.14 MWel, Heat 0.24 MWth	TRL 9 Commercial	(Bioenergy and Sustainable Technologies (BEST), 2023)
Ligento Nuernberg< Germany	Fixed-bed process in cocurrent flow	Wood chips (N/A)	Power 0.14 MWel, Heat 0.24 MWth	TRL 9 Commercial	(Bioenergy and Sustainable Technologies (BEST), 2023)
CHP Pyroforce Nidwalde, Stans, Switzerland, (started in 2007)	Two-zone downdraft Pyroforce gasification	Dried chips from demolition wood (N/A)	Power 1.38 MWel, Heat 1.2 MWth	TRL 9 Commercial	(Bioenergy and Sustainable Technologies (BEST), 2023)
CHP power plant, Kokemaen Laempoe Oy, Kokemäki, Finland, (started in 2004)	Condens Oy and VTT new type of fixed-bed gasification	Biomass residues, sawdust to large chips (N/A)	Power N/A, Heat (6 MWth)	TRL 9 Commercial	(Bioenergy and Sustainable Technologies (BEST), 2023)
Nong Bua dual fluidized bed gasification power plant	Dual fluidized bed steam gasification	Woodchips, cassava rhizomes, sugarcane leaf, rice straw, corn cobs, other agricultural residues and municipal organic solid wastes (N/A)	Power 1,0 MWel, Thermal 1.25 MWth. Overall efficiency (power and heat) 59.21%. District heating temperature 120°C/70°C	TRL 9 Commercial	(Siriwongrungson et al., 2022)
LiPRO Energy Gasification-CHP Plant, Germany (stated in 2012)	Multi-stage gasification (pyrolysis stage, gas cracking stage and gasification pyrolysis stage	Wood chips (22,5 -37,5 kg/h)	Power 30 - 50 kW, Heat 60 - 90 kW	TRL 9 Commercial	(Österreichische Biomasse-Verband, 2022)

	and a fluidized rising bed stage with rotating grid)				
Stadtwerke Rosenheim Gasification-CHP Plant, Germany (started in 2015)	Double staged gasification (pyrolysis stage and a fluidized rising bed stage)	Unadulterated wood, wood chips (42t/h)	Power 50 -180 kW, Heat 110-380 kW	TRL 9 Commercial	(Bacovsky D. et al., 2017, Allesina and Pedrazzi, 2021)
Mont-Godinne Hospital (Xylowatt), Special Purpose Vehicule (MGGE), Mont-Godinne, Belgium, (started in 2018)	NOTAR® medium scale down-draft gasification	Clean wood chips (690 kg/h) recycled wood (731 kg/h)	Power 0.75 MWel, Heat 1.2 MWth	TRL 9 Commercial	(Bioenergy and Sustainable Technologies (BEST), 2023)
CHP Urbas Sulzbach-Laufen, Sulzbach-Laufen, Germany, (started in 2009)	Downdraft gasification technology	Wood chips (N/A)	Power 0.13 MWel, Heat 0.28 MWth	TRL 9 Commercial	(Bioenergy and Sustainable Technologies (BEST), 2023)
Muensterland Energy Gmbh, Ladbergen, Germany (stared in 2011)	VIPP-VORTEX gasification	Wood pellets, wood chips, (N/A)	Power 6 Mwe, Heat 8.6 MWth	TRL 9 Commercial	(Bioenergy and Sustainable Technologies (BEST), 2023)
Micro-scale biomass gasification CHP Volter, Nurmes, Finland, (stared in 2012)	Downdraft gasification	Wood chips (N/A)	Power 0.04 MWel, Heat 0.1 MWth	TRL 9 Commercial	(Bioenergy and Sustainable Technologies (BEST), 2023)

RegaWatt Abensberg, Germany, (stared in 2010)	Fixed bed in countercurrent flow – Updraft gasification	Lignocellulosic biomass (N/A)	Power 2 MWel, Heat 4.3 MW	TRL 9 Commercial	(Bioenergy and Sustainable Technologies (BEST), 2023)
Puidoux Woodgasifier, Puidoux, Switzerland (stared in 2018)	Updraft gasification	Wood chips (N/A)	Power 0.89 MWel, Heat 4.5 MWth used for district heating	TRL 9 Commercial	(Bioenergy and Sustainable Technologies (BEST), 2023)
Kombi Power System Charmey, Val-de-Charmey, Switzerland (stared in 2020)	ReGaWatt updraft gasification	Wood chips (N/A)	Power 0.77 MWel and 0.12 MWel, Heat 4.5 MWth used for district heating	TRL 9 Commercial	(Bioenergy and Sustainable Technologies (BEST), 2023)
Skive CHP plant, Denmark, (stared in 2008)	Bubbling fluidized bed gasification	Wood pellets (28 MWth)	Power 6 MWel, Heat 13 MWth	TRL 9 Commercial	(Bioenergy and Sustainable Technologies (BEST), 2023)
Spanner Landshut, Landkreis Landshut, Germany, (stared in 2011)	Fixed-bed process in cocurrent flow gasification	Wood chips (N/A)	Power 0.025 MWel, Heat 0.5 MWth	TRL 9 Commercial	(Bioenergy and Sustainable Technologies (BEST), 2023)
Mont-Godinne Hospital (Xylowatt), Mont-Godinne, Belgium, (stared in 2018)	NOTAR® medium scale downdraft gasification	Clean wood chips (class A) (690 kg/h), recycled wood (731 kg/h)	CHPC (heat, power, cold), Power 0.75 MWel, Heat 1.2 MWth , Other 0.4 MWth	TRL 9 Commercial	(Bioenergy and Sustainable Technologies (BEST), 2023)
CHP Stadtwerke Rosenheim, Germany, (stared in 2015)	Fluidized bed reactor, combination of concurrent and eddy flow gasification	Wood chips (42 t/h)	Power 0.05 MWel , Heat 0.095 MWt	TRL 9 Commercial	(Bioenergy and Sustainable Technologies (BEST), 2023)

Steiner A. & Cie AG, Ettiswill, Switzerland, (stared in 2013)	Downdraft Spanner gasification	Wood chips (N/A)	Power 0.045 MWel, Heat 0.105 MWth	TRL 9 Commercial	(Bioenergy and Sustainable Technologies (BEST), 2023)
Stirling DK Carlow, Ireland, (stared in 2011)	Updraft gasification	Wood chips (N/A)	Power 0.035 MWel	TRL 9 Commercial	(Bioenergy and Sustainable Technologies (BEST), 2023)
CraftWerk Schwaz, SynCraft, Austria, (started in 2017)	Staged floating-fixed-bed gasification	Wood chips (1.3 MWth)	Power 0.4 MWel, Heat 0.615 MWth	TRL 9 Commercial	(Bioenergy and Sustainable Technologies (BEST), 2023)
CraftWerk Hatlerdorf, SynCraft, Dornbirn, Austria, (started in 2014)	SYNCRAFT®Werk Staged floating fixed-bed gasification	Wood chips (0.65 MWth)	Power 0.25 MWel, Heat 0.35 MWth	TRL 9 Commercial	(Bioenergy and Sustainable Technologies (BEST), 2023)
CraftWerk Innsbruck, SynCraft, Austria, (started in 2016)	Staged floating fixed-bed gasification	Wood chips (0.892 MWth)	Power 0.261 MWel, Heat 0.35 MWth	TRL 9 Commercial	(Bioenergy and Sustainable Technologies (BEST), 2023)
CraftWerk Vierschach, SynCraft, Austria, (started in 2014)	Staged floating fixed-bed gasification	Wood chips (0.95 MWth)	Power 0.3 MWel, Heat 0.4 MWth	TRL 9 Commercial	(Bioenergy and Sustainable Technologies (BEST), 2023)
Wegscheid Aschaffenburg, Landkreis Aschaffenburg, Germany, (started in 2011)	Fixed-bed process in cocurrent flow gasification	Wood pellets, wood chips (N/A)	Power 0.12 MWel, Heat 0.23 MWt	TRL 9 Commercial	(Bioenergy and Sustainable Technologies (BEST), 2023)
Wegscheid Bamberg, Germany, (started in 2011)	Fixed-bed process in cocurrent flow gasification	Wood pellets, wood chips (N/A)	Power 0.12 MWel, Heat 0.23 MWt	TRL 9 Commercial	(Bioenergy and Sustainable Technologies (BEST), 2023)

Wegscheid Bayreuth, Germany,	Fixed-bed process in cocurrent flow gasification	Wood pellets, wood chips (N/A)	Power 0.125 MWel Heat (N/A)	TRL 9 Commercial	(Bioenergy and Sustainable Technologies (BEST), 2023)
Wegscheid Passau, Landkreis Passau, Germany, (started in 2009)	Fixed-bed process in cocurrent flow gasification	Wood pellets, wood chips (N/A)	Power 0.12 MWel , Heat 0.23 MWt	TRL 9 Commercial	(Bioenergy and Sustainable Technologies (BEST), 2023)
WUN Bioenergy, Schönbrunn, Germany, (started in 2012)	Fixed-bed process in cocurrent flow gasification	Wood pellets, wood chips (N/A)	Power 0.36 MWel, Heat 0.54 MWth	TRL 9 Commercial	(Bioenergy and Sustainable Technologies (BEST), 2023)
Dall Energy CHP plant in Sindal, Denmark (stared in 2018)	Staged updraft gasification	Forestry by-products, wood processing industry by-products, garden & park waste (20-60% moisture content) (15,000 t/y)	Power 0.8 MWel, Heat 0.395 MWt	TRL 8 First-of-a-kind commercial	(Bioenergy and Sustainable Technologies (BEST), 2023)
Levenseat EfW, Edinburgh, United Kingdom, (started in 2020)	Outotec fluidized bed advanced staged gasification	Commercial and Industrial waste (215,000 t/y)	Power 12.5 MWel, Heat (N/A)	TRL 8 First-of-a-kind commercial	(Bioenergy and Sustainable Technologies (BEST), 2023)
Energy Works Hull, United Kingdom, (started in 2021)	Outotec fluidized bed advanced staged gasification	Commercial and Industrial waste (240,000 t/y)	Power 24 MWel, Heat 10 MWth	TRL 8 First-of-a-kind commercial	(Bioenergy and Sustainable Technologies (BEST), 2023)
ZAB Balingen Kopf Balingen Gasification-CHP Plant, Germany (started in 2011)	Fluidized bed	Sewage sludge (2300 t/y)	Power 80 kW, Heat 250 kW	TRL 8 First-of-a-kind commercial	(Bacovsky D. et al., 2017)

Swindon Advanced Bio-fuels Plant, United Kingdom	Oxy-steam fluidized bed gasifier	Refuse derived fuel and waste wood (8,000 t/y)	SNG 1,500 t/y, Hydrogen 500 t/y	TRL 8 First-of-a-kind commercial	(Bioenergy and Sustainable Technologies (BEST), 2024)
Sustainable Energy Centre KEW Technology Ltd., Wednesbury, United Kingdom, (stared in 2021)	Fluidized bed gasification (KEW's ACT process)	Organic residues and waste streams (14,000 t/y)	Diesel-type hydrocarbons (N/A) power 1.8 MW	TRL 8 First-of-a-kind commercial	(Bioenergy and Sustainable Technologies (BEST), 2024, KEW Technology, 2023)
Wegscheid Bayreuth, Germany,	Fixed-bed process in co-current flow gasification	Wood pellets, wood chips (N/A)	Power 0.125 MWel , Heat 0.23 MWt	TRL 6-7 Demonstration	(Bioenergy and Sustainable Technologies (BEST), 2023)
VIPP Demonstration, Hortlax, Sweden (stared in 2012)	VIPP-VORTEX gasification	Biomass pellets (N/A)	Power 1.2 MWel, Heat 2.2 MWth	TRL 6-7 Demonstration	(Bioenergy and Sustainable Technologies (BEST), 2023, Brandin et al., 2011)
Ecoloop GmbH, Lauingen, Germany	Fixed Bed/Counterflow Power	Wood chips (28 kg/h) EPS (expanded polystyrene) (11.4 kg/h)	Power 0.068 MWel, Heat 0.123 MWth	TRL 6-7 Demonstration	(Bioenergy and Sustainable Technologies (BEST), 2023)
Waste2Value BEST - Bioenergy and Sustainable Technologies GmbH, Wien-Simmering, Austria	Fluidized bed conversion technology with FT-synthesis	Biogenic residues and waste (1 MW)	FT liquids 44 t/y clean syngas	TRL 6-7 Demonstration	(Bioenergy and Sustainable Technologies (BEST), 2023)

(stared in 2022)					
BIOLIQ-Karlsruhe Institute of Technology (KIT), Germany (started 2010)	Double staged gasification (fast pyrolysis, high-pressure 40-60 bar entrained flow gasification)	Lignocellulosic biomass, ash rich biomass (wheat straw) (500 kg/h)	Bioliquid (DME) 2100 l	TRL 6-7 Deployment	(ETIP Bioenergy Working Group 2 – Conversion Processes and ETIP-B-SABS2 project team, 2020a) (Dahmen and Sauer, 2021)
BIOLIQ-Karlsruhe Institute of Technology (KIT), Germany (started 2014)	5 MW high pressure entrained flow gasification 40-80 bar	Lignocellulosic biomass, ash rich biomass (straw) (1 t/h)	Bioliquid (DME) 608t/y gasoline-type fuels 360 t/y	TRL 6-7 Deployment	(Bioenergy and Sustainable Technologies (BEST), 2024)
Syngas Platform Vienna, Austria (stated in 2022)	Advanced dual fluidized bed steam gasification	Wood chips, biogenic wastes, plastic wastes, sewage sludge, agricultural residues	1 MW fuel input Output: synthetic fuels such as FT diesel, sustainable aviation fuel (SAF), methanol and gaseous energy sources such as H_2 or SNG.	TRL 5-6 First-of-a-kind Demonstration	(Hochstöger D. et al., 2023, Kuba M. et al., 2024)
BioTfueL pilot, France, (started in 2021)	Entrained flow gasification	Torrefied biomass (forest waste, straw, green waste, dedicated crops) (N/A)	FT liquids 60 t/y, sustainable aviation fuels (SAF)	TRL 6-7 Demonstration	(Bioenergy and Sustainable Technologies (BEST), 2024, Morin M.)
CraftWerk Schwaz, SynCraft, Schwaz, Austria, (started in 2009)	SYNCRAFT®Werk Alpha floating bed gasification	Wood chips (N/A)	Power 0.1 MWel, Heat 0.5 MWth	TRL 4-5 Pilot	(Bioenergy and Sustainable Technologies (BEST), 2023)
FlexiSlag Pilot Plant, Freiberg, Germany	Slagging fixed-bed gasifier, 40 bar, BGL reactor	Biomass waste (2 t/h) coal, petcoke (2 t/h)	Heat 10 MWth syngas 2,300 m3/h	TRL 4-5 Pilot	(Bioenergy and Sustainable Technologies (BEST), 2023)

MAGNUS, Uni Stuttgart, Germany	Bubbling bed reactor	Solid fuels (e.g. wood, coal) auxiliary materials (e.g. lime, sand), waste	Clean syngas 0.33 MWth	TRL 4-5 Pilot	(Bioenergy and Sustainable Technologies (BEST), 2023)
Booster, TU Munich, Germany	Entrained flow gasification	Pre-treated (torrefaction and hydrothermal carbonization) and raw biomass and organic residues (N/A)	SNG 0.15 MW	TRL 4-5 Pilot	(Bioenergy and Sustainable Technologies (BEST), 2023)
CHP Agnion Biomasse Heizkraftwerk Pfaffenhofen, Germany (started 2001)	The agnion Heatpipe-Reformer gasification	Waste wood (80 000 t/y)	Power 6,1 MWel, Heat 28 MWth	TRL 4-5 Pilot	(Bioenergy and Sustainable Technologies (BEST), 2023)
Synthesis Cutec Clausthal-Zellerfeld, Germany, (started 1990)	Circulating fluidized bed gasifier (60 – 80 kg/h)	Straw, wood, dried silage, organic residues (N/A)	FT liquids 0.02 t/y	TRL 4-5 Pilot	(Bioenergy and Sustainable Technologies (BEST), 2023, Hrbek J., 2022)
MFC within ITZ-CC Project owner RWE Power AG (started 2022)	Gasification Technology (Type N/A)	Dried sewage sludge (130 kg/h), dried lignite and sewage sludge (130 kg/h), dried lignite and sewage sludge ash (130 kg/h)	Clean syngas 700 m^3/h, Phosphorus	TRL 4-5 Pilot	(Hrbek J., 2021)
ECN MILENA Gasifier, Nederland	Indirect gasification (MILENA-technology)	Wood, waste (N/A)	Clean syngas 200 m^3/h	TRL 4-5 Pilot	(Bacovsky D. et al., 2017)

Viking Gasifier, DTU, Denmark, 2002	Two Stage Gasifier (moving bed pyrolysis and downdraft fixed	Wood chips (N/A)	Power 200kWe, Heat 600 kWth	TRL 4-5 Pilot	(ETIP Bioenergy Working Group 2 – Conversion Processes and ETIP-B-SABS2 project team, 2020a) (Bentzen J. D. et al., 2004)
Ecoplanta Gaya, Lyon, France	methanization, pyro-gasification or even hydro-gasification	Forest residues, agricultural residues (N/A)	SNG 0.1 t/y	TRL 4-5 Pilot	(Bioenergy and Sustainable Technologies (BEST), 2024)
TRIJEN, TUBITAK, Turkey, 2013	Circulating fluidized bed gasifier and pressurized fluidized bed gasifier	Combination of hazelnut shell, olive cake, wood chip and lignite blends (0.2 t/h)	FT liquids 250 t/y	TRL 4-5 Pilot	(Bioenergy and Sustainable Technologies (BEST), 2024)
Technische Universtitat Darmstadt, Germany, 2010	Two circulating fluidized bed reactors (CFB 400 and CFB 600)	Lignocellulosic biomass (N/A)	FT liquids 1 MWth	TRL 4-5 Pilot	(Bioenergy and Sustainable Technologies (BEST), 2024, TU Darmstadt, 2021)
TU Wien advanced DFB steam gasification plant	Advanced dual fluidized bed steam gasification	Wood chips, biogenic wastes, plastic wastes (N/A)	100 kW fuel input Output SNG, H_2	TRL 4 Pilot	(Schmid et al., 2021, Benedikt F. et al., 2022)

2.5. Torrefaction

Sustainable development and economic expansion depend heavily on energy derived from fossil fuels. Due to population growth and industrialization, there is a significant increase in the energy demand globally, which results in the unregulated consumption of energy resources. By 2040, it is predicted that rising economic and population development will result in a about 37% rise in the world's energy consumption (Gajera et al., 2022).

As the electrical sector continues to grow quickly, interest in CO_2 emissions has started to grow. Roughly half of all CO_2 emissions come from the production of energy (Yang et al., 2024). The most significant greenhouse gas and component of the atmosphere is CO_2. The atmospheric concentration of carbon dioxide gas was approximately 315 parts per million in 1958, rising to 350 parts per million in 1986, and surpassing 400 parts per million in 2013. In 2040, carbon dioxide emissions are predicted to rise by over 40% when compared to 2010 levels. According to Zhang and Wang (2024), the combustion of fossil fuels including coal, oil, and natural gas produces roughly 44% of the world's carbon dioxide emissions today. It is obvious that alternative fuels must be found to replace conventional fossil fuels due to the rise in carbon dioxide levels and the decline in fossil fuel supplies.

Natural energy reserves are under strain from global industrialization, which is consuming enormous amounts of energy and depleting them at an alarming rate. Authorities and scientists are now looking for "clean" and renewable alternative sources as a result of this predicament. Renewable energy sources account for about 19% of the world's energy consumption; biomass accounts for 9% of this total, with modern renewable energy sources including wind, bio-fuel, geothermal, solar, etc., making up the remaining 10% (Mehmood et al., 2017). After coal, oil, and natural gas, biomass is currently the fourth-largest primary energy source. Bioenergy is a means of manufacturing bio-fuels that can be utilized in the transportation industry in addition to being used to generate heat and power, unlike solar and wind energy, which are exclusively used to generate electricity. Biomass is created when carbon dioxide and water are converted through photosynthesis to biomass. Photosynthesis is a worldwide process that produces bio-fuels from the standpoint of energy storage (Chen et al., 2021).

Heat conversion technologies for biomass have advanced quickly in recent years due to the fact that biomass is a renewable and carbon-neutral energy source (Yang et al., 2024). Biomass comes in a variety of forms, such as waste residues, animal dung, municipal wastes, organic sewage, and wastes from forestry and agriculture (Hu and Gholizadeh, 2019). Several processes, including gasification, pyrolysis, anaerobic digestion, fermentation, and transesterification, can transform biomass into gaseous or liquid fuels. It can also be burned directly to produce heat and electricity when used as solid fuel. Nonetheless, biomass is typified by a high moisture content, a low calorific value, a hygroscopic structure, and a big volume or low bulk density. These characteristics result in a low conversion efficiency as well as challenges with transportation, storage, grinding, and collection. For these reasons, biomass is typically utilized in power plants in combination with coal for cofiring, as opposed to being used alone (Chen et al., 2015, Sami et al., 2001).

Biomass is made easier to use in later conversion processes by pretreatments. Torrefaction and densification procedures including pelletization and briquetting are the most popular pretreatment techniques (Thengane et al., 2021). When biomass is subjected to torrefaction, a pretreatment method known as mild pyrolysis or high-temperature drying is used to increase the heating value of the biomass, remove fibrous features, and create a hydrophobic surface. Several experimental investigations have demonstrated the benefits of torrefied biomass. Furthermore, it is recognized that there is potential for using torrefied biomass in biomass applications (Park et al., 2015). The process of turning biomass or waste biomass into a carbon- and energy-rich bio-char for more effective usage in a variety of industries, particularly the energy industry, is known as torrefaction. A slow pyrolysis or mild carbonization process that enriches the heating value and energy content of biomass is known as torrefaction. Torrefaction is a pretreatment used to prepare biomass for use in advanced thermochemical processes including gasification, pyrolysis, and combustion, or for the creation of bio-char that can be used in a variety of industries. It is performed at low residence time process temperatures. The energy density of torrefied biomass is increased when it is subsequently made into pellets or briquetting.

The focus of this analysis is on the utilization of biomass potential and structure in the torrefaction process, as well as palletisation and torrefaction processes resulting from the pretreatments given to biomass. The types of torrefaction processes, the reactors used for torrefaction, the changes in the properties of the biomass produced during torrefaction (solid product, bio-char, or hydro-char) from wet and dry torrefaction, and the industries that use bio-char in conjunction with coal are the subheadings of the review.

2.5.1. General review and evaluation of Biomass types for Torrefaction Technology

A Evaluation of Waste Biomass Suitable for Torrefaction Technology

In general, biomass is defined as a biological or organic material that can be used as a renewable energy source through thermal or biochemical conversion processes. It can also refer to the entire mass of living matter within a given environmental unit or to plant material, vegetation, or agricultural waste used as an energy source (Achary et al., 2012). You may think of biomass as one of the sun's energy sources. To grow, plants take in carbon dioxide from the atmosphere, water, and nutrients from the soil. Through the process of photosynthesis, they subsequently transform these elements into hydrocarbons. Carbon is released into the atmosphere when biomass is burned for fuel since all of the carbon in it comes from carbon dioxide. As a result, biomass is referred to as a carbon-neutral fuel when burned (Saidur et al., 2011). Carbon, hydrogen, oxygen, nitrogen, and trace amounts of sulphur are typically found in biomass. Significant levels of inorganic matter can also be found in some forms of biomass, and depending on the kind of biomass, the quantity of ash from these inorganic materials can range from 1% in softwoods to 15% in herbaceous biomass and agricultural leftovers. Wood waste, sugar cane pulp, woody and herbaceous species, agricultural and industrial wastes, solid municipal waste, wastepaper, sawdust, biosolids, grass, food processing waste, animal waste, aquatic plants, and algae are just a few examples of the diverse natural and derived materials that can be used as biomass sources (Yaman, 2004). Table 19 lists the different forms of biomass and their corresponding sources. According to Nhuchhen et al. (2014), these sources include the forestry and agricultural sectors, main biomass sources, industrial and other wastes, and secondary sources.

Table 19. General classification of biomass resources (Nhucchen vd., 2014).

Supply sector	Type	Examples
Forestry	Dedicated forestry	Short rotation plantations (Willow, poplar, and eucalyptus)
	Forestry by products	Wood blocks and wood chips from thinning
Agriculture	Dry lingo-cellulosic energy crops	Herbaceous crops (Miscanthus, reed canary grass and giant reed)
	Oil, sugar and starch energy crops	Oil seeds for methylesters (Rape seed and sunflowers)
		Sugar crops for ethanol (Sugarcane and sweet sorghum)
		Starch crops for ethanol (Maize and wheat)
	Agriculture residues	Straw. prunings from vineyards and fruit trees
	Livestock	Wet and dry manure
Industry	Industrial residues	Industrial waste wood, sawdust from sawmills
		Fibrous vegetable waste from paper industries
Waste	Dry lingo-cellulosic	Residues from parks and gardens (prunings and grasses)
	Contaminated waste	Demolition wood
		Organic fraction of municipal solid waste
		Biodegradable landfill waste, landfill gas
		Sewadge sludge

Studies on the torrefaction of biomass are known to employ lignocellulosic materials, energy crops, agricultural residues, and forestry wastes. Algal biomass, such as micro- and macroalgae, and non-agricultural biomass have also been employed recently to stop the imbalance of food supplies and forest vegetation. Within the context of waste-to-fuel technology, wastes such as food waste, industrial wastes, and sewage sludge from municipal and industrial wastewater have also been studied as potential raw materials for torrefaction (Chen et al., 2021). Research has been conducted on the torrefaction of municipal solid waste (MSW) to find a solution for fossil fuel reserves and to lessen the pollution that these wastes cause to human health and the land due to the daily increase in population (Abdulyekeen et al., 2021).

Composition of lignocellulosic biomass

Both lignocellulosic and non-lignocellulosic components can make up biomass. The non-starch and fibrous portion of plants is called the lignocellulosic component, and it is mostly made up of cellulose, hemicellulose, and lignin. The non-lignocellulosic portion is made up of organic material that isn't cellulosic and is primarily utilized for food. The non-lignocellulosic component of any crop is its sugar, starch, protein, and oil content. Lignocellulosic biomass is comprised of various extractives, cellulose, hemicellulose, and lignin. Nevertheless, Nhuchhen et al. (2014) found that the biomass derived from animal waste is quite low in all three polymers.

The most common type of biomass that is not edible is called lignocellulosic biomass, and it primarily consists of agriculture and forestry wastes like rice straw and wood chips. Hardwood and softwood are the two kinds of woody biomass. Hardwood, including willow, poplar, and oak, grows more slowly than softwood, which includes fir, pine, cedar, and spruce. Hardwood has a more complex cell structure than softwood, with huge water-conducting holes or capillaries encircled by narrow fibrous cells. An annual grass lignocellulose is found in agricultural wastes including rice and wheat straw, corn stalks, and sugar cane bagasse. Miscanthus and switchgrass, two perennial bioenergy grasses, are significant sources of grass lignocelluloses. As seen in Figures 31 and 32, lignocellulosic biomass is mostly composed of cellulose, hemicellulose, and lignin, with trace amounts of extractives and ash. Depending on the type of biomass, the percentages of cellulose, hemicellulose, and lignin can range from 40–60%, 15–30%, and 10–25%, respectively (Wang et al., 2017).

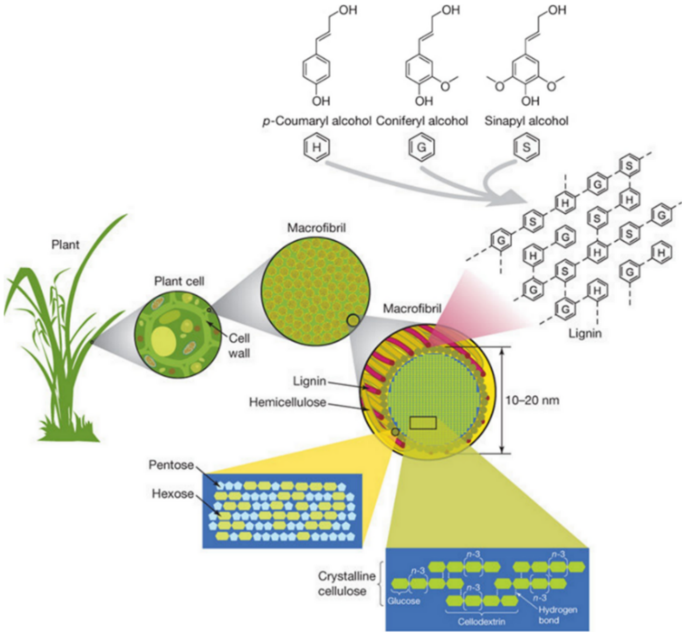


Figure 31. Structure of biomass (Amenaghawon vd., 2021).

Cellulose

The most prevalent organic polysaccharide on Earth, cellulose is a linear macromolecular polysaccharide made up of a lengthy chain of glucose units joined by β-1,4-glycosidic linkages. Cellulose concentration in woody biomass is approximately 45%, although it can reach 80–95% in cotton, flax, and chemical pulp. Cellulose is typically represented by the chemical formula $(C_6 H_{10} O_5)_n$, where n is the degree of polymerization (DP). For hardwood fibre, the average DP is at least 10,000–15,000, and it's likely more. The weak glycosidic connections that hold the glucose units in cellulose together tend to dissolve in acidic or hot environments. Three hydrogen bonds total—two intramolecular and one intermolecular—are present in each glucosyl unit of crude fibre. A large amount of cellulose packs into crystalline fibrils. The stability of cellulose fibrils is mostly attributed to van der Waals forces, which are thought to be the primary mechanism of interaction between the sheets. There are crystalline and amorphous regions in the cellulose ultrastructure, which are distinguished by the way the chain molecules are arranged. In the crystalline region of cellulose, the molecular organization is uniform and orderly; in the amorphous region, it is loose and disorderly. But there's no clear-cut difference between the two areas. Because of the packed cellulose structure, the crystalline area of cellulose has greater heat stability than the amorphous region. Furthermore, lignocellulosic fibre's thermal stability can be increased by intramolecular hydrogen bonding, which can stabilize cellulose molecules and prevent thermal expansion along the chains (Wang et al., 2017). The first phase of cellulose's breakdown is attributed to the creation of "active cellulose" via the depolymerization process, which typically occurs between 260 and 400 °C (Chen et al., 2021).

Hemicellulose

Hemicellulose, in contrast to cellulose, has an amorphous, branching structure and is composed of short-chain heteropolysaccharides. Even though the polysaccharide chain's structure resembles that of cellulose, hemicellulose only has an average degree of polymerization of 200. Hexoses (glucose, mannose, and galactose) and pentoses (xylose and arabinose), along with a few additional low-content saccharides (rhamnose and fructose), are the primary monosaccharide units that make up hemicellulose. Moreover, the hemicellulose structure contains acetyl groups and a few uronic acids (4-O-methyl-d-glucuronic acid, d-glucuronic acid, and d-galacturonic acid). The types of polysaccharides and the amount of hemicellulose are mostly determined by the sources of biomass. According to Wang et al. (2017), the hemicellulose content of hardwood, softwood, and herbaceous plants is 10-15%, 18-23%, and 20-25%, respectively. Hemicelluloses decompose at a temperature between 220 and 315 degrees Celsius (Chen et al., 2021).

Lignin

In contrast to cellulose and hemicellulose's carbohydrate structures, lignin's aromatic matrix gives its cell walls strength and stiffness. The amount of lignin varies depending on the kind of biomass and even on how a plant is shaped. For instance, the lignin contents of grass, hardwood, and softwood are, respectively, 10-15%, 20-25%, and 25-35%. Coniferyl (3-methoxy 4-hydroxycinnamyl), sinapyl (3,5-dimethoxy 4-hydroxycinnamyl), and p-coumaryl (4-hydroxycinnamyl) alcohols are the three basic units that make up lignin, an amorphous three-dimensional polymer. These are also known as syringyl (S), guaiacyl (G), and p-hydroxyphenyl (H) units. The number of methoxyl groups joined to an aromatic ring is the primary distinction between the three fundamental units. Methoxyl groups are absent from the H, G, and S units, present in one, two, and three of them, respectively. The common aromatic unit in lignin is referred to as a phenylpropane unit as these fundamental units consist of a phenyl group and a propyl side chain. The biomass species has a significant influence on the H/G/S unit ratio in lignin. A large percentage of guaiacyl units are found in softwood lignin, a combination of guaiacyl and syringyl units are found in hardwood lignin, and a mixture of all three units is found in grass lignin. Lignin is categorized as type-G (softwood lignin), type-GS (hardwood lignin), and type-HGS (grass lignin) based on the quantity of the three basic units. These units combine to form the lignin matrix through a variety of bonding interactions, and the addition of various functional groups to the propyl side chain results in incredibly complicated lignin structures (Wang et al., 2017). Throughout a broad temperature range of 100 °C to 900 °C, lignin exhibits thermal stability. As a result, lignin is not as changed throughout the torrefaction process, and the biomass produces a more solid product with a higher lignin concentration (Nhuchhen et al., 2014).

Extractives and inorganic minerals

Small quantities of extractives are also present in biomass, along with cellulose, hemicellulose, and lignin. These are not structural elements; they don't make up cell layers or walls. Biomass can be treated with either polar (water, methylene chloride, and alcohol) or non-polar (hexane, and toluene) solvents produce extractives.

The principal extractives found in lignocellulosic biomass are pigments, sugars, starches, tannins, oils, waxes, and resins. Very trace levels of inorganic minerals, primarily potassium, calcium, sodium, magnesium, silicon, phosphorus, sulphur, chlorine, etc., are also present in biomass. Traces of additional heavy metals, such as aluminium, titanium, vanadium, manganese, iron, cobalt, nickel, copper, zinc, and molybdenum, may also be present in biomass. varying biomasses have varying distribution and content of these minerals (Wang et al., 2017).

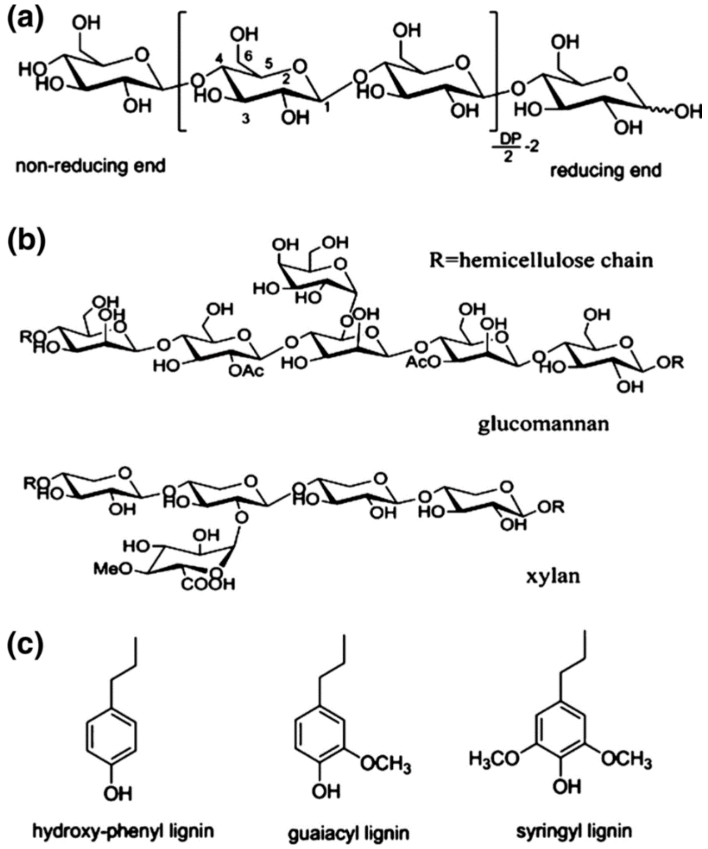


Figure 32. Structural units of cellulose (a), hemicellulose (b) and lignin (c) (Amenaghawon et al., 2021).

Pretreatments Applied to Biomass

Biomass can be treated in a variety of ways to regulate its chemical and physical properties. According to Chen et al. (2021), the basic pretreatments for raw materials are as follows: drying, grinding, pelletizing, impregnation with alkali and alkaline earth metals (AAEMs), treatment with ionic solutions and bio-solutions, leaching, or water washing (or demineralization).

To obtain dry-based samples, the samples are typically dried by placing them in an oven set between 50 and 105°C for eight to twenty-four hours. The step that uses the most energy is thought to be drying. The volatile materials created by torrefaction, or torgas, can be partially burned to provide heat for the torrefaction processes and pre-drying of biomass, preventing the need for excessive energy input during the drying process. Additionally, biomass can be heated directly or indirectly using flue gas (Chen et al., 2021).

To achieve the appropriate particle sizes, the dry samples are first ground in a mill or shredder and then sieved. Typically, a two-stage grinding procedure is used to reduce the size of biomass that is woody and herbaceous. To improve the material's flow in the conveyors, the shredder first smashes the wood chips or herbaceous biomass bundles into larger pieces. To prepare the biomass for biochemical and thermochemical conversion activities, it is processed smaller in size in the second stage of the grinding process (Safar et al., 2024). According to certain research, smaller particles have superior rates of convective and conductive heat transmission through the reactor wall, making them more susceptible to thermal deterioration. Large biomasses will hinder volatile diffusion during roasting, which will lead to uneven characteristics in the final products (Chen et al., 2021). The torrefaction process of biomass is impacted by the size of its particles. Nevertheless, residence time and temperature have a more significant impact on the torrefaction process than other factors (Safar et al., 2024).

The process of palletisation is defined as drying, shaping, and compressing biomass under high pressure to create cylindrical shapes. In addition to producing a consistent and steady fuel, palletisation also stops dust from forming. Increased volumetric energy density, easier storage and movement, lower moisture content, and lower transportation costs are the objectives of densification. The biomass particles' bulk density can be raised from 40–200 kg/m^3 to 600–1200 kg/m^3 by the densification process. Wood pellets typically have a bulk density of 500–650 kg/m^3 and a moisture content of 7–10% (Uslu et al., 2005). The energy density of raw biomass is increased by densification techniques like pelletizing or briquetting, but it's crucial to determine if it makes more sense to follow densification with torrefaction or the other way around. In these two scenarios, the energy needed will differ (Thengan et al., 2022). Figure 33 is a summary of the flow chart for the pelletizing process.

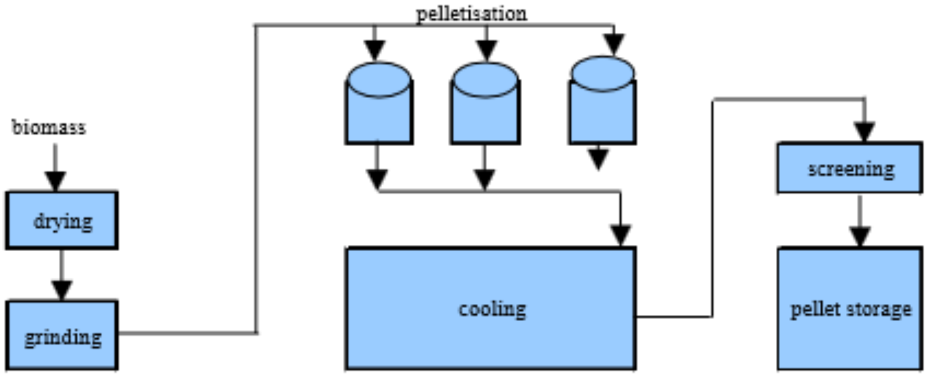


Figure 33. Pellet production stages (Uslu et al., 2005).

Doping or impregnation techniques are used to assess the impact of biomass on thermal degradation prior to the process because it is known that alkaline earth metals, such as K, Na, Ca, and Mn, have catalytic effects on thermal degradation. Certain alkali metals have been shown to lower the temperatures at which hemicellulose and cellulose decompose. Nevertheless, after combustion, the residual alkali metals (K and Na) in torrefied products interact with silica, sulphur, or chlorine and result in slagging and equipment fouling (Chen et al., 2021). Demineralization, as defined by Safar et al. (2024), is the process of removing metals from biomass by washing it with water and organic solutions prior to torrefaction.

It has been shown that many solvent types, including ionic liquids and mineral acids, can break the hydrogen bonds separating distinct polysaccharide strands. Exposure to solvents reduces the stiffness of the material and increases its sensitivity to the hydrolysis of the carbohydrate portion. It is well known that doping cellulose with mineral acids like H_2SO_4, HCl, and HNO_3 will greatly accelerate cellulose breakdown and reduce the temperature at which it must decompose. However, most acids are volatile and corrosive, which means that they release harmful fumes. They are therefore not recommended for high-temperature biomass torrefaction. Ionic liquids (ILs) have very low vapour pressures, moderate flammability, and great thermal stability at room temperature, in contrast to mineral acids. According to Sarvaramini et al. (2013), ILs are also effective heat transfer media, which may be a desirable attribute to improve heat transmission surrounding solid biomass. Depending on the anion and cation selection, the properties of ionic liquids can be adjusted. Since they often have extremely low vapour pressures, they qualify as green solvents. Their characteristics, which are essential for the breakdown of wood, include viscosity, melting point, dipolarity, and hydrogen bond basicity. Additionally, ionic liquids' corrosivity and toxicity must be taken into account when thinking about their potential uses in industrial settings (Mäki-Arvela et al., 2010).

Large-scale raw biomass exploitation is challenging due to a few of its intrinsic issues, which include low bulk density, high moisture content, hydrophilic structure, and low heating value (LHV) when compared to fossil fuel sources. These restrictions have a significant impact on the final logistics and energy efficiency. Very large volumes of biomass are needed since they have a lower energy density than fossil fuels. This makes it difficult to store, transport, and process feed in cogeneration, thermochemical, and biochemical conversion plants.

One of the main issues is the high moisture content in raw biomass, which raises production costs and decreases process efficiency. Biomass with a high moisture content naturally decomposes, causing quality loss and storage problems such as off-gas emissions. The uncertainty it creates in the physical, chemical, and microbiological characteristics of biomass is another effect of excessive moisture content. Another issue is irregular biomass forms, which are particularly problematic when fed into a system for gasification or co-combustion. Furthermore, biomass is less suited for thermochemical conversion processes since it contains more oxygen than carbon and hydrogen. These characteristics combined render raw biomass unsuitable for use in energy applications. Biomass must be pre-processed to get beyond these obstacles and qualify the material for energy use. Grinding is a popular pre-processing method that aids in achieving uniform particle size. Unfortunately, many grinders' performance is limited by the moisture level of biomass. Furthermore, if lower particle sizes are required, grinding can be very expensive and occasionally impractical for biomass with a high moisture content. A high moisture level can also lead to irregularly sized particles, particularly those smaller than 2 mm, which can cause an uneven reaction and lower conversion efficiency and cost. Furthermore, when employed in thermochemical processes like gasification, raw biomass has low LHVs and irregular particle size distribution because of its high moisture content, which makes it thermally unstable. This may result in inconsistent output and the buildup of condensable tars, which may cause problems like obstructions in gas lines. Pretreating biomass before applying it for final use is a feasible approach. Pretreatment helps modify the biomass's chemical makeup and physical characteristics, improving its suitability for conversion (Shankar Tumuluru et al., 2011).

2.5.2. Review of Torrefaction Technology

Raw biomass can be upgraded via torrefaction to produce a single class of solid bio-fuel. The temperature, operating pressure, reaction duration, and torrefaction medium all affect the chemical makeup of the solid product that is generated. There are three main categories for torrefaction processes: wet, dry, and ionic-liquid assisted. Furthermore, wet torrefaction is further defined as torrefaction in liquid and vapour phases, whilst dry torrefaction is subclassified as torrefaction in oxidizing and non-oxidizing settings. Compared to ionic-liquid assisted torrefaction, wet and dry torrefaction are more widely employed and have a wider range of applications. The right torrefaction technique can be chosen by considering factors including the kind and composition of the biomass, the intended use of the bio-fuel, and the quantity of biomass to be fed over time. Both wet and dry torrefaction can be used to process biomass, both lignocellulosic and non-lignocellulosic (Olugbade and Ojo, 2020;Gizaw et al., 2024).

A Dry torrefaction

The most widely utilized thermochemical conversion method for producing solid bio-fuels with reduced moisture content for use in the generation of energy and heat is the dry torrefaction of biomass. It can be referred to as a thermal pretreatment process that is used on raw biomass to transform it into a compact, homogenous solid biomass product with a higher heating value and enhanced energy density in a temperature range of roughly 200–300 °C in an oxygen-poor atmosphere. However, certain unfavourable outcomes of dry torrefaction include slag and fouling, corrosion, and an excessive amount of ash (Olugbade and Ojo, 2020; Gizaw et al., 2024).

Due to its low operating temperature, dry torrefaction—also known as mild pyrolysis—means that thermal deterioration takes place at a low temperature and under inert conditions. When air or oxygen is utilized as the carrier gas, dry torrefaction can also be performed in an oxidative environment (Piersa et al., 2022).

Thermal conversion of dry torrefaction can lead to improvements in dimensional stability, fungal resistance, hydrophobicity, durability, and absorption. Both wet and dry torrefaction can result in the production of mixed-value and higher energy content torrefaction solids. Nonetheless, there are some significant differences between the two biomass torrefaction processes. Compared to biomass products that undergo wet torrefaction, those that undergo dry torrefaction have a higher concentration of alkali metals. Furthermore, moist torrefaction products have a higher heating value (HHV) than dry torrefaction products. Because more dissolved organic matter is eliminated during wet torrefaction than during dry torrefaction, it is thermochemically more efficient and has a larger carbon content (Khempila et al., 2022).

While wet torrefaction is frequently used for biomass with high moisture content, such as animal dung, slugs, and municipal garbage, dry torrefaction is better suited for biomass residues with lower moisture concentrations. This is due to the fact that primary processes in dry torrefaction don't occur until the biomass has mostly lost its moisture. On the other hand, pre-drying is not necessary for wet torrefaction when samples with high moisture content are heated in water in a pressure chamber (Olugbade and Ojo, 2020). The O and C ratio gradually drops when the torrefaction temperature rises because it lowers the solid product's oxygen content (Liu et al., 2021). It is common for both torrefaction mechanisms to experience this state. However, compared to the dry torrefaction process, the wet torrefaction process loses more valuable components. The dry torrefaction process yields a lower mixed value product with a lower amount of inorganic components than the wet torrefaction method. Wet torrefaction is characterized by the dissolution of both inorganic and organic components in water under pressure, which is explained by the reduction of salt and mineral concentration in biomass. The distinction between wet and dry torrefaction is displayed in Table 20 (Gizaw et al., 2024).

Table 20. Main differences and general characteristics of dry and wet drying (Piersa et al., 2022; Gizaw et al., 2024).

Stage of process	General Properties	Dry torrefaction	Wet torrefaction
Process	Temperature	200–300 ∘C	180–265 ∘C
	Residence time	<1h	5 min to several h
	Pressure	Air	1-250 MPa
	Atmosphere	İnert	İnert
	Liquid medium	None	Water/steam
	Pre-drying	Yes	No
	Post-drying	No	Yes
	Toxic	Minimal	Non-toxic
Product	Product	Gas, tar, solid	Solid, gas, liquid
	Main product	Bio-char	Hydrochar
	Ash content	Higher	Lower
	Carbon content	Lower	Higher
	Moisture content	Lower	Higher
	Energy density	Lower	Higher
	Heating value	Lower	Higher
	Bulk density	Low	Low
	Hydrophobicity	Lower	Higher
	Grindability	Lower	Higher
	Combustion activity	More active	Less active
	Devolatilization activity	Less active	More active

Storage at open atmosphere	Possible	Possible
Purity of the product	Medium	High
Applications	Fuel and char	Fuel and char

B Oxidative torrefaction

It is also possible to perform the torrefaction process in oxidative settings, such as liquid or gas phase media. According to Olugabade and Ojo (2020), oxidative torrefaction is a complicated process that combines oxidation, carbonization, and evaporation. Oxidation and torrefaction happen simultaneously and are unrelated to one another. Because of the oxygen present and the exothermic reactions that take place during thermal decomposition, oxidative torrefaction responds more quickly than conventional torrefaction. Operating expenses can be decreased by using air or flue gas in the biomass torrefaction process, as nitrogen removal from the air is not required. The fuel properties of nitrogen-treated biomass are comparable to those of biomass torrefaction with a carrier gas that has low oxygen concentrations (<6 vol%). Nevertheless, compared to traditional torrefaction, oxidative torrefaction is less efficient. Research indicates that when torrefied at elevated process temperatures, like 300 °C, the solid bio-fuel's higher heating value (HHV) diminishes as the oxygen content rises (Piersa et al., 2022).

It is vital to consider the biomass's characteristics, such as moisture uptake and Meyer hardness when contrasting the typical torrefaction in an O_2-free environment with the oxidative torrefaction of biomass in a specific amount of O_2. The right torrefaction and densification conditions must be determined to produce durable and high-quality pellets from torrefied biomass. Furthermore, oxidative torrefaction in the presence of flue gas oxygen can raise particle density in comparison to biomass torrefaction in an inert environment. It indicates that biomass has a higher rate of mild hydrocarbon oxidation. This indicates that oxygen content has a significant role in the oxidative torrefaction of biomass. The key binder component lignin is removed oxidatively from biomass, which results in a modest drop in Meyer hardness as the oxygen content of the carrier gas for torrefaction increases. Increased surface area or pore volume, as well as a larger hydroxyl group content in particles torrefied under oxidative conditions, can also result in a decrease in hydrophobicity (Olugbade & Ojo, 2020).

C Wet Torrefaction

Another common thermal treatment technique for enhancing the characteristics and quality of biomass is wet (liquid and vapour) torrefaction. Wet torrefaction is less common than dry torrefaction, yet its significance and usefulness have long been recognized. Three products are produced during the process of wet torrefaction, commonly referred to as hydrothermal carbonization (HTC), which is conducted in a hot hydrothermal environment at temperatures between 180 and 260 °C and pressures of up to 5 MPa: gas, aqueous chemicals, and solid fuel. The product distribution is greatly impacted by the types of biomasses used, as well as by the process temperature and duration. Bio-char can be produced with less moisture than raw biomass during wet torrefaction because the hemicellulose in the biomass is hydrolyzed and depolymerized to produce monomers and oligomers with no impact on lignin (Piersa et al., 2022). Because the chemical processes and reaction conditions that take place during wet torrefaction differ greatly from those that occur during torrefaction and because the solid product produced by wet torrefaction is substantially different from that produced by dry torrefaction, wet torrefaction is frequently referred to as HTC. While the goal of the HTC process is hydrochar, bio-char is usually generated as a solid byproduct of the torrefaction process. Because of its superior higher heating value and reduced concentration of heavy, alkaline earth, and alkali metals, hydrochar is also frequently chosen over bio-char (Kambo and Dutta, 2015).

High moisture content biomass is more suited for wet torrefaction. Furthermore, compared to dry torrefaction, wet torrefaction is processed faster and at lower temperatures. As a result, more energy-intensive molecules are formed. Yet, wet torrefaction systems have drawbacks including excessive pressure, which drives up the cost of design (Sarvaramini et al., 2013). The wastewater produced during the process is the main drawback of wet torrefaction. There are alkaline chemicals in it, and the water's discharge pollutes the environment.

D Super-heated steam torrefaction process

This is the most recent technique pertaining to the process of torrefaction. Superheated steam is used as a pretreatment to open the fibres and improve the biomass polymer's suitability for further procedures like densification, fermentation, and hydrolysis. Superheated steam is therefore an effective and required method to enhance the recovery of sugars and other crucial biomass components. The procedure yields a solid product with better pelleting qualities, less moisture retention, and a higher heat value (HHV). The method's lack of need for carrier gas, like nitrogen or flue gas, as in dry torrefaction, is another benefit. There have only been a few studies conducted on the process of super-heated steam torrefaction thus far (Piersa et al., 2022).

E Ionic-liquid-assisted torrefaction

An alternative to conventional wet and dry torrefaction of biomass is ionic-liquid-assisted torrefaction. The goal is to accelerate the rate at which biomass is torrefied, improving the torrefied solid's quality in the process. More research is nonetheless required on topics like energy efficiency, which is shown to be lower than with the dry torrefaction process (Olugbade and Ojo, 2020).

The lignocellulosic biomass's complex polysaccharides are efficiently broken down into tiny pieces by pretreating it with an ionic liquid prior to torrefaction, which aids in further processing. Ionic liquids, which are essentially liquid ionic salts, are known to dissolve lignocellulose biomass quickly because of their strong hydrogen bond acceptor and high polarity. They can also be employed as a pretreatment agent before torrefaction. Because of their special qualities, which include near-volatility, high thermal stability, and recyclability, ionic liquids can dissolve cellulose in typical working circumstances (Sorn et al., 2019). In order to minimize fermentation caused by microbial or enzymatic activity, ionic liquids are employed as a green solvent in the torrefaction pretreatment process. They assist lower the cellulose crystallization rate and remove some lignin and hemicellulose (Gizaw et al., 2024).

The main drawbacks of this approach, despite the advantages of using ionic-liquids as pretreatment agents to aid in the torrefaction of biomass, are the process's high cost and the extraction of lignin and hemicellulose, which complicates the drying of biomass for industrial applications (Gizaw et al., 2024).

Influence of the process parameters on the product characteristics

Composition of biomass

Biomass has a complex chemical composition consistent with a mixture of organic and inorganic compounds, while exhibiting a microporous physical structure that directly affects the kinetics and transfer of heat and mass within the particles during torrefaction processes. However, the natural components of inorganic elements (e.g. potassium, calcium, sodium, silicon, and phosphorus) in biomass can affect the reaction rate and performance of the torrefaction process. The chemical composition of biomass is an important factor in determining the quality of torrefaction biomass (Safar et al., 2024). Biomass composition primarily consists of organic matter such as cellulose, hemicellulose, lignin, and extractives, and inorganic matter in the form of ash. The nature and source of biomass determine the relative proportions of these components (Thengane et al., 2024). Biomass components respond differently to torrefaction and therefore it is possible to see different performances for different feedstocks in the same reactor under the same operating conditions. Biomass types and biomass components are explained in detail in the A section.

Moisture content of biomass

Torrefaction is a deep drying process, but depending on the torrefaction environment, the moisture concentration can be reduced to 3%. The raw material moisture percentage usually varies between 10% and 50%. Torrefaction normally results in an equilibrium moisture concentration of 3%, a mass loss of 20–30%, and a retention of 80–90% of the initial energy content in the wood. Reducing the moisture content during torrefaction has three main benefits: 1) minimizing moisture levels during conversion processes, 2) reducing transportation costs by not carrying away unwanted water, and 3) preventing moisture absorption and biomass degradation during storage and transportation (Gizaw et al., 2024).

Torrefaction temperature

Temperature is the most important factor affecting the behaviour of torrefaction biomass. Torrefaction pretreatment is divided into three basic processes, namely mild, moderate and severe, corresponding to the temperatures of 473–508 K, 508–548 K and 548–573 K, respectively. With the increase of reaction temperature, the decomposition of hemicellulose and cellulose is accelerated, while since the thermal stability of lignin is relatively strong, changes in torrefaction temperature have only mild effects on lignin destruction (Yang et al., 2024). Hemicellulose in biomass is affected by mild torrefaction, while cellulose and lignin are almost unaffected. In contrast, severe torrefaction has a severe effect on the depletion of lignocellulosic materials (Chen and Kuo, 2011). In both dry and wet torrefaction, increasing temperature results in a solid with decreased mass yield and increased energy density, as well as increased carbon content, decreased oxygen content, and decreased volatiles (Yan et al., 2009). It has also been shown that increasing torrefaction temperature leads to a decrease in solid bio-char yield and an increase in volatiles yield, including liquid and non-condensable gases (Deng et al., 2009).

Heating rate

The heating rate (°C/min) used during the torrefication process affects the secondary decomposition reactions, which in turn affects the final solid, liquid and gaseous product distribution. The main reason for the distribution of reaction products is the decrease in the number of secondary reactions when higher heating rates were used. Also suggested that the effects of heat and mass transfer between particles would decrease with increasing the heating rate (Ribeiro et al. 2018).

Torrefaction time

The torrefaction process time is another important factor in determining the process performance and the severity of torrefaction. The residence time for the torrefaction process is generally in the range of 15-120 min depending on the biomass properties (e.g., composition, moisture, density). According to literature studies, a longer residence time can increase the carbon content yield and calorific value of bio-char. However, this will reduce the hydrogen and oxygen content, mass yield, and energy yield of the torrefaction products. Compared to other carbonization processes such as combustion, gasification, and conventional pyrolysis, torrefaction exhibits a longer reaction time to maximize the formation of carbonized material (Safar et al., 2024).

The Particle Size

The amount of heat required depends on the size, shape, and biomass properties. These parameters affect the heat transfer rate from the reactor to the biomass and both convective and conductive within the biomass, respectively. A larger biomass particle will have less surface area per unit mass, which will reduce the convective heat transfer rate. Larger particle may also have uneven heat distribution within the biomass due to the anisotropic and heterogeneous properties of the biomass. In addition, larger particle may face difficulties with volatile diffusion through it due to the high mass transfer resistance. Therefore, the quality of the torrefaction process may not be the same for all particle sizes. In small particles (sizes range from 0.23 to 0.81 mm), the mass loss due to torrefaction is higher than in larger particles due to both lower resistance to diffusion of volatiles and higher heat transfer rate in small particles (Nhuchhen et al., 2014).

Torrefaction atmosphere

Torrefaction atmosphere generally includes inert torrefaction, oxidation torrefaction and flue gas torrefaction. The main purpose of the inert atmosphere is to prevent the oxidation of various components during the torrefaction process and to ensure the integrity of the combustible components in the biomass particles. Due to the high cost of separating inert gases from air, the use of oxidative torrefaction is generally more extensive. When waste heat recovery is considered, flue gas torrefaction further reduces the cost of biomass torrefaction pretreatment (Yang et al., 2024).

In the study on oxygen concentration in the oxidative environment, it was stated that oxygen concentration did not significantly affect the composition of the solid product for low temperatures, while high oxygen concentration at high temperature (280 °C) affected some of the investigated properties (Rousset et al., 2012). In general, it has been emphasized that the torrefaction process with limited oxygen in carrier gases is not only economically viable compared to using 100% inert atmospheres, but also does not show a negative impact on the overall quality of the torrefaction-densified woody biomass (Riaz et al., 2022).

If the volatile substances obtained from torrefaction can be burned in a combustion chamber, the combustion flue gases from the burner can be recycled and used for torrefaction and pre-drying, the torrefaction process can be thermally self-sustained without the need for additional thermal energy input and inert gases, leading to significant savings in both energy and inert gases, and the process becomes economically viable.

Wang et al. (2013), in the study where the oxidative torrefaction of sawdust containing 3-6% O2 as carrier gas was investigated in a TG and fluidized bed reactor, it was stated that the oxidative torrefaction process produced torrefaction sawdust and pellets with similar properties to the normally torrefaction sawdust and corresponding pellets, especially in terms of density, energy consumption for pelletization, higher heating value and energy efficiency. For the moisture absorption and hardness of torrefaction pellets, the oxidative torrefaction process showed a slightly weak but negligible performance. Therefore, it is possible to use oxygen-laden combustion flue gases as carrier gas for torrefaction of biomass (Wang et al., 2013).

In addition to the above torrefaction atmospheres, it was stated that CO2 atmosphere can also be used for biomass torrefaction and that O2 and CO2 atmospheres are more effective than inert atmospheres on fuel quality. Industrial boiler flue gas mainly contains O2 , CO2 , H2O and a small amount of other gases, and the temperature of the flue gas is about 433 K- 623 K. Therefore, the combustion flue gas appears to be suitable for biomass upgrading. Using flue gas as a carrier gas for biomass torrefaction can not only effectively remove the oxygen element, but also recover the waste heat and reduce the energy consumption for biomass upgrading. In various torrefaction atmospheres, different chemical reactions occur on the surface of biomass particles. Oxidizing atmospheres generally cause deeper decomposition degree of organic content, faster release of volatile substances. Increasing the concentration of oxidizing agents will increase the cross-linking reaction and interaction of surface oxygen-containing functional groups (carbonyl, carboxyl and acid anhydride) (Yang et al., 2022).

Torrefaction pressure

The increase in pressure generally has positive effects on the removal of volatile substances and the increase of solid yield. The increase in reaction pressure in the inert atmosphere increases the probability of intermolecular collisions to promote the condensation reaction between macromolecules, mainly promoting the secondary polymerization reaction of low-carbon volatiles such as ethylene methane. Otherwise, during anoxic torrefaction processes, the increased reaction pressure tends to strengthen the diffusion ability of oxidant molecules and increases the contact rate between oxidant molecules and biomass particles. Increasing the pressure can also promote the polymerization of carbon chains, which can lead to the transformation of small aromatic rings into large rings. In addition, increasing the torrefaction pressure can also strengthen the cross-linking reaction of –OH groups, which can lead to stronger deoxidation of biomass. Increasing the pressure can also increase the decomposition rate of light volatiles and promote the polymerization reaction of organic structures in biomass particles, increasing the carbon content in the torrefaction sample. However, with the same energy consumption, the effect of increasing the pressure on the fuel quality of biomass is less than the effect of increasing the temperature. Increasing the torrefaction pressure is more likely to promote the deoxygenation and decomposition of macromolecular compounds and the polymerization of small molecular compounds such as alkanes and olefins (Yang et al., 2022).

2.5.3. Design of Torrefaction Technology

Torrefier is broadly classified into two types based on the heat transfer mode: (i) direct heating and (ii) indirect heating. The most common reactors such as moving bed, augur, entrained bed, microwave, fluidized bed, hydrothermal and rotary drum reactors fall into one of these two categories. The movement of biomass, the working medium and the heat transfer mechanism are the most important distinguishing features of reactors. These features determine the nature of the torrefined products and the total torrefaction time. For example, the rotation speed, the length of the drum and the inclination of the drum characterize the rotary drum torrefier. The rotation speed determines the heat transfer rate while the drum length affects the residence time. Torbed (fluidized bed) reactor, where the heat carrier fluid moves at a relatively high speed, is characterized by an intense heat transfer rate. This reactor can produce torrefied biomass in a much shorter residence time (about 80 seconds) when using fine particles. The main advantages and disadvantages of the different reactor types are outlined in the following section.

Presently, the development of torrefaction technologies follows current reactor mechanisms intended for gasification, pyrolysis, or drying. These reactors have been changed since it was determined that they are appropriate for the torrefaction process. There isn't a single ideal reactor design that works with every kind of feed, therefore choosing the right reactor for the job is crucial depending on the feed type (Chen et al., 2021). The primary characteristics that set the reactors apart are the heat transfer mechanism, the reactor's architecture, and the way the biomass is fed through it. Heating the biomass to the desired temperature and continuously transporting it are the duties of a torrefaction reactor.

Most pilot and commercial plants under construction use continuous reactors because batch torrefaction reactors can only operate at a limited capacity. Differentiating between reactors that are directly heated and those that are indirectly heated is one method of classifying torrefaction reactors (Figure 34).

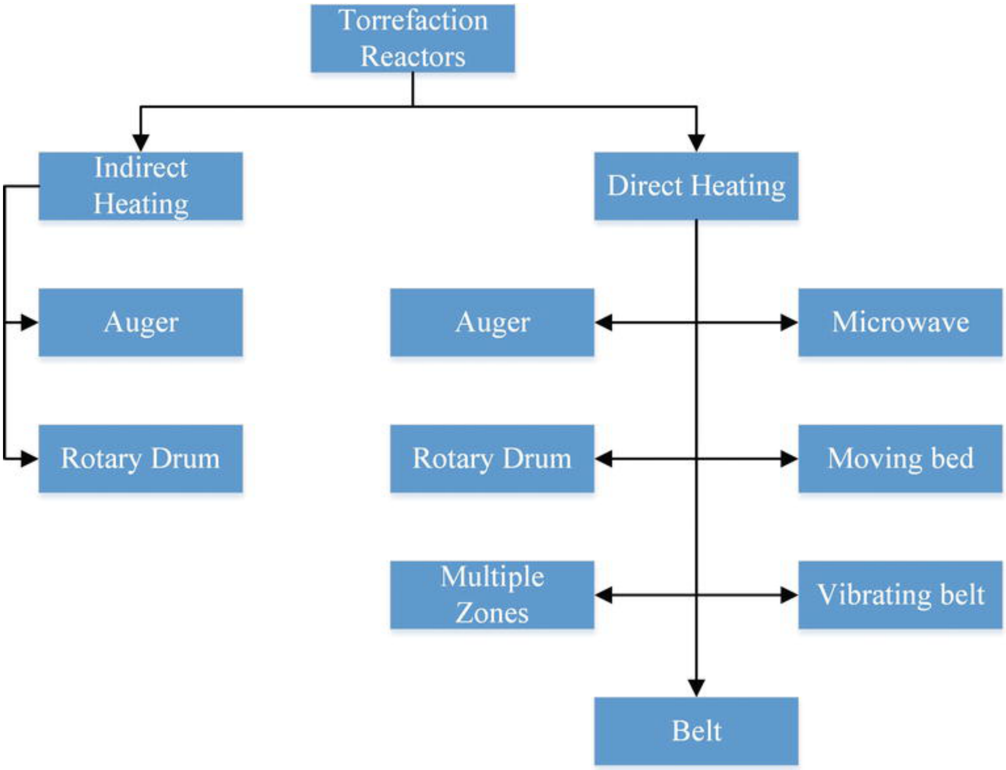


Figure 34. Torrefaction reactors classification (Stępień et al., 2017).

Direct contact with a heating medium that is either entirely oxygen-free or contains very little oxygen heats the biomass in directly heated reactors. Hot gases, hot solids, superheated steam, or electromagnetic radiation can all be used as the heating medium. Heat is transmitted through the wall surfaces in indirectly heated reactors; the biomass is not in direct contact with the heat-carrying medium. Therefore, it is simpler to inhibit combustion events that may occur during torrefaction because these types of reactors provide an oxygen-free environment. One or more of the following methods, including gas-particle convection, wall-particle conduction, electromagnetic radiation, particle-particle heat transmission, and liquid-aqueous heat transfer, can transmit heat to biomass particles. Reactors with augers and rotating drums use indirect heating. Conversely, direct heating reactors can be further classified into three subgroups based on the amount of oxygen present in the heating medium: reactors without any oxygen in the heating medium, reactors with a small amount of oxygen in the heating medium, and others (Stępień et al., 2017, Piersa et al., 2022).

A Moving bed reactor

According to Piersa et al. (2022), the moving bed reactor boasts a compact and uncomplicated design, accurate temperature regulation, a high heat transfer rate, high product quality, flexible fuel utilization, and minimal investment expenses. Due to gravity, the biomass that is fed into the reactor from the top descends (Figure 35a). A mechanism (such as a screw or conveyor) located at the bottom of the reactor is responsible for continually extracting the torrefied biomass. The biomass descends freely during the operation because there are no moving parts in the reactor. By immediately injecting hot gases into the lower portion of the moving bed, a temperature differential is created. The hot gases then counterflow—flow upward through the moving bed. By sending heat from the outside to the moving bed indirectly, the temperature gradient can also be changed. The greatest temperature that can be reached is 300°C, and the single cycle time varies between 30 and 40 minutes (Thengane et al., 2022, Stępień et al., 2017).

The moving bed reactor has the benefit of allowing biomass to fill the full reactor chamber. Consequently, the reactor volume can be greatly decreased for a given output capacity, lowering capital expenses. Because the biomass is not mixed evenly, the moving bed reactor has the drawback of frequently producing inhomogeneous zones during the heat transfer process. This is particularly true when using an indirect heating technique, such as heat transfer through the side or bottom walls.

B Fluidized bed reactor

A dense bed of fine biomass particles is found in a fluidized bed reactor (Figure 35b), which is typically filled with a solid substance that conducts heat, like sand with a high specific heat capacity. Inert hot gases blasted from the reactor's bottom are used to fluidize and heat the biomass. The raw biomass is broken down into small enough particles so that the reactor can fluidize them and distribute the temperature evenly throughout the bed. The process's reduction of biomass size, which raises energy consumption, is one of its main issues. These reactors fall into two categories for torrefaction: bubbling fluidized beds and circulating or toroidal fluidized beds. Compared to the moving bed, the bubbling fluidized bed offers superior heat transfer qualities because it allows for controlled heating of the solids. Compared to other reactor designs, fluidized bed reactors have higher heat and mass transfer rates, which result in quicker and more effective process conditions. By utilizing an appropriate velocity—typically higher than the minimum fluidization velocity for inert gases—fluidization requirements are met. Applications for biomass torrefaction do not commonly use this technology (Thengane et al., 2022; Tumuluru et al., 2021).

C Multiple hearth furnace (MHF) or Herreshoff furnace

The cylindrical multiple hearth furnace, also known as the Herreshoff furnace, is depicted in Figure 35c. Its interior is segmented into several levels, with trays fastened to a centrally located shaft that revolves around an axis of symmetry. An air lock at the end of the mechanical conveyor that feeds biomass into the reactor from above keeps oxygen from getting into the reactor. Pre-drying of the biomass is possible in a different drying technique. In this instance, the reactor alone does torrefaction. The reactor is separated into parts for torrefaction and drying in the event that an independent drying mechanism is not used. Depending on the number of hearths and shaft speed, the residence duration of the biomass in the reactor can range from 0.5 to 3 hours. The reactor's several levels aid in ensuring even mixing and slow heating. Gas burners or the direct injection of steam into each reactor layer provide the heating. Because the technology behind multiple hearth furnaces is easily scalable and adaptable to the specific needs of each customer, it is utilized on an industrial scale. It also offers benefits like mixing biomass and maintaining stable process temperatures. The technique has certain drawbacks, such as a lower rate of heat transfer to biomass than other direct reactors, a smaller capacity for frying biomass, a big reactor, and inadequate shaft sealing (Thengane et al., 2022, Stępień et al., 2017).

D Screw (auger) or belt conveyor reactor

It also offers benefits like mixing biomass and maintaining stable process temperatures. The technique has certain drawbacks, such as a lower rate of heat transfer to biomass than other direct reactors, a smaller capacity for frying biomass, a big reactor, and inadequate shaft sealing (Thengane et al., 2022, Stępień et al., 2017). Heat transfer is still not as good as it would be in a rotating drum, though, because the screw can be heated in addition to the outside wall, increasing the surface area available for more efficient heat exchange. Because the screw conveyor cannot be filled all the way to capacity for optimal performance, a greater reactor volume is needed for a given capacity of biomass processing. The conveyor's length and speed determine how long it stays in the reactor. These reactors have the advantages of being very inexpensive, easily scalable to huge industrial sizes, and requiring little in the way of inert gas. One drawback is the restricted capacity for production. A technique found in many of the industrial torrefaction systems currently in use is screw conveyor reactors. The reactor, which uses a conveyor belt rather than a screw conveyor to move biomass through the system, is another version that is most similar to an auger-based reactor or screw conveyor (Thengane et al., 2022, Stępień et al., 2017).

E Rotary drum reactor

The spinning cylinder in the rotary drum reactor (Figure 35e) has a little incline towards the bottom. This technology is straightforward and scalable. As the cylinder rotates, the biomass rolls into the upper end of the cylinder. The rolling motion causes the biomass particles to alternatively displace in touch with the gas inside the reactor and the hotter reactor wall, which leads to comparatively good homogenous heating and mixing. It is possible to supply process heat directly or indirectly. Under the first scenario, heat is typically generated by burning the gaseous product that is made during torrefaction and by bringing it back into the reactor. Heat is transferred indirectly through the walls of the drum. The length and angle of the drum inclination, as well as the rotation speed, can be used to control the process time in drum torrefaction reactors. One drawback of these reactors is that the friction between the biomass and the walls causes a large amount of fine dust to accumulate.

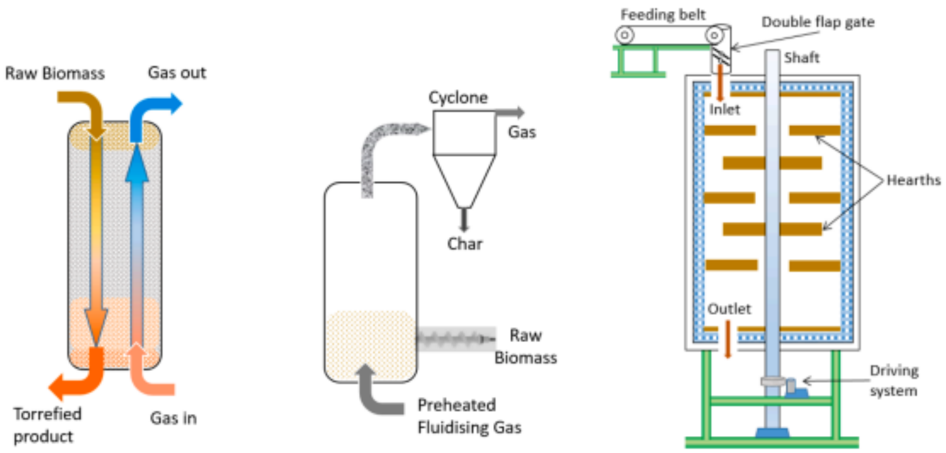
The reactor's maximum filling volume is restricted to roughly 30% in order to maintain the solid tumbling motion, which is another drawback. This implies that the reactor's volume will be at least three times larger than, say, a fully loaded moving bed reactor for a given production capacity, resulting in a higher capital cost. However, one advantage of the rotating drum design is that it is a reasonably well-established technology with additional uses, such pyrolysis and drying biomass. Because of this, the majority of businesses in Europe have created torrefaction technologies based on the rotary drum design, either by creating specially designed components or by using already-existing rotary drum suppliers (Thengane et al., 2022, Stępień et al., 2017).

F Microwave reactor

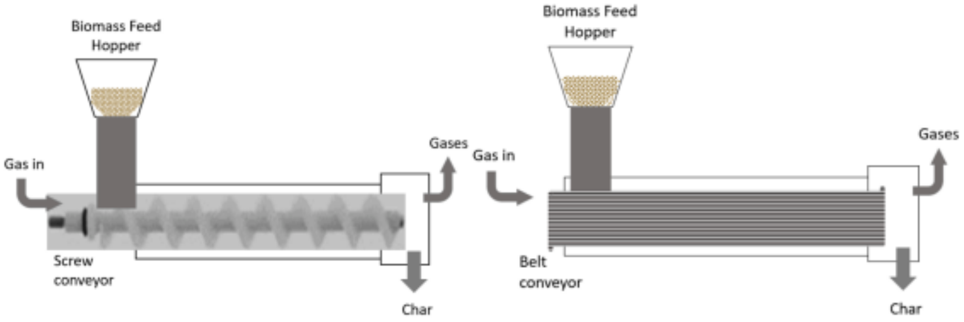
Radiation energy is employed in the microwave reactor (Figure 35f) to heat the biomass and bring it to the torrefaction conditions. The material is heated quickly and evenly with this method. According to Dhungana et al. (2012), microwave radiation is defined as electromagnetic waves that fall between 300 MHz and 300 GHz. Typical microwave ovens and reactors typically run at 2.45 GHz. The kind of material being processed, its size, ability to absorb microwave radiation, and reactor power all affect how long the process takes. For a given solid yield, it is possible to lower both the reactor size and the solid residence time thanks to the quick and uniform heating that microwaves provide (Thengane et al., 2022). Nevertheless, in thermally thick biomass particles, it has been discovered that this results in significant intraparticle temperature and drying inhomogeneity (Dhungana et al., 2012). The high energy consumption needed to produce microwave radiation—which is produced by electricity—is another significant drawback of employing a microwave reactor.

The heat or chemical energy included in the volatile gases (torgas) generated during the torrefaction process is not easily converted into electrical power. Due to the intricacy involved in producing microwave radiation, scaling up a design usually entails significant capital and operating costs (Thengane et al., 2022, Stępień et al., 2017).

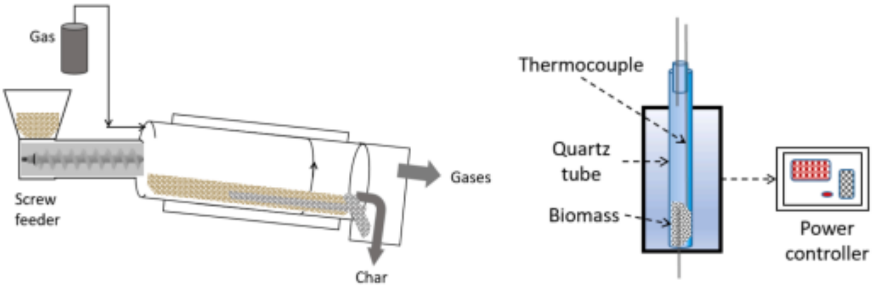
Table 21 compares several biomass torrefaction reactors, while Table 22 lists the various commercial-scale torrefaction reactors.



(a) Moving bed (b) Fluidized bed (c) Multiple hearth furnace



(d) Screw conveyor and belt conveyor



(e) Rotary drum (f) Microwave-based

Figure 35. Commonly used torrefaction reactors (Thengane et.al., 2022).

Table 21. Comparison of biomass torrefaction reactors (Piersa et al., 2022).

Reactor Type	Medium/Heat Source	Size of Heat Transfer Surface/Reactor Surface	Difficulties in Handling the Process	Movable or Special Elements	Limitation of Scale Up
With fixed bed	Flue gas, inert gas, or super-heated steam	Not applicable	Hard	Inert gas heat exchanger or super-heated steam generator; inert gas compressor	– Non-uniform heat distribution when the thickness of the biomass bed is large – Price of inert gas – High cost of building a super-heated steam generator
With rotating drum	Exhaust or Super heated steam	Not applicable	Hard	Drum and drive unit,super-heated steam generator	– High construction costs – Super-heated steam generator in reactor
With fluidized bed	Solid medium and/or inert gas	Not applicable	Hard	Gas/air compresson, biomass/ carrier solid separator	– Separation of biomass from solid medium – High construction costs for peripheral devices such as air/gas compressor and solids separator – Price of inert gas
With moving bed	Flue gas or Super-heated steam	Not applicable	Hard	Conveyor belt	– High construction costs of super-heated steam generator and reactor – No possibility to control the amount of oxygen in the exhaust gas
Microwave	Microwave	Not applicable	Hard	Microwave generator	– High construction costs of the reactor – High energy consumption
Fixed bed	Burning or electrical heater	High	Easy	No moving part	– Limited heat distribution when the thickness of the biomass in bed is large
Screw	Burning or electrical heater	High	Moderate	Screw and its drive set	– Limited heat distribution when the thickness of the biomass in bed is large
With rotating drum	Burning or electrical heater	High	Moderate	Drum and its drive set	– Limited heat distribution when the thickness of the biomass in bed is large
New reactor design (SHS)	Combustion	Small	Easy	No moving part	– Uniform heat distribution

Table 22. Summary of different torrefaction reactor designs at commercial scale (Thengane et al., 2022).

Reactor type	Advantages	Disadvantages	Companies
Moving bed	High degree of filling; Simple reactor design; Better heat transfer	Significant pressure drop; Difficult to control temperature; Sometimes heat transfer inhomogeneity	AREVA (France), LMK Energy (France), Torrec (Finland), Andritz/ECN (Denmark/Netherlans)
Fluidized bed and Entrained flow	Proven; High heat transfer, uniform; Easily scalable	Separation of biomass from solid heat carrier particles; fines losses	Topell (Netherlands)
Rotary drum	Proven; Low pressure drop; Possibility of both direct and indirect heating	Low degree of filling, heat transfer limitation	Andritz (Austria), CENER (Spain), Torr-Coal (Netherlands),
Screw or belt conveyor	Low cost, proven; Possibility for plug flow	Low degree of filling, heat transfer limitation	Arigna Fuels (Ireland), BioEndev (Sweden)
MHF / Herreshoff oven	Proven Design; Higher possibility of scale up; Close to plug flow; Good control; Possibility of adding fines	Lower heat transfer rate compared to other direct reactors; Limited volumetric capacity; Relatively large reactors; Require shaft sealing	CEA/CMI-NESA (France/Belgium)
Microwave	Homogeneous and rapid heating rate	High capital cost and sophistication; intra-particle inhomogeneity	Rotawave (United Kingdom)

Properties of torrefied biomass

While there are a number of different torrefaction techniques, the most common approach for pretreating solid biomass is non-oxidative (conventional) torrefaction, which has a lot of industrial applications. As a result, the typical torrefaction process is taken into consideration when describing the change in biomass properties following torrefaction.

The utilization of biomass in energy generation is limited by its hygroscopic nature, high moisture content, high atomic H/C and O/C ratios, low calorific value, poor grindability, big volume or low bulk density, increased biodegradation, and inhomogeneity features. It has been found that the torrefaction process applied to solid biomass can address the aforementioned drawbacks of raw biomass. Following the torrefaction process, biomass gains characteristics like a higher calorific value, improved grindability, higher volume and energy densities if the densification process is used, lower biodegradation, and higher homogeneity (Chen et al., 2021). It also has lower moisture content, atomic H/C, and O/C ratios.

Certain reaction processes that take place during thermal decomposition at higher temperatures are thought to be responsible for changes in biomass characteristics during torrefaction (Chen et al., 2014). The processes of biomass decarbonization, dehydrogenation, and deoxygenation are responsible for the mass loss of biomass resulting from thermal degradation. Figure 36 and Table 23 list the important mechanisms that take place during torrefaction and the alterations in biomass characteristics that follow.

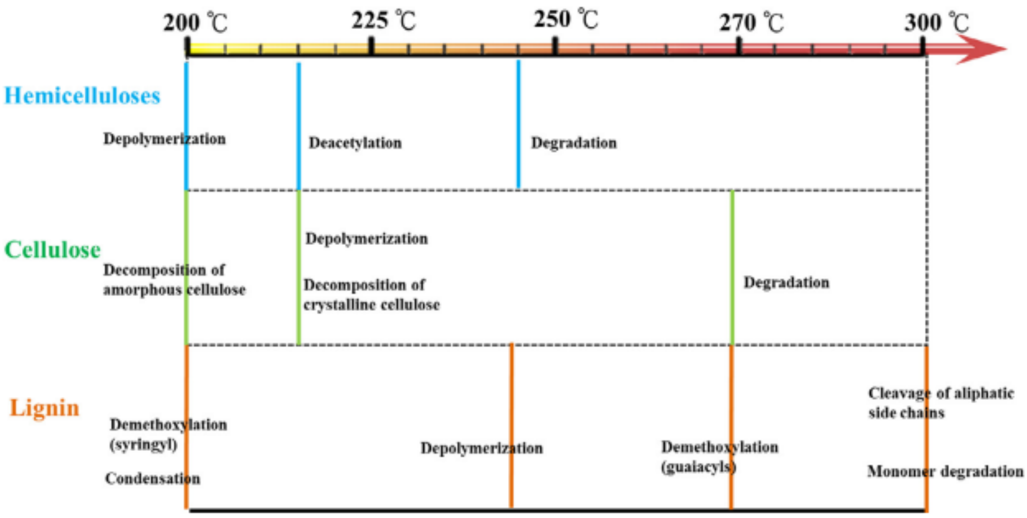


Figure 36. Reaction mechanisms occurred in the course of biomass torrefaction (Chen et al., 2021).

Table 23. Physicochemical transformation and property variations of biomass before and after torrefaction (Chen et al., 2021).

Raw biomass	Physicochemical transformations	Torrefied biomass property
High moisture content	Dehydration	Low moisture content
Hygroscopic	Dehydration Dehydroxylation Decomposition of amorphous cellulose Apolar tar in pores	Hydrophobic
Higher O/C and H/C ratio	Less extent decarbonization Dehydrogenation Deoxygenation Deacetylation Demethoxylation Devolatilization	Lower O/C and H/C ratio
Lower calorific value	Dehydration Carbonization Dehydrogenation Deoxygenation Dehydroxylation	Higher calorific value
Poor grindability	Hemicelluloses decomposition	Improved grindability
Higher biodegradation and poor storability	Hemicelluloses decomposition Lignin modification	Lower biodegradation and higher storability

Colour change

When the biomass is thermally decomposed, the raw material's colour changes as a visible cue. The conditions of torrefaction determine how the biomass changes colour. According to research, the temperature range of 150–300°C is when biomass turns from brown to black (Shankar Tumuluru et al., 2011). This results from the torrefaction process's modifications to the chemical composition. There are several possible reactions that cause torrefaction wood to change colour. First, several coloured byproducts are produced during the breakdown of hemicelluloses. Second, a number of processes, including oxidation, cross-linking, and condensation reactions brought on by the breakage of lignin's β-O-4 ether linkages and aromatic methyl groups, may be the cause of the accelerated colour change of torrefied biomass. Third, during heat breakdown, polysaccharides (such as amino acids, sugars, and phenolic substances) undergo enzyme-mediated (Maillard) reactions. Lastly, during the drying process, oxidative interactions between extractives (found in woody biomass) and the atmosphere may be the reason. The partial carbonization that is taking place on the wood's surface while it dries is also indicated by this colour shift (Chen et al., 2021).

Moisture content

Since the initial high moisture level during biomass combustion results in energy loss, moisture is a crucial component during thermochemical conversion. The moisture content of torrefied biomass is usually 1-3 % wb. According to Ribeiro et al. (2018), lowering the moisture content has three major benefits: 1) lowering the moisture level, which improves the efficiency of energy conversion processes; 2) lowering transportation costs because less water is transferred; and 3) preventing moisture absorption and biomass decomposition during storage and transportation.

Hydrophobicity

A reliable measure of the efficiency of the biomass torrefaction process is hydrophobicity. Utilizing an immersion test or equilibrium moisture value analysis, one can ascertain the hydrophobic quality of torrefied biomass. Stated differently, a decline in the equilibrium moisture content signifies a greater hydrophobicity of the biomass (Dyjakon et al., 2021). During the immersion test, raw biomass and torrefaction products are submerged in a specific volume of water for a predetermined amount of time. By comparing the ultimate moisture content of multiple materials following immersion, one can ascertain a material's hydrophobicity. One common method for figuring out the equilibrium moisture content of biomass is to leave it at a constant temperature and humidity level for the duration of the time needed to reach the equilibrium moisture content. Generally speaking, torrefaction increases the hydrophobicity of solid biomass. Furthermore, both temperature and residence duration affect the torrefaction process. As residence duration and torrefaction temperature rise, treated biomass may become less prone to absorbing moisture, hence altering its hydrophobic properties (Gizaw et al., 2024).

Because natural hydrogen bonds to the hydroxyl groups of the components of the cell wall that readily absorb water, raw biomass is hygroscopic. Biomass typically contains 30% to 60% moisture by weight, depending on the length of storage, how and when it is harvested, the temperature and humidity levels throughout storage, and whether it is stored indoors or outdoors. Because dehydration during the torrefaction process partially destroys the hydroxyl groups in the biomass and prevents hydrogen bonds from forming, the torrefied biomass is hydrophobic. Because the biomass is hydrophobic, storage deterioration is less likely to occur. The torrefied biomass's equilibrium moisture content significantly drops as a result. The biomass is more durable when there is less water absorbed. By evaluating the change in wettability of the biomass before and after torrefaction, contact angle and equilibrium moisture content tests can be used to measure the hydrophobicity of the biomass. TGA curves can also be used to assess the hydrophobic behaviour of torrefaction biomass. When compared to raw biomass maintained at less than 25°C and 65% relative humidity, it was discovered that the weight loss of torrefaction biomass between 25 and 100°C was negligible (Chen et al., 2021). Additionally, it was discovered that the hydrophobicity of the torrefaction biomass increased with increasing torrefaction intensity.

Grindability

Grindability is one of the key factors that determines how well torrefied biomass performs. The structure of biomass is extremely fibrous and dense. Torrefaction causes biomass to lose its dense structure primarily due to the depolymerization of cellulose and the degradation of the hemicellulose matrix (Chen et al., 2015), which shortens the fibers' length. It is also possible to shorten each particle's length without affecting its diameter (Shankar Tumuluru et al., 2011). Compared to torrefied biomass, grinding raw biomass requires more energy. The distribution of particle sizes is also impacted by this. The better the grindability, the smaller the required particle size and the less energy used for grinding (Olugbade and Ojo, 2020). Torrefied biomass chips were found to require 90% less energy for grinding than non-torrefied wood chips (Ribeiro et al., 2018).

Surface area

Since it influences the burning and transportation of biomass, particle surface area plays an important role in torrefaction processes. Because of their diverse and vast particle size distribution, different raw biomass sources have low surface areas. Smaller particle sizes result in more specific surface area (Gizaw et al., 2024). Torrefied biomass products typically have higher surface area and smaller, finer particle sizes than raw biomass (Xu et al., 2019).

Particle size distribution and sphericity

When examining the fuel's fluidity and the behaviour of combustion in co-combustion, particle size and sphericity distribution play a critical role. Research has demonstrated that biomass can undergo torrefaction to provide smaller, more uniform particles that resemble coal. Reportedly, when the temperature of torrefaction rose, the sphericity of biomass increased proportionately from 0.48% to 0.62%. In general, torrefied biomass has bigger surface areas or smaller particle sizes, making it suitable for co-combustion and combustion applications (Gizaw et al., 2024).

Densification (pelletization) of processed biomass

Densification, also known as pelletization, is the process used to compress biomass into solid particles with a uniform particle size distribution for briquettes or pellets. Changes in the types of raw materials utilized, variations in the climate and seasons, and other factors all have a significant impact on the quality of the pellets made from biomass. Nonetheless, the quality of the resulting raw material is enhanced by the torrefaction procedure that is used on the biomass prior to pelletization (Sarker et al., 2022). Because lignin acts as a binding agent, its concentration affects how pelletizable biomass is (Gizaw et al., 2024).

Bulk density and energy density

The torrefaction of biomass results in the loss of mass as solid, liquid, and gaseous products; this increases the porosity of the biomass. It has been discovered that this lowers the biomass's bulk density, which typically ranges from 180 to 350 kg/m3, contingent upon the non-torrefied biomass's starting density. It has been found that the energy density of the torrefaction biomass increases (by about 30%) after the torrefaction process, despite this drop in bulk density (Ribeiro et al., 2018).

Biodegradation

Raw biomass decomposes quickly because it is innately susceptible to fungal and microbial deterioration (particularly in humid environments). The biomass is more resistant to microbial destruction after it has undergone torrefaction. Increased durability follows after the torrefaction process due to the degradation of hemicelluloses, which are widely thought to be an essential source of nutrients for the growth of fungi that cause wood decay. Torrefaction biomass is generally resistant to fungus due to four factors: Its hydrophobicity was improved; it produced new volatile products and polynuclear aromatic hydrocarbons, which are derived from polyaromatic compounds formed during torrefaction; wood polymers were modified so that the enzymes involved in fungal degradation could not recognize the polymers; and hemicelluloses were degraded by torrefaction (Chen et al., 2021).

Van Krevelen diagram (Atomic H/C and O/C ratios)

The chemical makeup of biomass is dramatically altered during the torrefaction process. The elemental carbon content of the torrefied biomass increases as the torrefaction temperature rises, but the levels of hydrogen and oxygen drop as a result of the release of tiny molecules volatile components rich in hydrogen and oxygen, such as CO_2 and water. Consequently, the biomass fuel characteristics change towards coal and the H/C and O/C ratios drop. The Van Krevelen diagram's zones of coal, torrefied biomass, and raw biomass settlement are depicted in Figure 37.

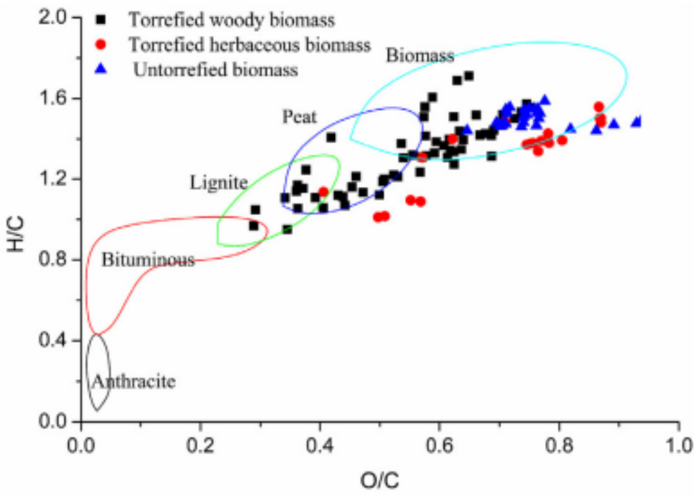


Figure 37. Van Krevelen diagram (Niu et al., 2019)

Torrefied biomass, particularly torrefied woody biomass, has chemical compositions similar to peat, lignite, and even subbituminous coal under certain conditions (high temperature and extended residence time), and it can be utilized for co-firing and gasification (Niu et al., 2019).

Heating value

Carbon (C), hydrogen (H), and oxygen (O) are the major elements in biomass; tiny amounts of nitrogen (N) and sulphur (S) are also present. These elements combine to form hemicelluloses, cellulose, and lignin. The primary source of heat released during the burning of biomass is carbon oxidation. When biomass is burned, hydrogen is also a significant source of heat; however, hydrogen is mostly found in biomass as either OH or C-H bonds. Although biomass's higher oxygen content lowers its calorific value, oxygen is good for combustion. Biomass has a larger hydrogen and oxygen concentration than coal, but a lower carbon, nitrogen, and sulphur content. Consequently, torrefaction is used on biomass to exclude undesirable elements (H and O) from the solid products, yielding calorific values (25–35 MJ kg^{-1}) that are comparable to those of coal. Furthermore, biomass has a lower calorific value than coal due to its high moisture content. Figure 38 provides an overview of the fuel characteristics of coal, torrefied biomass, and raw biomass (Chen et al., 2021).

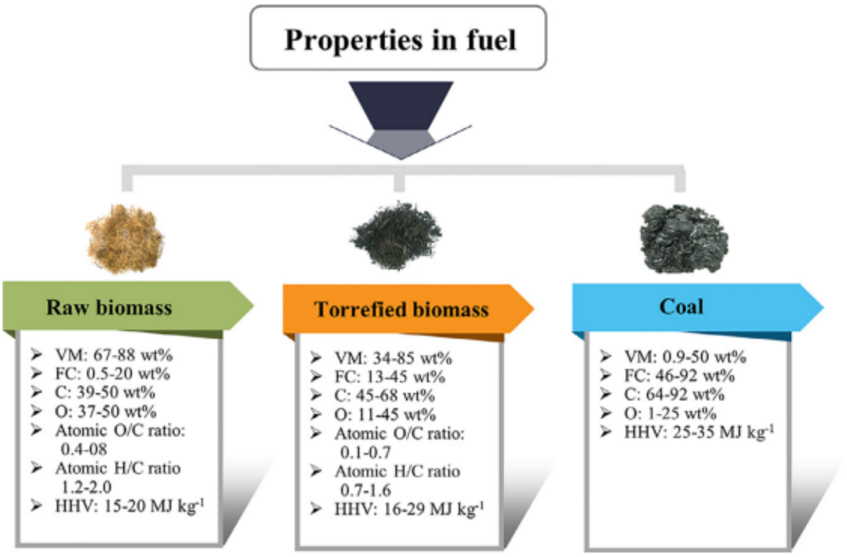


Figure 38. Comparison of fuel properties of raw and torrefied biomass and coal (Chen et al.,2021).

Application of Torrefied Biomass

As shown in Figure 39 and Table 24, the main uses of torrefied biomass are in metallurgy, co-utilization (co-combustion and co-gasification), densification, gasification, pyrolysis, combustion, and co-utilization.

Densification

Torrefied or raw biomass can be compressed using the densification process. Densification yields biomass in the form of compact, uniformly sized torrefaction biomass with or without additions (binders) (Sithole et al., 2023).

More importantly, pellets made from torrefied biomass can be more uniform and uniform in terms of handling, transportation, storage, combustion, grindability, and heating value, making them attractive for use as a coal substitute in many power plants. Densification through pelletization can improve the heat and power conversion properties of biomass (Olugbade and Ojo, 2020). When compared to untreated biomass, the mechanical strength and durability of torrefaction pellets diminish marginally as the torrefaction conditions increase. Nonetheless, torrefied pellets have improved combustion characteristics, increased hydrophobicity, and a higher heating value (Sarker et al., 2021).

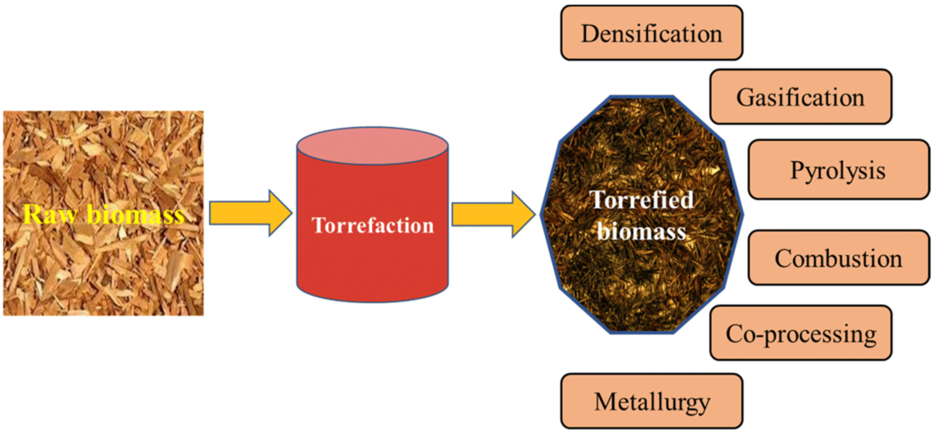


Figure 39. Application areas of torrefried biomass (Sarker et al., 2021).

Table 24. Market potential of torrefied biomass in different applications (Radrics et al., 2012, Thengane et al., 2022).

Application	Conversion Process	Technology/ Equipment	Pretreatment Requirements	Torrefaction Advantages	Market Potential
Power generation	Co-firing	Coal-fired boilers	High	Drop-in replacement; Higher co-firing rates	High
	Gasification	Entrained flow gasifier	Very high due to particle size	Size reduction; Fluidization; C/H/O ratio; dry	Limited
	Stand-alone Combustion (> 20 MWe)	Circulating fluidized bed boilers	Moderate	Limited; relatively expensive	Small
Industrial heating	Combustion	Blast furnaces	Moderate	Handling; C/H/O ratio; Energy content	High
Residential/ District heating	Combustion	Stoves/ Boilers	High, Decentralized	Transport savings	High

White pellet production technology can incorporate the torrefaction process. As shown in Figure 40, in this instance, the torrefaction process can be completed prior to palletisation. The torrefaction method has benefits and drawbacks when it comes to palletisation. Grinding requires less energy when the palletisation procedure is carried out after torrefaction. The torrefaction process's intensity, or temperature and torrefaction time, affects how much energy is needed for grinding. It is challenging to manufacture both white and black pellets since dusting that happens during grinding contaminates pellet lines. When grinding, dusting can occur, which might lead to an explosion or fire. Torrefaction wood palletisation is another challenge in this process. Dehydroxylation of lignin and a decrease in hemicellulose content will lessen hydrogen bonding during compression in extreme torrefaction procedures. High levels of torrefaction severity will also cause biomass's fibrous structure to diminish. As the intensity of the torrefaction increases, this condition will make it harder to densify the biomass.

Weak pellets will be formed, and it will be challenging to extract the torrefaction wood from the mold since the connectivity between the particles is weakened. Since torrefaction biomass is as dry as bone, it must be stabilized by adding water up to a 15% moisture content. Water used in combination with high mold and feeding temperature can aid in compressing the torrefaction result and converting it into pellets. Lignin serves as a naturally occurring binder since it softens at high pelleting temperatures. This isn't the case, though, if high temperatures have caused the biomass to undergo torrefaction. Torrefied wood has less calories when it is pelletized, however using binders and lubricants makes the process more expensive and increases the oxygen content of the pellet. Furthermore, combustion happens when it comes into contact with air and the friction force causes a temperature increase. As a result, an inert atmosphere should be used for the palletisation process (Kumar et al., 2017).

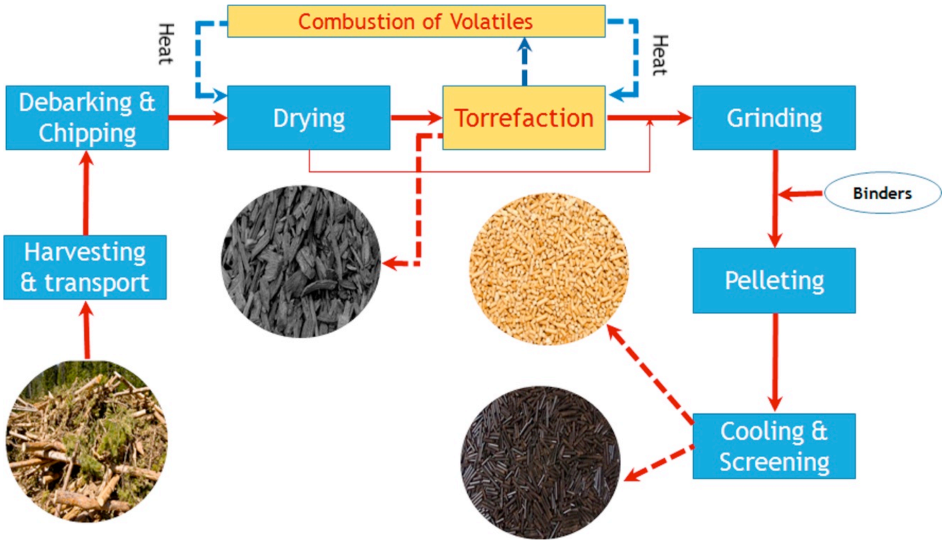


Figure 40. Integration of torrefaction as an upstream operation in a white pellet facility. Red solid arrows represent the primary process lines, and blue dotted lines represent the heat integration. Red dotted arrows represent the final products (Kumar et al., 2017).

The characteristics of coal, white wood and its pellets, and torrefied wood are contrasted in Table 25. Wood pellets (8–11 GJ/m^3) have an energy density that is higher than wood chips (2–3 GJ/m3), but it is still significantly lower than coal (18–24 GJ/m^3). Compared to wood pellets, the energy content of wood obtained through torrefying is lower. When palletisation and torrefying are combined, biomass can achieve an energy density of 15–18 GJ/m^3, which is similar to low-rank coal. Biomass gains hygroscopic qualities through torrefying, which enhances its stability and storage capabilities. During storage and transit, microbial activity and gas emission are encouraged by moisture absorption. Wood pellets cannot be stored outdoors like coal because they break down quickly in the presence of water. Biomass undergoes torrefaction, which confers hydrophobic characteristics that enable outdoor storage (Kumar et al., 2017).

Table 25. Properties of Wood Chips/Sawdust, Wood Pellets, Torrefied Wood Chips, Torrefied Pellets, and Coal (Kumar et al., 2017).

Properties	**Wood chips/sawdust**	**Wood pellets**	**Torrefied wood chips**	**Torrefied pellets**	**Coal**
Moisture content (% wt)	20-50	7-10	1-5	1-5	10-15
Calorific value (MJ/kg)	15-16	15-16	20-24	20-24	23-28
Volatiles (% db)	70-75	70-75	50-60	50-60	15-30
Bulk density (kg/m ^{3})	100-200	550-750	450-850	450-850	800-850
Volumetric energy density (GJ/m^3)	2-3	8-11	4-5	15-18	18-24
Hydroscopic properties	Hydrophilic	Hydrophilic	Hydrophobic	Hydrophobic	Hydrophobic
Biological degradation	Yes	Yes	No	No	No
Milling requirements	Special	Special	Classic	Classic	Classic
Handling properties	Difficult	Easy	Difficult	Easy	Easy
Product Consistency	Heterogeneous	Good	High	High	High
Transport cost	High	Average	Low	Low	Low

The densified products' physical mechanical property values serve as markers for how well they can withstand the damaging pressures encountered during loading, storage, and transportation. Particle size, external additives, moisture content, and operational parameters (compression pressure, residence time, and temperature) all affect the quality of briquettes or pellets. The most crucial briquette/pellet quality attributes are density, compressive strength, impact resistance, and moisture absorption or adsorption. Table 26 lists the limit values for the briquettes' and pellets' physical, mechanical, and chemical characteristics. Moreover, Table 27 lists the characteristics of the sawdust-torrefied pellet produced during the process and the pellets produced at the end of the sawdust-torrefaction process.

In addition to reducing mold wear, adding a binder to a raw material during briquetting improves the briquettes' cohesiveness and mechanical strength. In the end, this lowers the cost of storage and transportation. High-quality briquettes can be produced by adding 5-25% binder to the basic material. In briquetting or pelletizing, the following materials are typically used: organic (molasses, tar pitch, and starch binders), inorganic (clay, lime, gypsum, cement, sodium silicate, and sodium silicate), and composite/composite binders. A binder can be a liquid or solid that creates strong interparticle linkages by a chemical reaction, forming a film, bridge, or matrix. Good binders should generally be combustible, inexpensive, non-polluting, and acceptable to the environment.

The physicochemical and mechanical qualities of briquettes are influenced by the kind and quantity of additives utilized. Superior grade briquettes often have easy lighting, smokelessness, odorlessness, and a lengthy burning period. These rely on the type of binder and raw material utilized. Strong binders, as opposed to weak binders, minimize pore gaps in the densified product and bind the particles of the raw materials together. As a result, there is a decrease in oxygen infiltration and an increase in combustion product outflow, lengthening both the burning and ignition times (Evangelista et al., 2018).

Table 26. Limit values for physicomechanical and chemical properties of pellets/briquettes (Eling et al., 2024).

Quality parameter	Limit values	Test standards
Density	1000-1400 kgm^{-3}	German standard DIN 51731
Water resistance	95 %	ASTM 870-15
Shatter index	≥ 90	Shatter index
Compressive strength	>1.0 MPa	ASTM D2166-85
Durability	95 %	ISO 17831-2
Calorific value	15.5–19.50 MJ/kg	German standard DIN 51731
Moisture content	<12 %	German standard DIN 51731
Ash content	≤1.0%(minimum)≤ 3.0%(maximum)	ASTM D317-12
N	<0.3 %	German standard DIN 51731
S	<0.08 %	German standard DIN 51731
Cl	<0.03 %	German standard DIN 51731

Table 27. Comparison of torrefaction of densified wood (pellets) versus densification of torrefied sawdust (Peng et al., 2015, Thengane et al., 2022).

Properties	Untreated wood pellets	Torrefied wood pellets	Untreated sawdust	Pellets from torrefied sawdust
HHV (MJ/kg)	18.5	22.7	19.9	22.5
Bulk density (kg/m3)	650	530	650	700
Single pellet density (kg/m^3)	1190	930	1200	1250
Volumetric energy density (kg/m^3)	12	12	12.9	15.9
Meyer hardness (N/mm^2)	24	12	9	11
Saturated water uptake (% wt)	16	9	19	11
Energy yield (%)	100	83	100	78

Combustion

Because raw biomass agglomerates, slag forms, ash clinkers, and low energy content weakens with biomass moisture, burning it in coal-fired power plants requires specialized infrastructures or retrofitting. In contrast, in coal-fired power plants, torrefied biomass, also known as torrefied pellets, can be utilized either alone or in conjunction with coal. This demonstrates excellent fuel qualities, grindability, and comparatively low by-product production, all of which lower particle and greenhouse gas emissions (Sarker et al., 2021).

A separate biomass feeding mechanism is required for the co-combustion process because the coal mill is unable to grind the biomass small enough. Torrefied biomass can be pulverized and burned with coal, despite its outstanding flammability and grindability. For effective combustion and co-firing applications, torrefied biomass is preferred since it has a higher particle surface area and a smaller particle size than base biomass (Niu et al., 2019).

By bringing raw biomass's chemical and physical characteristics closer to those of bituminous coal through the torrefaction process, large substitution rates of biomass can be used in place of current coal-fired boilers without requiring significant alterations (Thengane et al., 2022).

One dependable way for power plants to cut back on the usage of fossil fuels is to co-fire coal and torrefied biomass. With less money needed for new infrastructure, the qualities of torrefied biomass can be used either alone or in conjunction with coal to lower greenhouse gas emissions (Sarker et al., 2021).

It was highlighted in the experimental study where torrefied biomass and coal were co-firing that torrefaction biomass can be fired at 100% without lessening boiler load fluctuations and that increasing the amount of torrefaction biomass during the co-firing process greatly reduced emissions of NOx and CO2. Figure 41 depicts the torrefaction-based functioning system (Li et al., 2012).

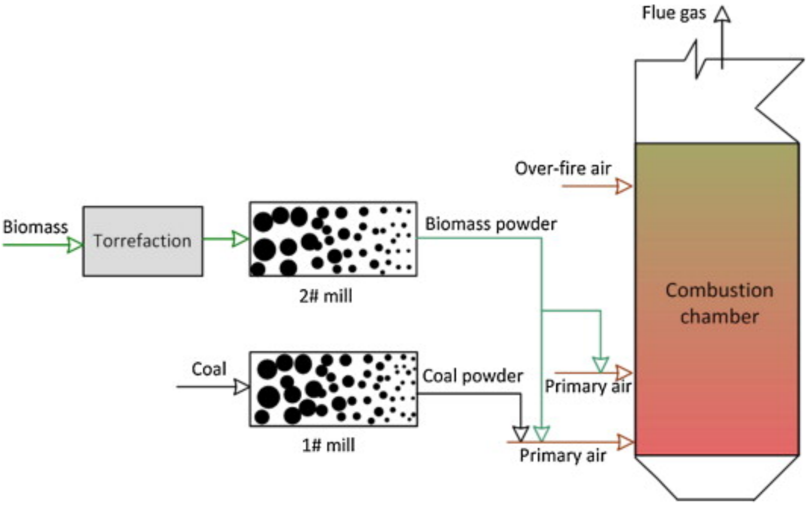


Figure 41. Co-firing system based on torrefaction (Li et al., 2012).

Gasification

By the process of gasification, solid or liquid raw materials are transformed into gaseous fuels or chemical raw materials that can be burned to create compounds with added value or to generate energy for power and heating. In order to achieve homogeneous and heterogeneous reactions with carbonized substances and rearrange the molecular structure of biomass, gasification necessitates the use of a medium known as a gasification agent, such as steam, CO_2, or O_2 (Lu et al., 2021). This allows solid biomass to be transformed into ideal products.

The moisture content and particle size of torrefied biomass are lower than those of the parent biomass. Thus, in a high-temperature flow reactor operating at 1400 °C, dried biomass with a size of several hundred microns can be gasified quickly in a matter of seconds. Torrefaction-gasification is more energy-efficient than two-stage pyrolysis-gasification since it requires less heat than higher-temperature pyrolysis (Niu et al., 2019).

Because oxygenated volatile chemicals are eliminated during the gasification process, torrefied biomass lowers the development of tar and improves thermal efficiency. Compared to raw biomass, torrefied biomass yields significantly more syngas in both quantity and quality. Fischer-Tropsch catalysis can be used to create high-value hydrocarbon fuels and chemicals from biomass or syngas produced from coal (Sarker et al., 2021). The sensible heat of the producer gas leaving the gasifier or the gaseous product of the pyrolyzer or torrefaction reactor can meet the heat requirements for the torrefaction process, which are lower than those for pyrolysis or gasification at higher temperatures (Thengane et al., 2022).

For instance, in a pilot plant (Figure 42) of Pressurized Entrained flow Biomass Gasification (PEBG) at approximately 270 kWth between 1200 and 1500 °C at the Energy Technology Centre (ETC) in Piteå, a study was carried out to determine whether torrefaction would significantly change the gasification plant performance and to determine whether feeding and operating torrefaction biomass dust into the gasifier would be feasible. The study made use of two torreified wood residues, one raw wood residue, and one torrefied stem wood. For all four gasification trials, the oxygen equivalent ratio (λ) and system pressure remained constant. It was observed that the pretreatment of torrefaction greatly decreased the energy required for grinding in order to reduce fuel size, hence increasing the efficiency of the gasification plant. Additionally, it was determined that while less severe and more severe torrefaction result in decreased carbon conversions, an intermediate torrefaction pretreatment can boost carbon conversion efficiency. Additionally, the results demonstrate that the fuel with the greatest degree of torrefaction had a much lower CH_4 production (Weilend et al., 2014).

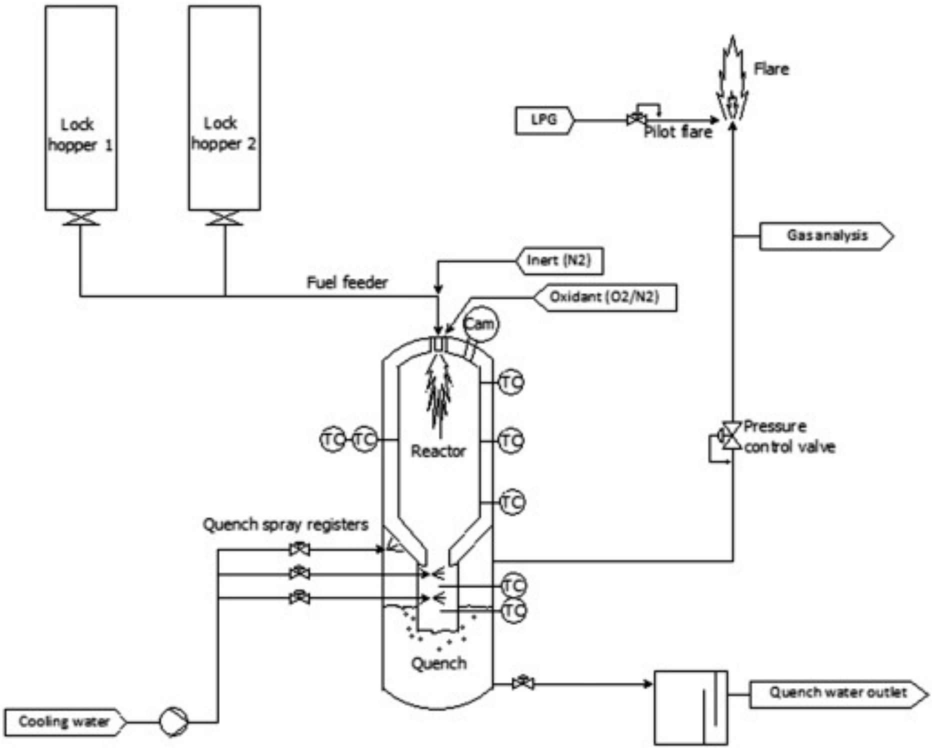


Figure 42. Schematic process flow diagram for PEBG process (Weilend et al., 2014)

Pyrolysis

One of the most popular thermal breakdown processes for raw materials is pyrolysis, which is accomplished by reducing the amount of oxygen in an inert environment like argon or nitrogen. The pyrolysis process yields a liquid product (pyrolysis bio-oil), a gaseous product (CO, CO_2, H_2, CH_4), and a solid product (carbonated). The typical weight ratio of moisture, aromatic compounds, oxygenated aliphatic compounds, and different oxygen and nitrogen molecules in pyrolysis bio-oil is between 15 and 30 percent. Since raw lignocellulosic biomass typically contains a high moisture content that acts as an adsorbent, it cannot be utilized directly in the pyrolysis process. In this instance, the biomass needs to be dehydrated first and then fed into the reactor systems for pyrolysis. Pyrolysis techniques are typically classified as Slow, Fast, or Flash depending on temperature variations and residence time (Javanmard et al., 2023).

Before pyrolysis, torrefaction is regarded as an efficient pretreatment method as well. After torrefaction, pyrolysis products can be produced in greater numbers and with higher quality. Due to the dehydration processes that occur during torrefaction, the water content of bio-oil made from torrefied biomass can be greatly decreased. The heating value, viscosity, and other fuel qualities of bio-oil can be increased by reducing its water and oxygen component content. In pyrolysis bio-oil, oxygen compounds include aldehydes, alcohols, and acids. Since these molecules decrease with torrefaction intensity, bio-oil's oxygen content can be decreased by increasing torrefaction intensity (Sarker et al., 2021).

Metallurgical Applications

The biggest industrial source of CO_2 emissions is the iron and steel sector. The industry uses a lot of fossil fuels and has an energy intensity similar to that of steel production. The use of biomass in the steel industry has been identified as a viable area for development, and the volume of energy used in this industrial sector presents a strong potential for bio-fuel use and bio-fuel development (Proskurina et al., 2017). To mitigate adverse environmental effects, the steel industry is contemplating substituting fossil coke with reductants derived from biomass. Bio-char produced by gasification and pyrolysis was previously primarily thought of as biomass-based reductants. Torrefied biomass has garnered more attention lately as a potential bioreductant. This direction has already been the subject of several investigations. Torrefied biomass has potential benefits over conventional coke or coal produced by pyrolysis and gasification (Doddapaneni et al., 2023).

An efficient way to lower the amount of CO_2 emissions in the blast furnace ironmaking process is to replace fossil carbon with carbon derived from renewable biomass. Biomass must be thermochemically treated prior to being used in the blast furnace because the steel industry requires high-quality solid fuel (Suopajärvi and Fabritius, 2013). Research has indicated that carbonized materials produced at temperatures above 300 °C are appropriate for injection into the blast furnace when it comes to torrefied biomass (Sarker et al., 2021).

Other applications

Bio-char made from torrefied biomass can be either acidic (low pH), which is appropriate for usage in very alkaline soils, or alkaline (high pH), which acts as a liming agent to prevent soil acidification. The crops will also influence the choice and rate of torrefied biomass application since various plants and crops require varied soil pH levels for optimal growth. Furthermore, it has been observed that torrefied biomass contributes nutrients like potassium (K), inhibits the build-up of harmful elements, and boosts the availability of water-soluble elements (K, Na, and P) that are readily assimilated by plants and, in certain situations, can even function as a fertilizer on their own (Thengane et al., 2021).

Because of the structural changes caused by torrefaction, biomass can now be used in a wider range of carbon-related processes, such as industrial carbonization and polymer compounding. By using the Fischer Tropsch process, torrefied biomass can be used to create syngas of the necessary grade, which can then be catalytically or enzymatically transformed into useful chemicals. Given its characteristics, torrefied biomass can be a sustainable adsorbent for the removal of different types of pollutants from the air (PAHs, for example) and water (oil spills, for example) (Thengane et al., 2022).

Limitations of the use of torrefied biomass in industry

Because of its structure or post-processing, torrefied biomass presents a variety of challenges in applications where it is utilized either alone or in conjunction with coal. These are the following:

Finding the right binding to provide the briquettes with the required density and durability is a challenge in the densification of torrefied biomass. The primary cause is the thermal breakdown of biomass during torrefaction, which breaks down components like lignin. Lignin decomposes and loses its binding ability at high temperatures (high torrefaction temperatures) in the range of reactive (temperature range of 150 to 200^{o}C) and destructive regions (200-300^{o}C). This results in poor densification and lower durability for torrefied biomass at high temperatures. It has been determined that using conventional binders in the densification process is costly, lowers the pellets' heating value, and affects the food supply chain. Additionally, it has been noted that whereas torrefied pellets have a similar hardness to raw pellets, they have a reduced bulk density (Aaimiri et al., 2019).

A less complicated method that transforms biomass into a commodity fuel with better homogeneity, energy density, hydrophobicity, and grindability is dry inert torrefaction mixed with densification. This fuel may be processed similarly to coal and can be used directly to replace coal. However, the removal of alkalis from biomass is severely limited by dry torrefaction. The biggest barrier to using low-quality biomass in combustion systems is its increased maintenance costs, which are mostly brought on by the significant and more frequent dangers of sintering, slagging, fouling, and corrosion that come with the biomass's alkalis and chlorine content. The addition of additives, combining high alkali biomass with materials with higher aluminosilicate and sulphur content to raise the ash fusion temperature in the mixture, or lowering the alkali content through washing techniques are some ways to lessen the effects of alkali content in biomass (Abelha et al., 2019).

Another problem for solid fuels like coal or torrefied biomass is that they can self-heat, which poses a safety risk when stored in small areas. Self-heating is the process by which exothermic events, including oxidation, release heat more quickly than the bulk material disintegrates. This results in an increase in temperature. Temperature increases often promote heat production and can naturally result in self-ignition, or the critical stage of self-heating, which raises hazards and risk concerns. The thermal runaway of exothermic reactions marks the change from self-heating to self-ignition. Actually, self-heating happens when the bulk material gets big enough, or when the cooling capacity becomes sufficiently limiting (Elvangelista et al., 2014). According to one study, oxidation below 100 °C initiated the biomass's self-heating process following torrefaction (Itoh et al., 2018).

Persistent organic pollutants (POPs) including dibenzofurans and polychlorinated dibenzo-p-dioxins (PCDFs) may occur within the temperature range employed for torrefaction (200–350 °C), according to prior research on wood burning and other thermochemical processes. For PCDDs and PCDFs to develop, the feedstock must contain chlorine or chlorinated precursors, such as chlorinated benzenes and phenols. The concentration of PCDDs in torrefaction products was found to be 2–5 times that of the feedstock in the study that examined the possible formation of polychlorinated dibenzo–p–dioxins (PCDDs) and dibenzofurans (PCDFs) from solid and volatile components (liquid and gaseous products) obtained during the torrefaction process. Analysing homologous profiles revealed that the PCDDs found in the torrefaction products were partially produced by physical transformation brought on by the volatilization and recondensation of PCDDs present in the feedstock, as well as partially by de novo creation. In contrast to PCDDs, there was less net PCDF creation during the torrefaction process (Gao et al., 2017).

Advantages and disadvantages of torrefaction process

Advantages and disadvantages for torrefaction process are presented in Table 28.

Table 28. The advantages and disadvantages of torrefaction process.

Feedstock	**Technical conditions**	**Key Product**	**Advantage**	**Disadvantage**	**Level of Conversion Efficiency**	**Level of Capital Cost**	**Level of Operational Cost**
Suitable feedstock: e.g.: Wood Chips Agricultural Residues Corn Stover Pine Sawdust Straw *Feedstock size:*		Torrefied biomass	Improved Energy Density, Enhanced Hydrophobicit, Reduced Volatile Matter, Better Grindability, Improved Storage and Handling, Increased Improved Enhancing energy efficiency in thermochemical conversion technologies using torrefied biomass	High Energy Consumption, Limited Feedstock Variety (Low-Lignin Biomas....add,), Complex Process Control, Cost of Equipment and Operation, Potential Emissions, Potential Production of Char	Moderate to High	Moderate to High	Low to moderate

2.5.4. The technology status of Torrefaction Technology

Torrefaction technology, a promising method for biomass pretreatment, has seen significant development but faces challenges in commercialization. Despite its potential, the commercialization of torrefaction technology has been slower than expected. This is due to issues with reactor design and ensuring consistent product quality (Tumuluru et al., 2021). However, there is a strong market pull for torrefaction technology. Commercially, many setups have been established in Europe and worldwide. In Table 29 is presented TRLs levels of some torrefaction technologies implemented in Europe.

Table 29. Biomass waste torrefaction technology readiness levels (TRLs) (Thengane et al., 2022).

Plant Name	Torrefaction type	TRLs
AREVA (France), LMK Energy (France), Torrec (Finland), Andritz/ECN (Denmark/Netherlans)	Moving bed	TRL 6–8
Topell (Netherlands)	Fluidized bed and Entrained flow	TRL 6–9
Andritz (Austria), CENER (Spain), Torr-Coal (Netherlands),	Rotary drum	TRL 6–9
Arigna Fuels (Ireland), BioEndev (Sweden)	Screw or belt conveyor	TRL 4–6
CEA/CMI-NESA (France/Belgium)	MHF / Herreshoff oven	TRL 3–5
Rotawave (United Kingdom)	Microwave	TRL 1–3

2.6. Hydrothermal Liquefaction (HTL)

2.6.1. General review and evaluation of Biomass types for Hydrothermal Liquefaction Technology

Hydrothermal Liquefaction (HTL) is a thermochemical conversion method that transforms biomass with high moisture content into bio-crude oil, a promising alternative to petroleum-based fuels. Water imposes a dual role in HTL while under sub- and supercritical conditions (250 – 450^{o}C, 4-22 MPa) it acts both as a solvent and a catalyst and contributes to the depolymerisation of long carbon chains (Wikberg H. et al., 2015 and Yin S. et al., 2010) biomass types exhibit different levels of suitability and efficiency in HTL, largely depending on their composition and physical properties.

A Evaluation of Biomass types for Hydrothermal Liquefaction Technology

Waste biomass suitable for Hydrothermal Liquefaction Technology

The most used waste biomass types are demonstrated below.

Lignocellulosic waste biomass: This category includes a wide range of agricultural and forestry residues such as straw, corn stover, woodchips and sawdust (Zhang S. et al, 2020 and Bautista-Peñuelas E. et al., 2023). Lignocellulosic waste biomass is the most extensively studied biomass for HTL, while it is considered inexpensive and abundant. However, its high lignin content can reduce bio-crude yields and pretreatment is often required for efficient processing. Dedicated energy crops (e.g. miscanthus, switchgrass) also fall in this category, though their total value is reduced regarding sustainability and costs.

Algae (although is not waste biomass): Both macroalgae and microalgae have been tested and are considered promising for HTL due to their high lipid content, rapid growth rates and the ability to grow in diverse environments (Cheng F. et al., 2019 and Matricon L. et al., 2023). While algae-based HTL can result in high bio-crude yields, the economic feasibility is still a challenge due to the high cost associated with algae cultivation and harvesting. Significant research is ongoing to make the overall process more commercially viable.

Sewage sludge: As a byproduct of wastewater treatment plants, sewage sludge is produced in large quantities and the fact that it is rich both in organic material and moisture makes it an ideal feedstock for HTL (Kapusta K., 2018 and Fan Y. et al., 2022). Additionally, recent research on co-liquefaction of sewage sludge with other feedstock sources has shown promising results leading to a bio-crude oil yield increase (Xu D. et al., 2019). However, the variability in sludge composition can result in inconsistent product quality.

Other waste biomass feedstocks: Hydrothermal Liquefaction is a highly suited method for the conversion of organic liquid biomass into liquid bio-fuels, as it eliminates the need for the energy intensive step of drying. Non-recyclable plastics, food residues and manure are amongst the feedstock that has been tested through HTL technology (Seshasayee M. S. and Savage P. E., 2020, Poravou C. A. et al., 2022 and Aierzhati A. et al., 2022). Although these feedstocks can be processed using HTL, their efficiency varies, and additional water is often added to maintain optimal moisture content.

Feedstock preparation

Depending on the feedstock used and the sample total mass, pretreatment might be necessary to ensure that biomass enters the process in a homogenous and efficient form (Summers S. et al., 2024 and Zhang R. et al., 2019). Grinding or homogenization may be part of the pretreatment steps of the process. Moisture level differs through the various biomass types and is usually set to a standard ratio for comparison reasons. The addition of extra moisture is also applied in several cases, while alternative sources of process water have been investigated. However, the required moisture level is expected to be a minor preprocessing step for the avoidance of its high cost.

2.6.2. Design of Hydrothermal Liquefaction Technology

The design of Hydrothermal Liquefaction (HTL) technology includes several critical components and steps aimed at optimizing the process. These range from the selection and preparation of waste biomass, the main HTL process itself, to the subsequent separation and upgrading of the produced bio-oil.

Hydrothermal Liquefaction (HTL) typically occurs in high-pressure reactors, which can operate in either batch or continuous mode. The process is carried out under conditions determined by the critical point of water, with sub- and supercritical conditions (250–450°C, 4–22 MPa) applied for residence times ranging from 10 minutes to 4 hours, often in a reducing environment. In the past decade, the addition of catalysts has been extensively studied to increase bio-crude oil yields and optimize product ratios (Lappalainen et al., 2020 and Malins et al., 2015). A key observation is that process conditions influence each feedstock differently, impacting the overall outcome.

The HTL process generates bio-crude oil along with liquid, gaseous, and solid byproducts. Separation involves using organic solvents to extract the bio-crude oil, while filtration is used to remove solid residues. This step is crucial for isolating valuable bio-crude and managing byproducts efficiently.

A Influences of various operating parameters on bio-crude quality

The effect of temperature on the yield of HTL products is characterized by a sequential relationship. Initially, as the temperature rises, there is a corresponding increase in bio-crude yield, driven by enhanced reaction kinetics and the breakdown of biomass components (Tian et al., 2017). However, this trend is not linear, as further increases in temperature beyond a certain peak can inhibit the HTL process by causing the breakdown of liquid products into gases and promoting side reactions that generate undesirable byproducts (Tian et al., 2017). Therefore, selecting the optimal temperature for HTL is crucial. Careful consideration of these factors ensures that the process conditions not only maximize bio-crude yield but also enhance the quality of the end products. Optimizing temperature is essential for facilitating efficient biomass conversion while minimizing the formation of unwanted compounds, ultimately leading to a more sustainable and economically viable bio-crude production process.

Pressure plays a significant role in the hydrothermal liquefaction (HTL) process for bio-crude production. Elevated pressures can significantly enhance the reaction rate and increase bio-crude yield by ensuring that water remains in a liquid state at high temperatures, which is essential for hydrothermal reactions (Tian et al., 2017).. Higher pressure also improves the solubility of gases such as hydrogen and carbon dioxide in the reaction medium, facilitating critical chemical processes like hydrodeoxygenation, necessary for bio-crude upgrading (Shah et al., 2022). Additionally, optimal pressure levels contribute to reducing the oxygen content and increasing the hydrogen content of the biocrude, resulting in a higher heating value and improved fuel properties (Nava-Bravo et al., 2024). Furthermore, maintaining high pressure enhances the overall efficiency of the HTL process by minimizing unwanted byproduct formation and optimizing biomass conversion into bio-crude (Deepika et al., 2024).

Residence time, or the duration of the reaction, plays a crucial role in the HTL process for bio-crude production. Optimizing residence time is essential for maximizing bio-crude yield. While shorter residence times may prevent complete biomass conversion, excessively long durations can trigger secondary reactions that degrade the quality of the bio-crude (Shah et al., 2022). The energy content and stability of bio-crude are significantly influenced by residence time. Well-optimized residence times strike a balance between maximizing yield and ensuring high-quality bio-crude (Deepika et al., 2024). Achieving this balance is critical for the effective utilization of bio-crude as a renewable fuel source. Moreover, residence time affects the kinetics of hydrothermal reactions (Borazjani et al., 2023). Sufficient time is required for the breakdown of biomass components and the formation of biocrude; however, prolonged residence times may lead to the generation of unwanted by-products, which can adversely impact the efficiency of the process

(Borazjani et al., 2023). By carefully controlling residence time, the HTL process can be optimized for both yield and quality, contributing to more sustainable bio-crude production.

The heating rate in the HTL process plays a critical role in determining both the yield and quality of biocrude. A faster heating rate facilitates the decomposition of biomass, resulting in a more efficient conversion into bio-crude (Borazjani et al., 2023). Moreover, the kinetics of the reactions involved in the HTL process are positively impacted by faster heating rates (Shah et al., 2022). Lastly, maintaining higher heating rates can also reduce the formation of solid byproducts, which are typically undesirable by-products in the HTL process (Borazjani et al., 2023). In summary, the heating rate is a key parameter that influences not only the yield and quality of bio-crude but also the overall efficiency of the hydrothermal liquefaction process.

Catalysts (both homogeneous play a vital role in enhancing the efficiency of the HTL process for bio-crude production (Shah et al., 2022). One of the primary benefits of using catalysts in HTL is the significant increase in bio-crude yield. Metal-based catalysts, such as nickel and cobalt, are particularly effective in enhancing the conversion efficiency of biomass into bio-crude (Shah et al., 2022). By facilitating more complete reactions, these catalysts help maximize the amount of usable energy extracted from the biomass feedstock. In addition to improving yield, catalysts also enhance the quality of the produced bio-crude (Rasaq et al., 2024). They achieve this by reducing the oxygen content while increasing the hydrogen content, resulting in a bio-crude with a higher heating value and improved fuel properties (Rasaq et al., 2024). Furthermore, the implementation of catalysts in the HTL process can significantly reduce the formation of unwanted by-products (Moreira-Mendoza et al., 2024). By minimizing these by-products, catalysts not only streamline the process but also contribute to the stability of the final bio-crude product, ensuring its suitability for further applications. Catalysts also allow for more favourable reaction conditions by lowering the necessary temperature and pressure for the HTL process (Deepika et al., 2024). This reduction leads to improved energy efficiency and cost-effectiveness, making the overall process more economically viable. In summary, catalysts are instrumental in optimizing the hydrothermal liquefaction process, enhancing bio-crude yield and quality while minimizing by-products and improving overall efficiency.

Bio-crude characteristics

Bio-crude oil produced through HTL possesses several unique properties that position it as a promising intermediate for renewable fuel production. One key characteristic is its heating value, which typically ranges from 30 to 40 MJ/kg (Deepika et al., 2024). Although this is lower than that of petroleum crude, it remains significant for various energy applications.

Bio-crude oil is characterized by a high concentration of organic materials, encompassing aromatic hydrocarbons, phenols, fatty acids, alcohols, heterocyclic compounds, aldehydes, esters, ketones, amides, and amines (Shahbeik et al., 2024). The physicochemical properties of bio-crude exhibit average contents of carbon, hydrogen, nitrogen, oxygen, and sulphur at 58, 7.4, 3.9, 23.4, and 1.79 wt%, respectively (Shahbeik et al., 2024). Notably, the high carbon content plays a key role in achieving an acceptable heating value. However, due to its high oxygen and nitrogen content, bio-crude can be more corrosive than petroleum crude. This necessitates the use of corrosion-resistant materials in processing equipment to prevent degradation and ensure safe operations.

The average viscosity, total acid number, and density of bio-crude oil, as reported in the literature, are approximately 650×10^{-6} m^2/s (at 40 °C), ~67 mg KOH/g oil, and ~970 kg/m^3, respectively (Shahbeik et al., 2024). The viscosity of bio-crude oil is significantly higher than that of petroleum crude, which can affect its handling and processing; however, these issues can be mitigated through refining techniques (Kannan et al., 2020). This adjustment is crucial for optimizing the biocrude's suitability for a variety of applications, ensuring its effective use as a renewable fuel source.

Bio-crude oil upgrading

The use of bio-crude oil as a drop-in bio-fuel is challenged by the presence of oxygen and other heteroatoms, which result in high water content, increased acidity or corrosiveness, a low hydrogen-to-carbon (H/C) ratio, and suboptimal combustion characteristics (Shahbeik et al., 2024). To address these issues, various upgrading techniques are necessary. These include phase separation to reduce water content, hydrotreating to lower the levels of water, ammonia, hydrogen sulphide and viscosity, esterification to decrease acidity, hydro/catalytic cracking to improve the H/C ratio and cetane number, and emulsification to enhance fuel stability (Shahbeik et al., 2024, Elliott D. C. et al., 2013 and Summers S. et al., 2024).

Once separated, the bio-crude typically undergoes hydrotreating. Hydrotreating is a widely used method in petrorefineries that operates at moderate temperatures (300–450 °C) and high hydrogen pressures (up to 20 MPa) in the presence of a catalyst (NiMo, CoMo and HZSM-5) to remove water, ammonia, and hydrogen sulphide (Shahbeik et al., 2024). While hydrotreatment effectively upgrades biocrude, it faces challenges such as high coking rates, equipment corrosion from by-products like water, ammonium hydrosulfide, and hydrochloric acid, along with the associated costs and safety concerns of hydrogen supply (Shahbeik et al., 2024).

Solvent-catalytic esterification is a process used to upgrade bio-crude oil, and it involves a few key elements: 1) Mild Conditions: process is typically carried out at moderate temperatures (around 50-100°C) and atmospheric pressure, 2) Polar Solvents: such as methanol or ethanol, which are effective in dissolving the bio-crude and facilitating the esterification reaction, 3) Catalysts: Acidic catalysts (sulfuric acid or solid acid catalysts (e.g., zeolites) which help in converting free fatty acids in the bio-crude into esters, which are more stable and have better fuel properties, and 3) Enhanced Properties: The esterification process reduces the acidity and viscosity of the biocrude, making it less corrosive and more suitable for use as a fuel. The resulting esters have higher energy content and improved combustion characteristics.

The solvent-catalytic esterification is conducted under mild conditions (around 50-100°C) and utilizes polar solvents (methanol or ethanol) and acidic catalysts (e.g., zeolites) to enhance bio-crude oil properties (Shahbeik et al., 2024). The process enhances the fuel properties of biocrude, such as increasing its heating value and reducing its viscosity. This makes the bio-crude more suitable for use as a transportation fuel.

Catalytic cracking utilizes a specific catalyst to reduce the oxygen content of bio-crude oil in the presence of hydrogen at temperatures ranging from 500 to 550 °C (Shahbeik et al., 2024). This process effectively breaks carbon-carbon bonds, converting heavier hydrocarbons into lighter fractions (Shahbeik et al., 2024). This method reduces the oxygen content while increasing the hydrogen content (Moreira-Mendoza, C.A., 2024). However, it has limitations, including lower carbon recovery yields and rapid catalyst deactivation. Additionally, unlike hydrotreating, catalytic cracking typically produces low-energy bio-fuels due to the reduction in carbon content.

To address the limitations, hydrotreating and catalytic cracking are often combined into hydrocracking (Shahbeik et al., 2024). In hydrocracking, C–C bonds are targeted to produce lighter molecular weight saturated hydrocarbons under harsher conditions (>350 °C, 0.69–13.8 MPa), utilizing hydrogen donor solvents or hydrogen/carbon monoxide along with strong solid acid catalysts such as $Ni/Al_2O_3–TiO_2$ and H-Z. Nevertheless, challenges such as reactor clogging, catalyst deactivation, high costs, and the need for sophisticated equipment must be addressed to ensure the successful and efficient performance of hydrocracking (Shahbeik et al., 2024).

Active research is also focused on valorising byproducts, particularly the aqueous and solid phases. The nutrient-rich aqueous phase offers potential for various applications, while solid residues could be repurposed as soil amendments or used for further energy recovery.

2.6.3. The technology status of Hydrothermal Liquefaction

Hydrothermal Liquefaction technology is promising in terms of the production of liquid bio-fuels, offering a sustainable pathway to transition from conventional fuels to alternative ones, without the need of tremendous infrastructure modifications. However, reaching the critical conditions of water requires exceptional energy consumption and costly equipment. Thus, HTL is currently running mostly in lab or pilot-scale reactors, in an experimental development status.

For the moment, in an international level a few companies have initiated pilot and demonstration HTL plants. Steeper Energy (Canada, Denmark), Licella (Australia) and Algenol Biotech (USA) are some indicative examples of pilot-scale constructions (Lappalainen J. et al., 2020, Malins K. et al., 2015, Elliott D. C. et al., 2013, Summers S. et al., 2024 and SundarRajan P. et al., 2021).

The main challenges in the HTL developmental path are the economic feasibility, the feedstock optimization and the final product quality. Attempting economic feasibility, scientists have investigated the efficient utilization of byproducts in several different applications or even the use of Concentrated Solar Power for the coverage of the process energy needs, instead of electric energy. A combination of these solutions would significantly reduce the overall costs and provide a sustainable, environmentally friendly bio-fuels production line.

2.7. Hydrothermal Carbonisation (HTC)

Hydrothermal carbonisation (HTC) is a thermochemical process where biomass is heated at temperature in the range 160 – 250 °C in presence of water in confined system, at pressure 2 – 6 MPa with a process duration starting from few minutes up to 24 hrs (Funke & Ziegler, 2010; González-Arias et al., 2022). Water under pressure and temperature typical of HTC process is under subcritical conditions and thus acts both as solvent and reaction catalyst facilitating hydrolysis reactions of polysaccharides, lignin and other high molecular weight organic substances (proteins, nucleic acids) as well as disintegration of physical properties of biomass (Nicolae et al., 2020). During HTC exothermic reactions take place resulting in decarboxylation (removal of oxygen containing functional groups of organic matter, like-COOH) and dehydrogenation (removal of H containing functional groups). Formed low-molecular weight substances are subjected to further transformation, including condensation reactions and formation of aromatic and even condensed aromatic structures (Pauline & Joseph, 2020; S. Wu et al., 2023). As main product of HTC process a carbonaceous material – hydrochar (HC) is formed characterized by higher oxygen containing functional groups and lower specific surface area of in comparison with bio-chars obtained from pyrolysis (Cavali et al., 2023; Masoumi et al., 2021). During HTC high molecular weight soluble substances similar to natural organic matter called artificial humic substances are formed. Artificial humic substances can find applications, similar to natural humic matter, in agriculture, environmental technologies and other fields (Yang et al., 2021). Changing HTC process parameters shift can be achieved towards one or another group of HTC products.

2.7.1. General review and evaluation of Biomass types for Hydrothermal Carbonisation Technology

HTC commonly is used for processing of plant material, but also biomass of lower organisms (bacteria, yeasts, fungi etc. as common in wastewater treatment activated sludge) or higher organisms (animal fats etc.) can be used. In HTC all types of organic residues can be considered as potential sources: green waste, agricultural waste, forestry waste, municipal solid waste, waste from food processing industry and waste from markets (De Mena Pardo et al., 2016; Romano et al., 2023). Quality criteria for waste materials to be used in HTC process includes: 1) amount of organic carbon, nitrogen; 2) moisture; 3) inorganic residues (De Mena Pardo et al., 2016). For each waste type a set of quality criteria, with minimum and maximum values tolerable for the HTC process can be identified, especially for pilot and industrial scale applications.

As source materials for HTC process any lignocellulosic biomass material can be used and many examples of HTC versatility and robustness in respect to biomass has been demonstrated (Jain et al., 2016; Tekin et al., 2014) using as starting material orange peels, oak tree leaves, wood, nut shells, straw, olive oil waste, corn stalks and many other biomass wastes (Bao et al., 2024; Cavali et al., 2023; González-Arias et al., 2022; Peng et al., 2023; Zhou et al., 2023). Also algae biomass can be used in HTC process to produce hydrochar and humic like substances. In general, HTC process can be used for processing of agricultural, forestry, fishery, food production, processing wastes and presently no barriers have been found in respect to limitations of biomass use in HTC process. Among the huge range of organic wastes, 5 main wet substrates are considered to be most prospective for processing in HTC process (Zhuang et al., 2022): 1) sewage sludge from municipal wastewater treatment plants; 2) digestate from anaerobic digestion plants; 3) green waste; 4) household wastes; 5) organic fraction of municipal solid waste.

Sewage sludge (activated sludge) is dominantly a biomass formed by different groups of microorganisms (bacteria, moulds, yeasts etc) and organic matter, inorganic sediments, nutrients, water, and a range of contaminants possibly containing also pathogenic microorganisms. Sewage sludge is a waste of the wastewater treatment with global annual production estimated at 45 million tons (Giwa et al., 2023) and thus can be considered as one of major organic waste streams. In comparison with dry thermochemical processing methods, HTC provides possibility to use wet sludge mass, achieve destruction of microorganisms, organic pollutants, even microplastics and provides possibility to produce products with diverse applications (Cui et al., 2024; Kowalski et al., 2024; Nahar et al., 2024). Presently the use of HTC for sewage sludge processing/utilisation seems to be one of the most promising direction of applications (Liu et al., 2022; Paiboonudomkarn et al., 2022).

Organic substrate for HTC process before processing must be homogenised (milled) and mixed with water, if the substrate is injected in liquid phase, with moisture content up to 85%. Most of difficulties of biomass pre-treatment are related to the heterogeneity of the raw material over time and among different biomass types. Contaminations and/or varying compositions can cause fundamental problems and hinder a HTC process. A great flexibility of the HTC process can be ensured with respect to the biomass feedstocks and thus biomass processing using HTC do not much depend on the feedstock and short term and long term changes are possible without any major modification or adjustment of the HTC process (De Mena Pardo et al., 2016; Romano et al., 2023). Not only the characteristics of the biomass, but also its contamination with inert inorganic material such as stones, metal pieces, sand or dust is of importance and the limits for the inorganic material should be established, especially when hydrochar is employed as bio-fuel also with respect to mechanical properties (De Mena Pardo et al., 2016; Romano et al., 2023).

2.7.2. Design of Hydrothermal Carbonization Technology

The hydrothermal carbonization of biomass consists of 4 main phases: hydrolysis, dehydration and decarboxylation, condensation and polymerization, aromatization. (Pauline & Joseph, 2020) During hydrolysis phase, the sub-critical conditions increase the ionic constant of water, making it more efficient in bond cleavage. Each biomass component has a different hydrolysis onset temperature: hemicellulose hydrolysis starts at 180 °C, cellulose at 230 °C and lignin above 260 °C (Reza et al., 2014). The result of the hydrolysis phase is a mixture of monosaccharides and oligomers, as well as phenolic compounds derived from lignin. Inorganic compounds, mainly alkali and alkali earth metals, can also be released in the water during this phase; these inorganic compounds can promote the hydrolysis itself, but hinder the subsequent reactions (Funke & Ziegler, 2010). During the dehydration and decarboxylation phase, the small compounds formed during hydrolysis further react losing water and CO_2, thus forming organic compounds such as aldehydes, furans and acids (e.g. acetic, lactic, propionic and formic acid) and lowering the pH of the reaction medium (Sevilla & Fuertes, 2009b). These reactions are favoured by low pH values that are caused by the reaction products themselves; for this reason, the dehydration and decarboxylation phase is often referred to as autocatalytic (Titirici et al., 2012). The organic compounds dissolved in the water phase then follow the reactions of polymerization and condensation, starting to form solid particles (Sevilla & Fuertes, 2009b). The formed solid particles can undergo the aromatization process that causes the growth of aromatic structures. When the aromatic structures reach a critical concentration, they start to nucleate and enlarge forming the hydrochar that agglomerates in microspheres (Xia et al., 2000). Given the right conditions of temperature and residence time, the microspheres increase in size (Sevilla & Fuertes, 2009a); the final temperature of the process regulates the equilibrium among hydrochar, liquid products and gas (Lin et al., 2016).

The outcome of HTC process in terms of products yields and properties is strongly dependent on both feedstock characteristics and process variables, such as temperature, pressure, reaction time, pH, heating rate and biomass to water ratio (substrate concentration). In the following the influence of each process variable is clarified:

- Temperature: it is a critical factor in HTC process that must be contained in a specific range. At low temperatures (~200 °C) some components of the biomass do not undergo hydrolysis, causing the occurrence of pyrolysis-like reactions (Bobleter, 1994). On the other hand, a too high temperature can shift the water state from subcritical to supercritical conditions, raising the gaseous products yield at the expenses of hydrochar yield like in the case of supercritical water gasification (Savage, 1999). However, higher temperatures also causes a reduction in both O/C and H/C ratios of hydrochar, leading to a higher energy density, which is relevant for its use as solid fuel (Peng et al., 2023).

- Pressure: it increases during the HTC process with the increase of temperature but can also be increased by inert gas introduction in the reactor vessel. A higher pressure contributes to keep the water in subcritical conditions and increase the rate of biomass hydrolysis (Akhtar & Amin, 2011).
- Reaction time: together with temperature it is a crucial process parameter, as they both define the HTC severity. A sufficient residence time is needed for the polymerization and condensation reactions to happen (Kang et al., 2012). While temperature mostly influence hydrochar yield, reaction time is more relevant in defining hydrochar morphology.
- pH: normally, water pH tends to decrease during HTC due to the release of acidic species; low pH favours the hydrochar formation, so the process is considered to be autocatalityc (Titirici et al., 2012). There is also the possibility of altering the water pH, and it has been observed that both very high and very low pH values can effectively change the reaction pathways and, consequently, products distribution and properties (Lu et al., 2014).
- Heating rate: in HTC process the heating rate must be moderate; high heating rates promotes the formation of liquid products at the expense of hydrochar yield, thus are usually employed for Hydrothermal Liquefaction (HTL) processes (Akhtar & Saidina Amin, 2012).
- Substrate concentration: the ratio solid/liquid is a less explored variable, even if it appears to be relevant. Varying the substrate concentration affect mainly the energy and material transfer properties of the system, affecting the rate at which hydrolysis reactions occur: the more the solid, the more the time needed to form the hydrochar (Funke & Ziegler, 2010). Substrate concentration also affect hydrochar morphology (Li et al., 2011).

A key aspect of HTC design is the reactor choice, since the system must be able to reach and sustain the desired operational conditions. The most common configuration at lab scale is autoclave or batch reactor (Ischia & Fiori, 2021), which is convenient to realize and operate; moreover, it can be coupled with several heating sources, giving the possibility to explore unconventional techniques such as microwave (Holliday et al., 2022) or solar assisted heating (Ischia et al., 2020). On the other hand, the use of a batch reactor dictates the need for interrupting the process to cool down and refill the system, implying low productivity (Ho et al., 2024). For this reason, the use of continuous reactor is almost mandatory for the scale up of HTC process; however, this introduces several technical difficulties, among which the main one is the design of a feeding system that can introduce the feed into the high pressure zone of the reactor. Several literature papers considered possible configurations for lab and pilot scale HTC continuous reactors, such as:

- Twin-screw extruder (Figure 43) (Hoekman et al., 2017), in which the biomass is feed from one side and the produced slurry is recovered from the other side of the reactor. The pressure increment is obtained thank to the peculiar geometry of the screw that transport the biomass along the reactor body. In this configuration the process water is pre-heated and feed in the middle of the reactor.

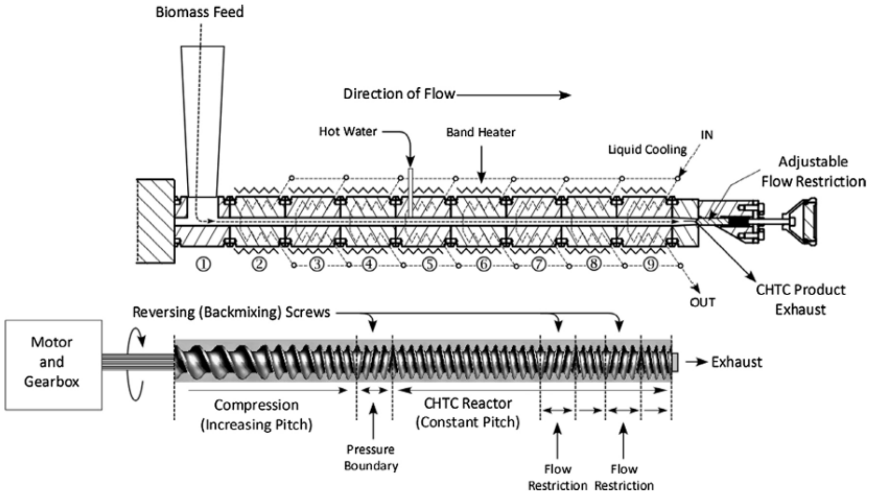


Figure 43. Twin-screw reactor configuration, from (Hoekman et al., 2017)

- V-shaped tubular reactor (Figure 44) (Hoekman et al., 2014), made up by two auger transporters connected to form a V. The first auger is the biomass feeder, while the second auger carries the hydrochar outside of the reaction zone and to the collection vessel. The whole system is pressurized, but the reaction zone is confined to the bottom of the V zone, where the hot water is retained.

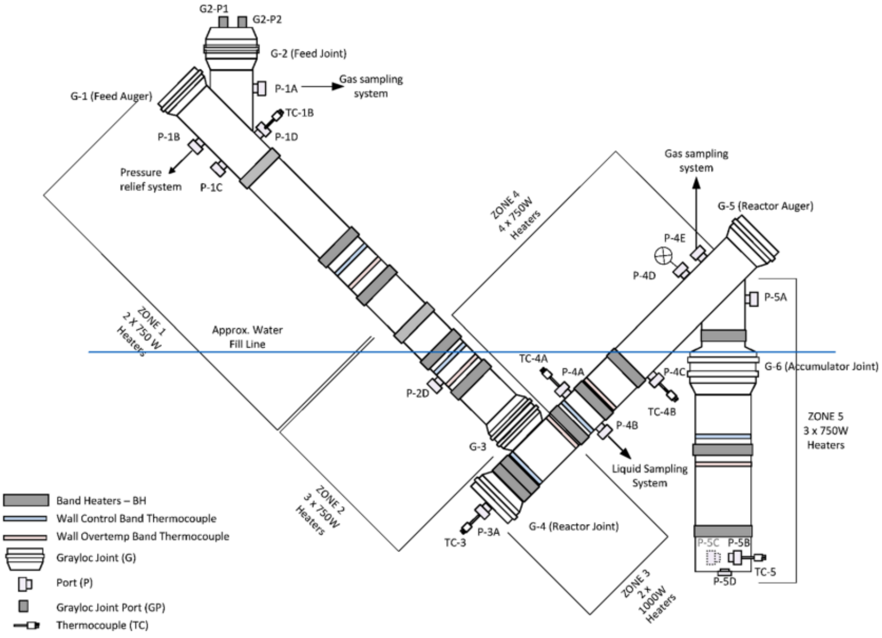
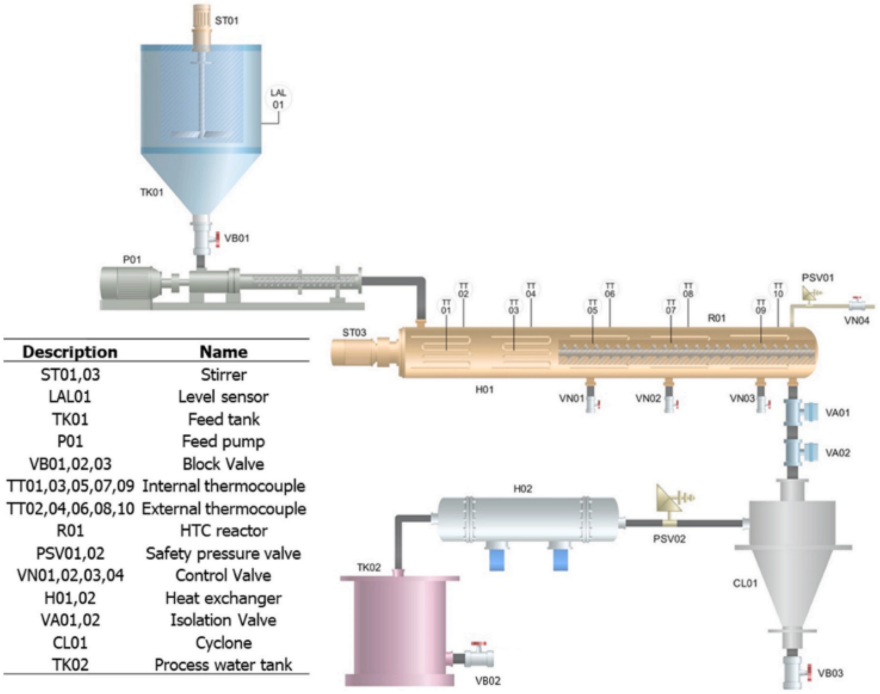


Figure 44. V-shaped tubular reactor configuration, from (Hoekman et al., 2014).

- Agitated tubular reactor (Figure 45) (Ipiales et al., 2024), that is a stainless-steel tube containing an agitation system to avoid solids deposition along the reactor walls. In this case, the feed is pressurized trough a screw pump feeder and the pressure gradient generated between the inlet and the outlet of the reactor keeps the slurry moving.



Description	Name
ST01,03	Stirrer
LAL01	Level sensor
TK01	Feed tank
P01	Feed pump
VB01,02,03	Block Valve
TT01,03,05,07,09	Internal thermocouple
TT02,04,06,08,10	External thermocouple
R01	HTC reactor
PSV01,02	Safety pressure valve
VN01,02,03,04	Control Valve
H01,02	Heat exchanger
VA01,02	Isolation Valve
CL01	Cyclone
TK02	Process water tank

Figure 45. Agitated tubular reactor configuration, from (Ipiales et al., 2024).

There is also notice of successfully implemented HTC continuous systems in high TRL plants, even if no technical details have been disclosed (Heidari et al., 2019).

Finally, regarding products utilization, hydrochar have low surface area and porosity, however use of surface modification and activation can help to transform this material for specific applications (Islam et al., 2022; Masoumi et al., 2021). Process water and also ashes contain plant nutrients and they could be used as fertiliser in agriculture and forestry (artificial humic substances). This should be relatively easy for agro-industrial residues and phosphorus from the ashes and potassium and nitrogen from the process water can be returned as natural fertilizer (Khalaf et al., 2023). The use of hydrochar as fertilizer and soil conditioner is also promising (Masoumi et al., 2021). It is known that a high carbon content of the soil is beneficial for plant growth. With an optimized application of hydrochar (or modified hydrochar) to the soil a second business model is possible which is a more environmentally sound application of hydrochar, low value wet feedstocks which can be converted into a soil conditioner (Carrasco et al., 2022). A promising application is the use of hydrochar as adsorbent (Ansone-Bertina et al., 2024). Thereby, different cases can be explored. It has already been demonstrated that, in principle, hydrochar can be transformed into active carbon (Zhang et al., 2024). This material possesses a high surface area, a high carbon content and a low oxygen content. This makes hydrochar per se a promising adsorbent material with properties different from classical, commercial active carbon (L. Wu et al., 2021). However, for commercial products two conditions have to be fulfilled.

The production of hydrochar for this application will be limited to certain raw materials and quality control of these materials has to be rigorous. In order to guarantee the quality of the adsorbent, characterization of hydrochar has to be standardized with respect to the chemical structure. In addition, for this type of higher value material also the inorganic content might play a role. For instance, if the material should be applied for water purification, it has to be assured that no undesired metal leaching occurs. Therefore, it can be speculated that, when adsorption applications are proposed, the production of the corresponding adsorbents has to be optimized for particular feedstocks.

2.7.3. The technology status of Hydrothermal Carbonisation

One of the primary benefits of HTC is its capability to process wet biomass without requiring energy-intensive drying, a common limitation in other biomass conversion technologies such as pyrolysis or gasification (Maniscalco et al., 2020, Ischia et al., 2024). This feature makes HTC particularly effective for managing various types of organic waste, including sewage sludge, agricultural residues, and food waste, which generally have high moisture content. The ability to transform these waste streams into valuable products like hydro-char, biogas, and liquid bio-fuels positions HTC as a versatile technology with applications in multiple sectors, including energy production, agriculture, and waste management (Cao et al., 2021, Wang et al., 2019, Khan et al., 2019). Recent advancements in HTC technology have concentrated on enhancing process efficiency, optimizing reactor designs, and broadening the range of feedstocks that can be effectively treated. For example, continuous feed reactors have been developed to facilitate large-scale, industrial applications of HTC, addressing a key challenge in scaling up the technology from laboratory to commercial scales. These technological innovations have significantly improved the feasibility of HTC for large-scale operations, making it a competitive option for biomass conversion in both developed and developing countries.

There are multiple influencing factors in HTC products. Understanding how biomass behaves under hydrothermal conditions, particularly with the help of various catalysts, such as alkaline and transition metals, is a crucial first step in unravelling the complex liquefaction mechanism of lignocellulosic biomass and its impact on product quality and yield. The use of different catalysts and thermal operating conditions can enable the production of various lignocellulosic HTC products (Rasaq et al., 2024). Moreover, the process parameters, which include temperature, water content, pH, and retention time, determine the characteristics of the final products. Lower solid products are produced at higher temperatures, the carbon concentration rises, while the hydrogen and oxygen content declines (Sivaranjanee et al., 2023).

The environmental benefits of HTC have significantly driven interest in this technology. Hydro-char, the primary product of HTC, can be utilized as a solid fuel, a soil amendment, or a precursor for activated carbon, depending on its properties and the feedstock used. Moreover, the HTC process contributes to carbon sequestration by stabilizing carbon in a solid form that resists decomposition. This potential for carbon sequestration aligns with global efforts to mitigate climate change by reducing atmospheric CO_2 levels (Hu et al., 2010, Farru et al., 2024). Additionally, the liquid by-products of HTC, which are rich in valuable nutrients, can be recovered and used in fertilizers, enhancing the overall sustainability of the process.

Despite its numerous advantages, HTC technology still faces several challenges that need to be addressed to realize its full potential. These challenges include the variability in feedstock properties, which can affect the consistency and quality of hydro-char, the energy requirements for maintaining the high-pressure, high-temperature conditions necessary for the process, and the economic feasibility of scaling up the technology to industrial levels. Additionally, the market for hydro-char and other HTC-derived products is still developing, and there is a need for more comprehensive economic and environmental assessments to support the widespread adoption of HTC. A recent paper reported a detailed global inventory of existing HTC facilities, highlighting their geographical distribution and application trends (Farru et al., 2024). Most of the companies are located in Europe, followed by Asia and North America. With significant participation from HTC companies—over 62% of those surveyed (15 companies)—the study offers a comprehensive overview of various companies, their business models, regulatory challenges, and the overall state of HTC technology. The existing HTC plants and companies worldwide are summarized in Table 1 of reference (Farru et al., 2024). One can observe the dominance of companies located in Europe, with a total of 19 companies (79.2%). Among these, nine are based in Germany; two each in Italy, Spain, Switzerland, and the United Kingdom; and one each in Sweden and the Netherlands. In Asia, three companies are located in Japan, and one in the Republic of Korea. Finally, only one company is based in North America, specifically in the USA. Figure 46 presents a choropleth map illustrating the distribution of HTC companies and plants worldwide (Figure 46a), with detailed views for Europe (Figure 46b) and Asia (Figure 46c) (Farru et al., 2024).

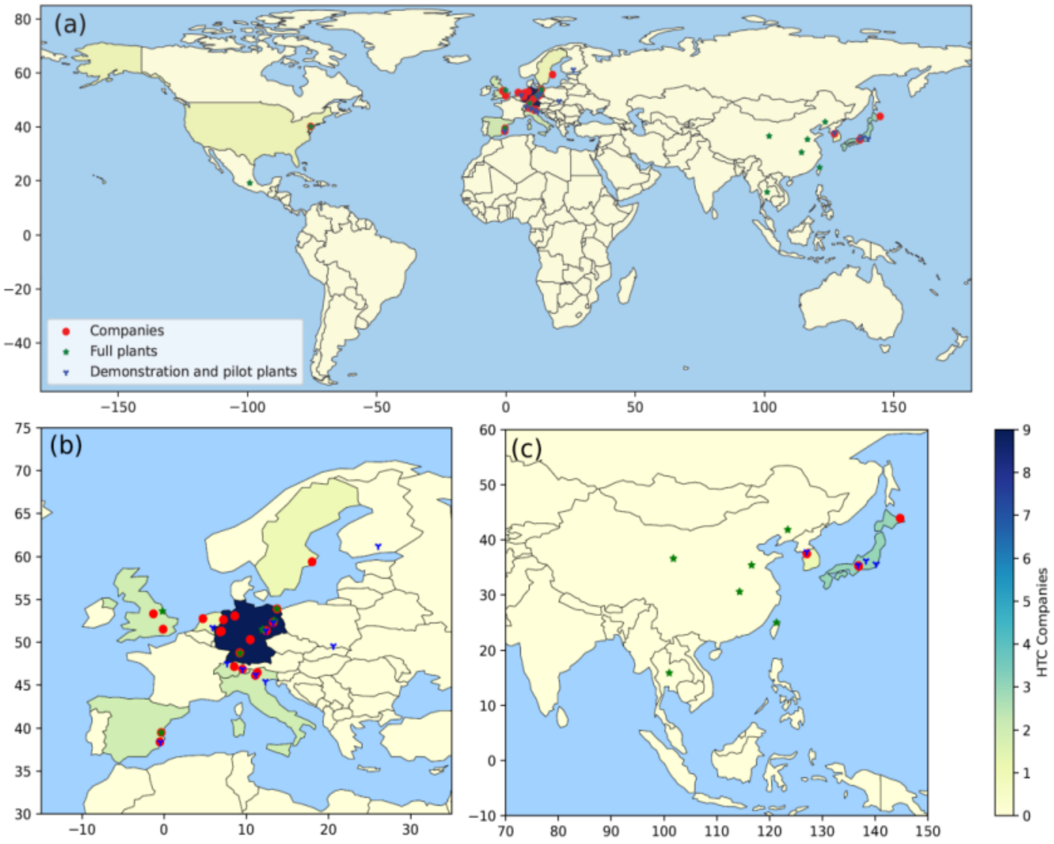


Figure 46. Distribution of HTC companies and plants: (a) worldwide, (b) in Europe, (c) in Asia. The figure has been reproduced with permission from reference (Farru et al., 2024).

Overall, the prospects for HTC are promising, with ongoing research and development efforts focused on overcoming the current challenges and unlocking its full potential. As the world continues to seek sustainable solutions for waste management and renewable energy, HTC is poised to play a significant role in the transition to a circular economy and a low-carbon future.

HTC technology has been advancing across different stages of development, with its Technology Readiness Level (TRL) varying based on the application and scale (Munir et al., 2018, Cebi et al., 2022, Kota et al., 2022).

Laboratory and Pilot Scale (TRL 4-6):

HTC technology is extensively explored at the laboratory and pilot scale, with significant research aimed at optimizing process parameters, understanding feedstock variability, and improving product quality. Recent advancements have focused on scaling HTC from lab settings to pilot plants. For example, pilot-scale HTC reactors have been developed to process various biomass types, such as sewage sludge, agricultural residues, and food waste. These efforts are critical in addressing operational challenges and refining the process for larger-scale applications. In Europe, particularly in Germany, pilot plants have been established to treat municipal waste, while in the United States, similar efforts have focused on agricultural residues.

Pre-Commercial and Demonstration Scale (TRL 6-7)

As of the early 2020s, HTC technology has progressed to the pre-commercial stage, with demonstration plants being built to validate the technology in real-world conditions. These projects are crucial for proving the economic viability and technical reliability of HTC at a scale approaching industrial applications. For instance, in Switzerland and the Netherlands, demonstration plants have been integrated with existing waste management systems to convert municipal solid waste and industrial by-products into hydro-char. These plants serve as important steps toward full-scale commercialization, providing insights into process integration and economic performance.

Commercial Deployment (TRL 8-9)

Although full commercial deployment (TRL 9) is still emerging, some companies are advancing toward this stage by establishing commercial-scale HTC plants. These facilities, designed to handle large volumes of biomass, produce hydro-char for specific markets such as energy production or soil enhancement. In countries like Denmark and Italy, commercial-scale HTC plants are being developed, marking significant progress towards achieving TRL 9. These developments focus on overcoming technical challenges related to reactor design, process optimization, and feedstock logistics, as well as addressing regulatory and market acceptance.

2.8. Plasma Technology

Plasma is often described as the fourth state of matter, a fully or partially ionised gas or a quasi-neutral gaseous state in which the densities of positive and negative charges are equal and the internal electric field strength is zero. Plasma is generated by applying an external electrical energy source to a gas (Air, O_2, water vapour, N_2, Ar, CO_2 or mixtures of these gases), resulting in the formation of charges. Electrons and ions are produced in the gas phase when electrons with sufficient energy collide with neutral atoms and molecules in the carrier gas. The main parameters of plasma are: temperature, concentration of charges, and pressure (Ayesha Tariq Sipra, 2018), with plasma often being categorised as hot or cold plasma. Plasmas are generated by a variety of methods, such as high-intensity electric arcs, microwaves, shock waves, radio-frequency induction and laser or high-energy particle beams. In addition, plasma can be generated by heating gases in a furnace at elevated temperatures (Vineet Singh Sikarwar, 2020) or plasma can be generated through electricity and involves a large potential difference applied across two electrodes, for example, using a dielectric barrier discharge process (DBD) (Gao, et al 2021).

The use of plasma is an alternative thermochemical technology suitable for the physical/chemical degradation of a wide range of organic and inorganic material such as municipal, industrial and hazardous wastes (B. Ibrahimoglu, 2020). Plasma degradation converts wastes/biomass into primarily syngas and char. The use of high temperature plasma gasification process, (usually between 1500 °C and 5500 °C, in some cases up to 14 000 °C) guarantees the fully conversion of toxic and harmful compounds (e.g. dioxins, furans, polycyclic aromatic hydrocarbons, volatile substances) into primary and harmless elements (in the gas phase). In addition, the formation of tar and carbon in the plasma gasification process is limited (L. Mazzoni, 2017). The plasma gasification process enables the production of cleaner conversion products, a key advantage that plasma can offer over conventional gasification processes (A. Sanlisoy, 2017), along with high conversion efficiency up to 99.99%. The major disadvantages associated with the use of plasma are the energy requirements and the initial capital cost associated with the reactor technology.

2.8.1. General review and evaluation of Biomass types for Plasma Technology

Plasma technology has advantages for the treatment of a wide range of waste types, including hazardous waste and biomass waste. In addition, plasma technology has no limitations in the treatment of organic and inorganic waste. Using a high temperature environment ensures reduced generation of greenhouse gases. In work (Dovilė Gimžauskaitė, 2022), authors have carried out a detailed analysis of the results of the most recent studies, which show the diversity of usage feedstock for plasma gasification (Table 30). The table presents information not only on biomass, which is the primary focus of this report, but also on various types of waste. This inclusion addresses the lack of data on different categories of waste biomass, and the additional waste types provide more data for comparison purposes. As can be seen from the data in the table, a variety of solid and liquid feedstocks are used for plasma gasification, including biomass. However, the primary interest in plasma technology is focused on the conversion of various wastes that are difficult to process using standard gasification technologies due to their high energy demands and specific requirements. Dimitrakellis et al, 2020, reviewed the use of plasma technology for the conversion of lignocellulosic biomass. They reviewed the used of plasma technologies, for the pretreatment of biomass (Table 31), plasma assisted liquifaction, plasma pyrolysis and plasma gasification.

Table 30. Summary results of feedstock usage in different plasma gasification technologies (Dovilė Gimžauskaitė, 2022).

Discharge type	Power, kW	Gasifying agent type and content, g/s	Additional gas	Feedstock type and content, g/s	LHV MJ/Nm^3	H_2, vol%	CO, vol%	H_2/CO ratio	Thermal efficiency, %
Rotating direct current (DC) arc plasma	15	CO_2, 0.24	None	Textile dyeing sludge, 0.6	8.91	27.5	48.58	0.57	n.d.
Transferred-arc plasma	160–190 A	Ar, 20–30 L/min	None	Petroleum sludge, 20 g per batch	7.40–7.86	43.79–50.97	8.45–11.18	3.92–5.99	n.d.
DC arc plasma	120	Steam, 0.3	CH_4	Lignite, 8.3–16.7	8–11	±50–62	±22–29	1.72–2.68	n.d.
DC arc plasma	137	Steam, 0.44	CO_2	Wood sawdust, wooden pellets, 8.3	±10–12	±39–45	±47–50	±0.83–0.9	59
DC arc plasma	100	Steam, 0.39	CO_2, O_2	RDF, 5.6–16.7	n.d.	29–58.5	33.8–56.1	0.58–1.72	58
DC arc plasma	97–140	Steam, 0–2.9	CO_2, O_2	Pyrolytic oil, 2.4–2.9	9.4–12.1	19–57.7	32.7–53.2	0.36–1.76	58–59
DC arc plasma	33.3	Steam, 2.78–3.33	None	Hard wood shaving, 0.42	9.28	55.2	14.5	3.81	n.d.
DC arc plasma	22.4	Steam, 2.78–3.33	None	PB&MDFB* 0.69	9.18	56.4	14.1	4	n.d.
DC arc plasma	26.3	Steam, 2.78–3.33	None	Peach pits, 0.86	10.74	57	18.8	3.03	n.d.
DC arc plasma	39	Steam, 2.78–3.33	None	Almond hulls, 1.03	7.99	52.4	11.7	4.48	n.d.
DC arc plasma	27.2	Steam, 2.78–3.33	None	Grape pomace, 1.33	9.45	59.1	14.1	4.19	n.d.
DC arc plasma	31.1	Steam, 2.78–3.33	None	Coffee ground, 1.56	9.75	77	4.1	18.78	n.d.
DC plasma	120	Steam, 5	None	RDF, 8.06	10.9	53	29.8	1.77	n.d.
DC plasma	120	Steam, 6.42	None	RDF, 8.06	10.7	53	27.2	1.95	n.d.
DC plasma	120	Steam, 2.4	CO_2, Ar	RDF, 8.06	10.5	37	42	0.88	n.d.
DC plasma	120	Steam, 1.88	O_2, Ar	RDF, 8.06	10.4	45	37	1.22	n.d.
DC arc plasma	56	Air	None	Crude glycerol, 5.6	7.32	29	27	1.07	74.1
DC arc plasma	62.4	Water vapor	Air	Crude glycerol, 5.6	9.82	51.16	24.74	2.07	76.1
DC arc plasma	48.8–55	Water vapor, 2.63–4.48	Ar	Crude glycerol, 2	10	50	25	2	58–75
DC arc plasma	45–61	Water vapor, 2.4–4.5	Ar	Pure glycerol, 4	9.83–10.64	46	25	1.84	n.d.
DC arc plasma	56	Water vapor, 2.63–4.48	Ar	Pure glycerol, 2–4	11	47	25.2	1.86	52

DC arc plasma	48–56	Water vapor, 2.63–4.48	Ar	Pure glycerol, 2	n.d.	47	25	1.9	51
Rotating DC arc plasma	24.1	Water in glycerol	Ar	The mix of pure glycerol and water, 0.5	11	56	38	1.47	40
MW plasma	2	Steam/O2, 7.2 mL/min/2.6 L/min	N_2	Pure glycerol, 2–3.5 L/min	12	57	35	1.63	n.d.
DC arc plasma	49–56	Water vapor, 2.63–4.48	Ar	Wood, 1.2	n.d.	45.2	21	2.2	45.6

***PB&MDFB** - Particle Board and Medium Density Fiber Board (wood products made from wood fibres and adhesives)

Table 31. Summary of plasma pretreatment of lignocellulosic feedstock (Dimitrakellis et al 2022).

Substrate	Plasma treatment	Main results
Wheat straw	Dry treatment, parallel-plate DBD, air, AC HV, 20–25 kHz, 1.5 min	84% total sugar yield after enzymatic hydrolysis
Wheat straw	Dry treatment (remote), coaxial DBD, air and O_2, pulsed AC 18.4 kHz, 230 W, 1–7 h	95% delignification, 78% glucose yield after enzymatic hydrolysis, 52% ethanol yield
Wheat straw	Liquid treatment (above-liquid plasma), DI water, commercial plasma jet, Ar/O_2 1%, 20 min	1.8-fold increase in reducing sugar production after enzymatic hydrolysis
Sugarcane bagasse	Liquid treatment (above-liquid plasma), Aq. Na_2CO_3 + NaOH, DBD with non-contact electrodes, air, AC HV 3.5 kV, 60 Hz, 2 h	58.5% lignin solubilization at pH 12, 51.3% glucose and 38.5% xylose yields after enzymatic hydrolysis
Bagasse	Liquid treatment (above-liquid plasma), ionic liquid, plasma jet, He, pulsed DC 3 kV, 10 kHz, 4 h	2-Fold increase of solubility in [Emim]Oac
Japanese cedar	Liquid treatment (above-liquid plasma), ionic liquid, plasma jet, He, pulsed DC 3 kV, 10 kHz, 4 h	Enhanced solubility of cellulose due to lignin disruption, selective extraction
Cornstalk	Dry treatment, parallel-plate DBD, N_2/steam, AC HV 3 kV, 2 h	1-Step hydrolysis through acidification, 76.65% conversion, 32.37% sugar selectivity
Miscanthus grass	Liquid treatment (microbubbles), DBD, air, AC 16.4 kV_{rms}, 21.2 kHz, 10% duty cycle, 3 h	0.5% acid-soluble lignin, 26% sugar release (2.5-fold increase) after enzymatic hydrolysis
Water hyacinth	Liquid treatment (in-liquid plasma), $FeCl_3$ solution, 450 V, 30 min	Lignin reduction from 23.7 to 18.4% crystallinity reduction from 31.2 to 25.1%, 126.5% increase in sugar yield in enzymatic hydrolysis
Cassava starch waste (CSW)	Liquid treatment (in-liquid plasma), H_2SO_4, pulsed 0.4 kV, 30 kHz, 300 min	1-Step plasma and hydrolysis, TRS yield 99% and glucose yield 47.9%
Spent coffee waste	Dry treatment, parallel-plate DBD, $FeCl_3$, H_2SO_4, air, AC HV 70 kV, 50 Hz, 2 min	Lignin removal/0.496 g reducing sugar per g SCW after enzymatic hydrolysis/74% fermentation efficiency (2-fold)
Brewer spent grain	Liquid treatment (submerged DBD jet), air, AC HV 28 kV, 10 min	2.1-Fold increase in reducing sugar yield after enzymatic hydrolysis

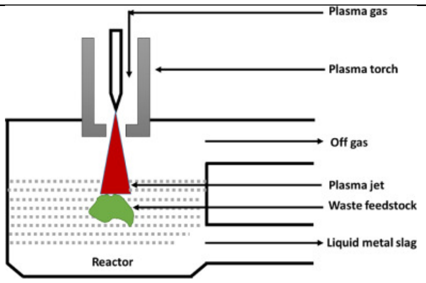
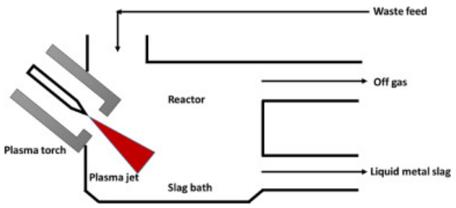
Plasma treatment of biomass has been initiated with the aim of using biomass more efficiently for energy and fuel production(Hrabovsky, 2011). providing a superior quality of syngas for advanced fuel and energy production technologies, without CO_2, methane, tars or other components. The need to produce clean, compositionally controlled syngas leads to the use of technologies that rely on an external energy supply to gasify the material. is the medium with the highest energy content and therefore a much lower plasma flow is required to provide sufficient energy compared to other media used for this purpose. This results in minimal plasma gas contamination of the syngas produced and easy control of the syngas composition.

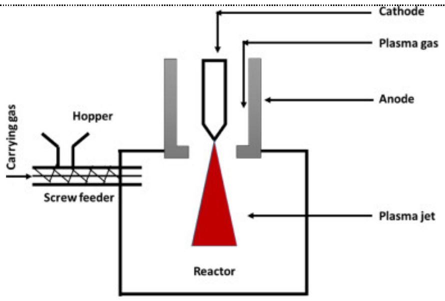
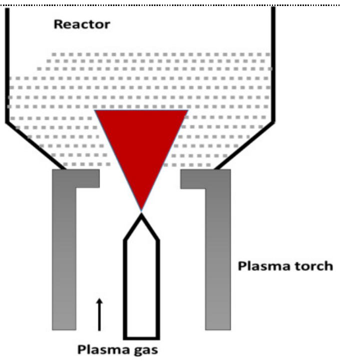
Feedstock preparation is also important for higher process efficiency and feedstock conversion conventional gasification, depending on the type of reactor used, feedstock preparation is also required. This usually involves drying, compaction, crushing, homogenisation, etc. Since gasification is aimed at the production of synthetic gases as an intermediate for the synthesis of further bio-fuels or biochemicals, the cleaner the feedstock, the fewer technological and operational problems are involved.

2.8.2. Design of Plasma Technology

Thermal plasma gasification is usually carried out in fixed or moving bed reactors and entrained flow reactors. The main reactor type are presented in a Table 32.

Table 32. Comparison of different designs of plasma reactors (Vineet Singh Sikarwar, 2020).

Reactor type	Principal scheme	Advantages / Disadvantages
Fixed/moving bed	 	Advantages: simple reactor design, efficient heat transfer to the waste and continuous contact with the plasma, allowing treatment of almost any type of waste. Disadvantages: the continuous contact of the plasma stream with the waste limits further development in areas where selectivity of intermediates is desirable.

Entrained flow bed		Advantages: the short residence time of the solids in the plasma results in fast heating and quenching rates. Reactor efficiency and relatively uniform flow structure. Disadvantages: low energy efficiency on account of conductive, convective and radiative losses; electrode pollution of DC plasma reduces the product purity and also limits the generation of desired intermediate products.
Plasma spout bed reactor		Advantages: higher rate of mixing, better solid-fluid contact, improved heat and mass transfer with high conversion efficiencies with short residence times. Disadvantages: lack of bed stability

Plasma gasification technology offers several advantages for different feedstock treatments. Some key advantages can be identified as follows:

- **Versatility**: It can process a wide range of waste types, including municipal solid waste, biomass, hazardous waste and even difficult-to-treat materials such as plastics and tyres.
- **High conversion efficiency**: High temperatures Plasma gasification's (up to 10,000°C) break down waste into its basic molecular components, maximising energy recovery.
- **Environmental benefits**: Unlike incineration, plasma gasification does not produce greenhouse gas. It also prevents the formation of harmful by-products such as dioxins and furans.
- **Reduction in landfill use**: When converting waste into syngas and other valuable by-products significantly reduces the need for landfill.
- **Clean disposal**: Ensures the clean destruction of hazardous waste, preventing it from entering landfills and potentially contaminating the environment.

Figure 47 shows a basic structural diagram of a plasma gasification system, with typical feedstock preparation, sorting facilities and outputs generated using municipal solid waste for energy recovery.

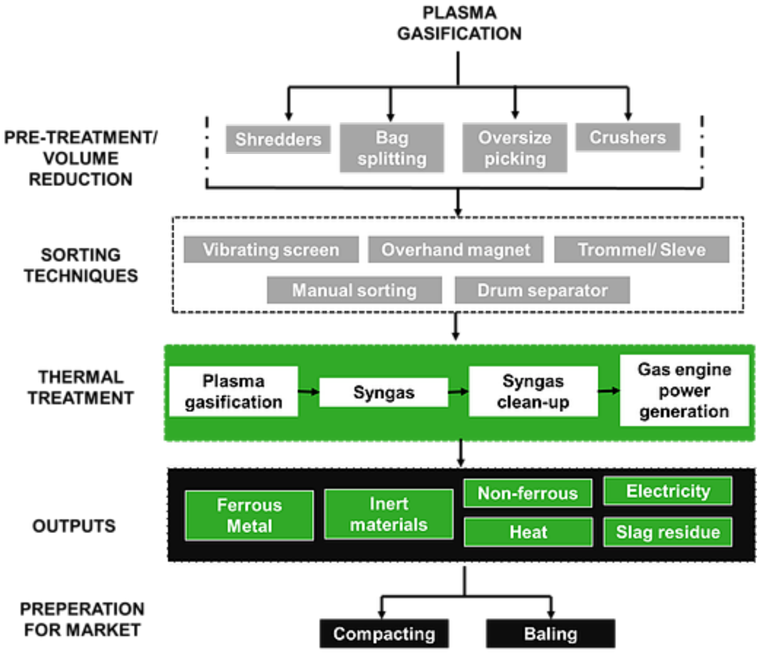


Figure 47. Generic technology flow diagram showing key components for plasma municipal waste gasification ((DEA), 2024).

In the work of (Dovilė Gimžauskaitė, 2022) the characteristics of waste-to-energy technologies (Table 33) were compared, which reveals the main difference of key technological parameter between existing WtE and advanced plasma gasification technologies.

Table 33. Plasma gasification technology against other thermal treatment technologies (Dovilė Gimžauskaitė, 2022).

Parameter	Incineration	Pyrolysis	Gasification	Plasma gasification
Type of waste	General waste stream (MSW, RDF)	Relatively homogeneous waste streams such as wood, agricultural residues or sewage sludge		Any kind of waste (organic, inorganic)
Waste volume reduction, %	Up to 80	Up to 50–90	Up to 75–90	Up to 90
Residence time	45–90 min	10–100 min	30–60 min	few s for the gas phase, min or h for the liquids and solid (e.g., 30 min—3 h)
Typical reaction temperature, °C	850–1200	300–800	800–1600	1500–5500
Useful conversion products	Steam/heat	Bio-oils, producer gas, bio-char	Synthesis gas	Syngas
Products customisation	Production of electricity or heat	Production of electricity, heat, synthesis gas, or chemicals	Production of electricity, heat, chemicals and liquid fuels	Production of electricity, heat, H2, NH3, CH3OH, or other liquid hydrocarbons
Contaminants and residuals	Dioxins, furans, PM, SOx, NOx, fly ash, metals, glass	H_2S, HCl, NH_3, HCN, tar, PM, coke, pyrolytic water	H_2S, HCl, NH_3, HCN, PM, tar, heavy metals, alkaline compounds	Lower production levels of NOX, SOX, tars, chars compared to gasification or incineration. Vitrified slag.
Operational and maintenance costs, United States/year	8.2	7.2	6.9	8.5
Capital costs for technologies in the United States (15 MW output), United States$/kW	7000–10,000	8000–11,500	7500–11,000	8000–11,500
Net energy production to the grid, kWh/ton of MSW	544	571	685	816
The efficiency of plants, %	15–29	17–24	15–30	29–33

Overall benefits	Can handle large amounts of waste. Utilization of bottom and fly ash of incineration plants in road construction, cement production and recovery of ferrous and nonferrous substances.	Recovers up to 80% energy from waste. Produce high-quality fuel. Reduces flue gas treatment. Reduces land requirements. - Generated products have higher calorific values.	Limited formation of dioxins, NO_x, and SO_x compared to incineration. Bottom ash often produced as vitreous slag that can be used in road construction.	No organic waste size requirements. Production of benign vitrified slag, which can be used in the construction material. Steady-state conditions, fast start-up, and shutdown.
Overall limitations	Corrosion of the incineration system by alkali metals in solid residues and fly ash. Required pollutant/emissions control system. Social opposition.	Cleaning of by-products. Corrosion of metal tubes used in pyrolysis.	Organic waste size requirements (particle diameter up to 100 mm). Organic waste with a high content of moisture cannot be used as a feedstock. Produced syngas often contains a large amount of tar.	The requirement for appropriate organic waste sorting. Electrodes erosion. Limited society awareness of plasma technology leading to safety concerns. Limited technology commercialization. Insufficient understanding of processes.

2.8.3. The technology status of Plasma Gasification Technology

Recent developments in advanced syngas production and purification systems, catalysts, modular plant designs, improved materials and alternative energy sources have focused on improving the efficiency, environmental performance and economic viability of plasma gasification. Plasma gasification has emerged as a viable technology for waste management and energy recovery(Vedraj Nagar, 2024). Only thermal plasmas have been employed at commerical scalr whereas non-thermal plasma reactors are still in development, with only lab- or pilot-scale installations launched(Dimitrakellis et al. 2022). The Gasification and Syngas Technologies Council reports that there are over 272 gasification plants in the world, of which only 5 report using plasma technology (Alter NRG Corp.,100 t/day, Wuhan, China(T.N. Generation, 2016); Maharashtra enviro power ltd., 72 t/day, Pune, India(R. Kaushal, 2022); Hitachi Metals Ltd., 150 t/day, Mihama-Mikata, Japan(Kaushal, 2024); Alter NRG, Westinghouse plasma gasification unit, 200 t/day, Tees Valley, UK(Tighe, 2016); InEnTec., 25-150 t/day, Oregon, USA(O'Neill, 2021).

In the conclusion, the use of plasma has potential as an initial step in biorefining technology, especially for the conversion of different waste to energy, fuels or other valuable chemicals. The benefits of plasma gasification in the treatment of different organic waste including waste biomass have been assessed in different studies and indicated an added value in an overall economic assessment. Although the investment and operational costs of plasma technology are very high, this problem can be solved by optimising process parameters and producing valuable products. The study of Gun et al., 2022) identified six main plasma technology challenges: fundamental process understanding, operational cost, commercialisation, community readiness level, energy-intensive process, and waste sorting difficulties. Solving these challenges should open options for plasma technology scaling up in the future, perhaps using government incentives and initiatives.

Conclusion

Thermochemical conversion technologies, including direct combustion, pyrolysis, gasification, torrefaction, hydrothermal liquefaction, hydrothermal carbonization, and plasma technologies, present significant opportunities for transforming biomass into valuable products. Each of these methods offers distinct outputs and advantages:

Direct Combustion: This process generates heat and electricity while producing ash as a byproduct. It is a straightforward method for utilizing biomass for energy.

Pyrolysis: This technology converts biomass into bio-char, bio-oil, and syngas. The products can be utilized for various applications, including soil enhancement and energy generation.

Gasification: Gasification produces syngas, which can be employed for power generation or as a chemical feedstock. This process allows for a more efficient energy conversion compared to direct combustion.

Torrefaction: This process yields torrefied biomass, which is easier to store and transport, improving the logistics of biomass utilization.

Hydrothermal Liquefaction: This method produces bio-crude oil, which can be further refined into bio-fuels. It effectively utilizes wet biomass, making it a versatile option for feedstock.

Hydrothermal Carbonization: Hydrothermal carbonization generates hydrochar, a product that can be used as a soil amendment or as a fuel source, enhancing its environmental benefits.

Plasma Technologies: Plasma conversion can produce syngas, bio-oil, and various chemicals, offering a high degree of flexibility in product outputs.

The key takeaways from the presented analysis:

1. Comprehensive Carbon Utilization: In contrast to biological processes that convert only a portion of the biomass, thermochemical methods are capable of utilizing all the carbon in the feedstock. This capability results in higher overall conversion efficiency, making these technologies particularly valuable.
2. Sustainability and Environmental Impact: Thermochemical conversion technologies contribute significantly to waste biomass utilisation. Furthermore, they have the potential to generate bio-fuels and bio-chemicals with a zero or very low carbon footprint, aligning with global efforts to combat climate change.
3. Challenges and Opportunities: Despite their many advantages, thermochemical conversion technologies encounter several challenges, including the necessity for efficient process control, the management of high moisture and ash content in feedstocks, and the assurance of

consistent product quality. Addressing these challenges requires ongoing research and development efforts to improve the commercial viability of these technologies.

In summary, thermochemical conversion technologies represent a promising approach for waste biomass valorisation, characterized by flexibility, efficiency, and sustainability. However, it is imperative to address the associated technical and economic challenges to facilitate their widespread adoption and commercialization.

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KEY ENABLING TECHNOLOGIES ACCORDING TO FEEDSTOCK TYPE

Part III

Physicochemical Technologies

CA 20127

Waste biorefinery technologies for accelerating sustainable energy processes (WIRE)

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Table of contents

List of acronyms

AD	Anaerobic digestion
AFEX	Ammonia fiber explosion
AGS	Aerobic granular sludge
ARP	Ammonia recycle percolation
CDE	Carbon dioxide explosion pretreatment
CFCs	Chlorofluorocarbons
CG	Crude glycerol
ED	Electro-kinetic Disintegration
EG	Expandable graphite
EPSs	Extracellular polymeric substances
FAME	Fatty acid methyl esters
FFAs	Free fatty acids
HPH	High-pressure homogenization
LCB	Lignocellulosic biomass
LHW	Low-pressure hot water
LP	Lime pretreatment
MAE	Microwave-assisted extraction
MSW	Municipal solid waste
OMW	Olive mill waste
PCMs	Phase change materials
PHAs	Polyhydroxyalkanoates
PLE	Pressurized liquid extraction
POL	Liquefied coffee grounds derived polyol
PU	Polyurethane
SAA	Soaking aqueous ammonia
scCO2	Supercritical carbon dioxide
SCF	Supercritical fluids
SCW	Supercritical water
SFE	Supercritical fluid extraction
SP	Steam pretreatment
TRL	Technology Readiness Level
UAE	Ultrasound-assisted extraction
UFA	Unsaturated fatty acids

WOP	Wet oxidative pretreatment
WWTPs	Urban wastewater treatment plants

List of figures

List of tables

Executive summary

Physicochemical processes play an integral role in biorefineries and support a variety of applications, each contributing to the system at multiple scales. These processes are instrumental in optimizing the conversion of biomass into valuable products and can be tailored for specific outcomes, including improving feedstock quality, enhancing product stability, and increasing energy efficiency. Mechanical treatment processes, such as grinding, milling, and sieving, are frequently applied at various stages of biorefinery operations, either as pre-treatment to prepare feedstocks for subsequent processing or as post-treatment to ensure the quality and consistency of end products.

Additionally, biochemical processes like hydrolysis, extraction, and esterification are key reactions within biorefineries. These processes contribute to the production of intermediate and final products, including biofuels, biochemicals, and other value-added products. Hydrolysis, for example, is widely used to break down complex organic compounds into simpler, usable molecules. Extraction processes help isolate specific bioactive compounds, whereas esterification is commonly employed in the production of biodiesel. Such physicochemical processes not only create bio-based alternatives to fossil fuels but also promote circularity by generating products that can be reintroduced into the production cycle.

Each of these processes is at a different stage of development and industrial maturity, with some having been well-established and others only recently gaining traction as emerging technologies. Advances in technology and the push for sustainable development models drive the innovation of newer processes with a stronger emphasis on ecosystem preservation and energy efficiency. Certain novel processes have shown promise in potentially replacing older, less sustainable ones. For instance, energy-efficient hydrolysis methods, bio-based extraction techniques or no-solvent extraction protocols offer greener alternatives that align more closely with eco-conscious manufacturing practices.

Physicochemical chapter focuses on the current conditions of both traditional and developing physicochemical processes, providing a comprehensive evaluation of their principles, practical applications, and industrial relevance. The chapter aims to highlight the future development of in physicochemical processes and their use in biorefineries, emphasizing processes that lead to sustainable development, reduce environmental impact, and improve resource utilization.

3. General review of Physicochemical Conversion Technologies

Physicochemical conversion technologies in waste biorefineries play a critical role in accelerating sustainable energy processes. Global society's efforts to transition to a sustainable and circular bioeconomy have highlighted these technologies, which offer simultaneous solutions to two significant challenges: waste management and renewable energy production (Cherubini, 2010). This approach directly aligns with the United Nations' Sustainable Development Goals, particularly "Affordable and Clean Energy" and "Responsible Consumption and Production."

Various physicochemical conversion technologies used in waste biorefineries include mechanical processing, extraction, transesterification, supercritical processes, and hydrolysis. These technologies play different but complementary roles in converting waste biomass into valuable energy products and chemicals (Dahiya et al., 2018).

Mechanical processing serves as a fundamental pre-treatment step in waste biorefineries. Size reduction techniques such as grinding, milling, shredding, and pelletizing increase the surface area of biomass, facilitating access to chemical and biological agents. This step significantly affects the efficiency of subsequent conversion processes (Cheng & Timilsina, 2011). In recent years, innovative mechanical processing methods have been developed, such as high-pressure homogenization for cell wall disruption in microalgae, ball milling to enhance enzymatic hydrolysis of lignocellulosic biomass, and extrusion pre-treatment to increase biogas production from agricultural residues (Zabed et al., 2019).

Extraction techniques are used for the selective separation of valuable components from waste biomass. Methods such as conventional solvent extraction using organic solvents, supercritical fluid extraction, pressurized liquid extraction, and microwave-assisted extraction have been effective in extracting high-value compounds like lipids, polyphenols, and pectins from biomass (Chemat et al., 2017). For example, lipid extraction from microalgae for biodiesel production, extraction of phenolic compounds from olive mill waste, and pectin extraction from citrus peel waste are successful applications of these techniques.

Transesterification has long been used for biodiesel production from waste oils and fats. This reaction involves the conversion of triglycerides to fatty acid methyl esters (FAME) using alcohol in the presence of a catalyst (Meher et al., 2006). Recent research has focused on developing effective heterogeneous catalysts to simplify product separation and enable catalyst reuse. Additionally, innovative reactor designs such as oscillatory flow reactors and microreactors aim to improve reaction efficiency by enhancing mixing and heat transfer (Guan et al., 2009).

Supercritical processes leverage the unique properties of fluids above their critical points to enhance extraction and reaction efficiencies. The most commonly used supercritical fluids in waste biorefinery are water (SCW) and carbon dioxide (scCO2) (Brunner, 2009). Supercritical water is used in the hydrolysis of lignocellulosic biomass for bioethanol production, gasification of wet biomass for hydrogen production, and oxidation of organic waste for water treatment. Supercritical CO_2 is applied in the extraction of valuable compounds from food waste, pre-treatment to enhance enzymatic hydrolysis of lignocellulosic biomass, and simultaneous lipid extraction and transesterification for biodiesel production (Loppinet-Serani et al., 2010).

Hydrolysis plays a vital role in breaking down complex biomass structures into simpler, fermentable sugars. This process is critical for the production of bioethanol and other fermentation-derived products. Acid hydrolysis and enzymatic hydrolysis are the two main hydrolysis methods commonly used (Taherzadeh & Karimi, 2007). In recent years, there has been a focus on developing more efficient and thermostable enzymes and investigating the synergistic effects of enzyme cocktails. Additionally, physicochemical hydrolysis methods such as steam explosion and liquid hot water pre-treatment have been effective in breaking down lignocellulosic biomass (Alvira et al., 2010).

The integration of these physicochemical conversion technologies in waste biorefineries offers a sustainable approach to resource recovery and energy production. Each technology presents unique advantages and challenges, with their selection depending on factors such as feedstock characteristics, desired products, and process economics (Mohan et al., 2016). Future research directions should focus on developing new catalysts and enzymes for improved selectivity and efficiency, optimizing process conditions and exploring synergistic effects of combined technologies, addressing scalability issues, and reducing energy inputs for improved economic feasibility.

As the world transitions to a circular bioeconomy, the development of these physicochemical conversion technologies will play a key role in accelerating sustainable energy processes and mitigating environmental challenges related to waste management (Venkata Mohan et al., 2016). The successful implementation of these technologies has the potential to create a paradigm shift in how we view and utilize waste resources, paving the way for a more sustainable and resource-efficient future.

3.1. Pretreatment of waste biomass used in physicochemical conversion technologies

Waste biomass pretreatment is a critical step in enhancing the efficiency of subsequent conversion processes in physicochemical transformation technologies. Various pretreatment methods have been developed for biomass conversion. Pretreatments of waste biomass in physicochemical conversion technologies aim to optimize the efficiency and effectiveness of subsequent conversion processes.

There are several unit processes or operations by which biomass is prepared for energy or alternative material production. Among them are size reduction, drying, hot water extraction, and chemical pretreatment such as acid hydrolysis, alkaline treatment, and oxidative pretreatment (especially preferred for modifying the structure of lignin), as well as several biological pretreatment processes (to break down lignin and hemicellulose), carbonization, pyrolysis, microwave, ultrasound treatment, Steam Explosion, supercritical processes or fractionation. All of these are necessary and inseparable preliminary operations or processes to achieve well-characterized energy or products.

The use of pretreatment methods are crucial for reducing the complexity of biomass structure and making it more suitable for conversion operations in industrial production. The use of these pretreatment processes provide:

1. Enhanced Biomass Accessibility: Methods like alkali-based treatments and microwave pretreatment induce structural changes in lignocellulosic biomass, including cellulose swelling, lignin structural deformation, and partial cellulose decrystallization. These changes improve enzyme or chemical accessibility to biomass, facilitating subsequent conversion processes (Akhtar et al., 2015).
2. Improving Hydrolysis Efficiency: Pretreatments such as enzymatic pretreatment and acid hydrolysis break down complex biomass components into simpler sugars, easing their conversion into biofuels. Enzymatic approaches provide a more environmentally friendly and efficient alternative to traditional chemical methods, enhancing the hydrolysis efficiency of lignocellulosic biomass (Akhtar et al., 2015).
3. Reduced Mass Transfer Limitations: Supercritical technology and other pretreatment methods help overcome mass transfer limitations encountered in other techniques by enhancing solvent penetration into the biomass's crystalline structure. This penetration improves the efficiency of subsequent conversion processes by accelerating mass transfer rates (Akhtar et al., 2015).
4. Delignification and Cellulose Conversion: Methods like alkali pretreatment effectively achieve delignification and cellulose conversion, critical steps in enhancing biomass conversion efficiency (Akhtar et al., 2015).
5. Increase Sugar Yield: Some pretreatment methods, such as steam explosion and acid hydrolysis, have been shown to increase sugar yields from biomass. These methods break down complex carbohydrates into simpler sugars, thereby enhancing overall sugar yields crucial for biofuel production (Zulqarnain et al., 2021).

6. Optimize Enzymatic Transesterification: Enzymatic transesterification processes, preceded by suitable pretreatments, lead to higher biodiesel yields. These pretreatments prepare biomass for efficient enzymatic reactions, improving biodiesel production efficiency (Taher et al., 2011; Akhtar et al., 2015).
7. Enhanced Biofuel Production: Overall, pretreatments of waste biomass in physicochemical conversion technologies aim to enhance biofuel production efficiency, reduce environmental impact, and promote sustainable energy practices. These pretreatments play a vital role in converting waste biomass into valuable biofuels and bioproducts, contributing to a more sustainable bioenergy sector (Sudalai et al., 2024).

Alkali-based treatments are widely used to induce structural changes in lignocellulosic agricultural residues, including cellulose swelling, lignin structural deformation, and partial cellulose decrystallization, facilitating subsequent hydrolysis processes (Kumar et al., 2009). This pretreatment method is crucial for breaking down the complex structure of biomass and improving its conversion efficiency. Microwave pretreatment has emerged as an effective approach for biomass pretreatment, utilizing both thermal and non-thermal effects to disrupt the recalcitrant structures of lignocellulose (Hassan et al., 2018). The unique heating mechanism of microwaves causes an explosion effect among biomass particles, enhancing their breakdown and improving sugar yields during hydrolysis processes. This method offers a rapid and efficient way to prepare biomass for biofuel production, demonstrating its potential in enhancing conversion efficiency. Moreover, dry and wet torrefaction processes have been employed as pretreatment methods for biomass conversion, leading to the formation of biochar, bio-oil, and gaseous products (Ruiz et al., 2020). Dry torrefaction, conducted at specific temperatures under oxidative or non-oxidative conditions, modifies the biomass structure, making it more amenable to subsequent conversion processes. Wet torrefaction and hydrothermal carbonization also result in upgraded solid fuels and high-carbon content charcoal suitable for various applications. Enzymatic pretreatment has shown promise in enhancing the hydrolysis of lignocellulosic biomass by breaking down complex components into simpler sugars, facilitating their conversion into biofuels (Kucharska et al., 2018). Enzymatic approaches provide a more environmentally friendly and efficient alternative to traditional chemical methods, contributing to the sustainability of biomass conversion processes(Qian et al., 2022). In summary, pretreatments of waste biomass using physicochemical conversion technologies are essential for optimizing the efficiency and sustainability of biomass biorefinery processes. By employing a combination of alkali-based treatments, microwave pretreatment, torrefaction processes, enzymatic approaches, and researchers and practitioners can enhance the conversion of waste biomass into valuable biofuels and bioproducts, contributing to a more sustainable bioenergy sector.

3.1.1. Mechanical treatment

Mechanical treatment is one most overlooked unit operation in any industrial and biorefinery process. Although mechanical treatment can be one of the energy consuming operations, usually it does not require chemical consumption and may be a major product quality control steps in the whole process. Mechanical treatment have the potential to gain high quality biomass for biorefineries. Mechanical treatment is often one of the first steps in treatment and further steps are relying on it. Mechanical treatments could separate lignocellulosic material which could later go into solubilization and separation of cellulose and lignin (Costa et al., 2018).

Mechanical treatment have use at the preliminary or post processes such shereding of cellulosic feedstock or dewatering of any sludge.

A typical mechanical pretreatment using for agricultural waste feedstock given in Figure 1.

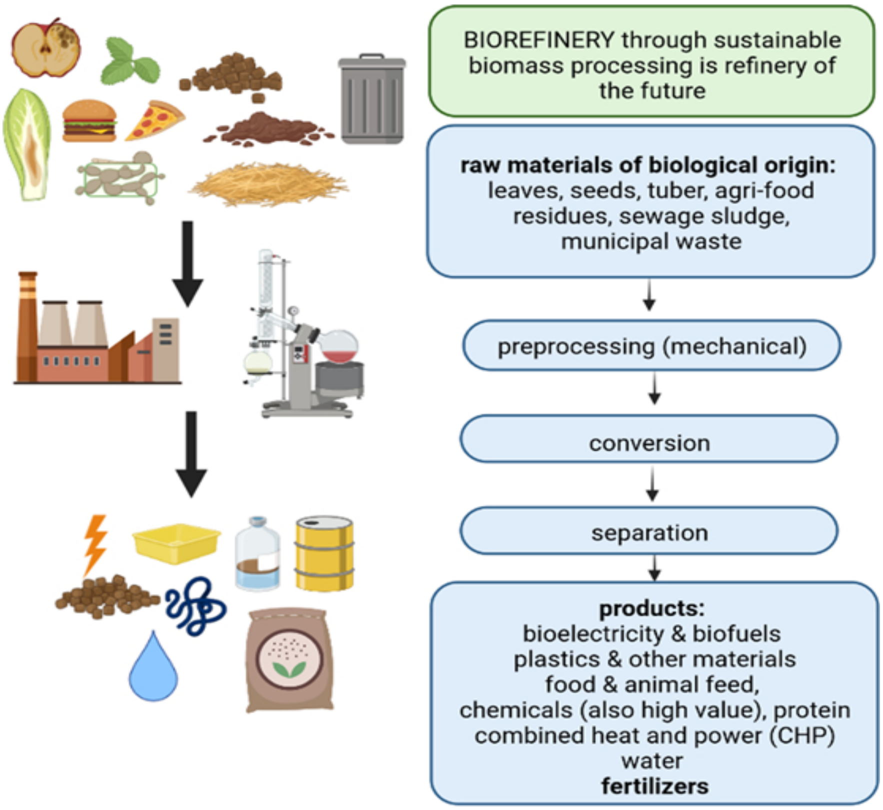

Figure 1. Mechanical pretreatment using for agricultural waste feedstock (Chojnacka, K., 2023).

Generally, green biomass processing require separation operations these liquid-solid separations (may be fractinations as well) is achieved using mechanical pretreatments (Sieker et al. 2011). These pretreatment methods help to reduce (or increase) the water content needed in the process, thus decreasing the costs for further processing and transportation. Moreover, mechanical pretreatments avoid the formation of inhibitory compounds which may affect the uncontrolled microbial growth (Nielsen et al. 2015).

3.1.1.1. General review and evaluation of biomass types for mechanical treatment

Mechanical pretreatment of biomass involves physical processes that modify the structure, size, or composition of biomass to enhance its subsequent processing, particularly in biochemical and thermochemical conversions. These pretreatments are crucial for improving the efficiency of biomass conversion into biofuels, chemicals, and other valuable products. The main effects of mechanical pretreatment are i) reduction of particle size, ii) solubilisation, iii) biodegradability enhancement, iv) formation of refractory compounds and v) loss of organic material (Carlsson et al, 2012). Methods and expressions used for quantifying these effects differ among publications. In light of this, it has been reported that the larger the particle diameter, the less energy generation there is, implying that the substrate's increased bioavailability and utilization is inversely proportional to particle size (Akunna et al., 2018). Along with particle size reduction, disruption occurs when physical/mechanical pretreatment mechanisms include the application of intense external pressure that exceeds the internal pressure of cells (Tyagi et al., 2011), resulting in the release of intracellular material in the bulk medium. Nonetheless, despite the beneficial aspects of mechanical disintegration, most of the methods belonging in this category are energy intensive (Ariunbaatar et al., 2014). Moreover, excessive reduction in particle size may cause process issues (e.g. viscosity, high water holding, filter clogging, liberation of inhibitory compounds, etc..). Depending on the pretreatment conditions, and on the particle-size reduction tools used in the process, the pretreatment process may also cause the biomass to shear and reduce the degree of polymerization, increasing the available accessible area to chemicals, enzymes and microbes (Arce and Kratky, 2022).

Mechanical pretreatments can involve the processing of different types of biomass to enhance their conversion into valuable products (biofuels or bioproducts). The types of biomass used for mechanical pretreatments include:

A) lignocellulosic wastes:

Lignocellulosic wastes including energy crops (i.e. sorghum, triticale, ryegrass, miscanthus, etc..) and wastefrom farming activities, such as crop residues, straw, and husks. They contain high levels of lignocellulosic material, which is challenging to break down although abundant in agricultural settings. Lignocellulosic biomass is composed of three major polymeric components: cellulose, hemicellulose, and lignin, this last one existing as a natural resistant bio-composite. The recalcitrant nature of lignocellulosic biomass presents a technical challenge for releasing fermentable sugars from the biomass, and a major hurdle in its use in biorefinery. Indeed, pretreatment of lignocellulosic biomass is the initial step in exposing the cellulose and hemicellulose content for hydrolysis (Bhatia et al., 2018). According to a review on mechanical pretreatments on lignocellulosic biomass done by Kratky and Arce (2022), *milling* is the most used mechanical pretreatment technique among the references found by the authors (68%), followed by *grinding* (16%), *refining* (9%), *ultrasonication* (4%), and *extrusion* (3%).

B) Animal manure

Animal manure rich in organic matter and nutrients, it is a valuable feedstock in particular for energy recovery in anaerobic digestion processes. It typically contains a lower lignocellulosic content than plant residues, but mechanical pretreatments can still improve its biodegradability and biogas yield. A meta-analysis conducted by Anacleto et al. (2022), revealed that cattle manure prevailed in studies investigating manure from herbivore diets. The lignocellulosic content in cattle manure is higher than in swine and chicken manure, mostly due to its lignin content because of the use of straw as litter in stables, which reaches values on average two to four times higher than in manure from herbivores. Lignin is a recalcitrant compound composed of polymeric structures of low degradability, which makes fermentation difficult, requiring pretreatments such as *grinding*. *shredding, cavitation* or *extrusion* to weaken the intra and intermolecular hydrogen bonds (You et al.,2019).

C) Biowaste

Biowaste intended as waste generated from left over food in households and canteens, or food not optically acceptable, or beyond to the expiration date, removed from the supply chain. Food waste can come from retails (i.e. supermarkets and restaurants), and consumers. The composition of biowaste depends on several factors, including the disposal management in the different EU countries. For example, in Austria and Germany, food wastes generated in households, including also non-edible parts (e.g. bones, eggshells, napkins), are often disposed together with garden wastes (e.g. leaves, grass cuttings, branches, seeds) (Alessi et al., 2020). The most commonly researched treatment technologies for biowastes comprise anaerobic digestion (AD) and composting (Lohri et al., 2017). Among other factors, the optimal performance of industrial AD systems depends on the composition of the biowaste and its biogas potential. Particularly in the case of biowaste, impurities, such as plastics, glass shards and stones, can compromise the efficiency of the process; it might cause malfunctions of mechanical devices, abrasion, pipe clogging and formation of sediments at the bottom of digesters. Particularly, the formation of sediments in the digester can affect the performance of the AD process and reduce the quality of the digestate, i.e., the remaining material after AD, limiting its further use and commercialization as compost or liquid fertilizer (Alessi et al., 2020). Therefore, in order to remove the impurities, most biowastes must be treated mechanically prior to AD (Carlsson et al., 2015). The pretreatment also reduces the size of the particles, increases the bioavailability and results in a more homogeneous substrate. Typically, the first step of a biowaste mechanical processing is the *bag opener* or *shredder*, which aims at separating the biowaste trapped inside plastic bags and making it more homogeneous. Other standard processes include *sieves*, *presses* and *metal separators*, which are used for separating the different fractions, depending on size and composition. An optimal treatment produces a clean substrate to be transferred into the digester, with only minor losses of organic material together with the removal of impurities (Alessi et al., 2020).

D) Sewage sludge

Sludge has a complex floc structure and composition of extracellular polymeric substances (usually denoted as EPS) as well as hard cell walls, which can obstruct the efficient performance of energy recovering processes. Moreover, it contains toxic substances, such as (in)organic contaminants and pathogens, which pose significant environmental threat, as well as odor and hygiene concerns; therefore, both its pretreatment and disposal are crucial (Mitraka et al., 2022). Mechanical pretreatments can enhance dewaterability of sewage sludge (and so reduce its volume), can contribute to (in)organic contaminants removal, stabilization with odors and pathogens removal, and improve its biodegradability for subsequent processes, like could be anaerobic digestion. Some of the most commonly applied mechanical processes for sludge pretreatment include, among other common ones, the ultrasonication process, the high-pressure homogenization (HPH) process, the microwave irradiation process, and the electro-kinetic disintegration process (Ariunbaatar et al., 2014). *Ultrasonication* is commonly employed for sludge pretreatment and results in its disintegration through cavitation phenomenon. *Microwaves* are a form of electromagnetic radiation, which occur at a frequency range of 300 MHz to 300 GHz; it is preferable to conventional heating strategies and it is associated with its minimal or no heat losses. Through MP, sludge's floc and EPS structure is disrupted, bound organic matter is released, and the cell walls, which are no longer protected within the EPS matrix, are destroyed. *High-Pressure Homogenization (HPH)* involves high pressures, abrupt pressure alterations and typical effects of fluid/dispersion dynamics such as the formation of mixing eddies due to high turbulence, cavitation phenomenon, and shear forces. *Electro-kinetic Disintegration* (ED) technology, also known as "pulsed electric field", uses high-voltage pulsing electric fields ranging between 20 kV and 30 kV, aiming to disrupt the sludge flocs and cell membranes, and solubilize the complex organic matter (Mitraka et al., 2022).

E) Aquatic biomass

The macromolecular composition (lipids, proteins and carbohydrates) and the cell wall structure of algal biomass make this substrate interesting for energy and products recovery. The algal cell wall is mostly composed of polysaccharide-based compounds, with multilayers of cellulose and hemicellulose, with consequent slow biodegradability and/or low bioavailability (Carrere et al., 2016). This resilient cell wall impedes the energy recovery, since organic matter retained in the cytoplasm is not easily accessible to microorganisms. In eukaryotic microalgae, the cell wall is generally composed of a microfibrillar layer of cellulose, which may be surrounded by an amorphous layer. Outside the outer amorphous layer a laminated polysaccharide cover may be present. Its composition can be more or less complex, containing: 25-30% cellulose, 15-25% hemicellulose, 35% pectin and 5-10% glycoproteins. The cell wall structure depends on the microalgae species (Gonzalez-Fernandez et al., 2011). Mechanical pretreatment including physical methods aim at size reduction or cell wall disruption by provoking physical damage; *microwaves* are more commonly used for microalgae biomass; *ultrasound* pretreatment relies on the cavitation produced by soundwaves to break the cell wall from the inside out. Although it cannot break chemical bonds, microwaves can break hydrogen bonds of the macromolecules, altering their structures and damaging the cell wall (Jankowska et al., 2017; Rodriguez et al., 2015). The pretreatment effectiveness strongly depends on the applied conditions and to the algae species (Carrere et al., 2016).

3.1.1.2. Mechanical Pretreatment Technologies

Among physical pretreatments, mechanical pretreatments allow a good increase in terms of energy recovery yield in particular for some biomass types, and do not have issues related to use of harsh chemicals, like chemical treatments, or to slowness and uncertainty of the process, like biological ones. The only drawback might be the energy requirement in relation to the final effect on substrates, and this aspect is one of the most important parameter describing the technical outlook of mechanical pretreatments. In fact, the energy efficiency of the mechanical pretreatments needs to be evaluated for different substrates and the knowledge about the required intensity of disintegration to maximize the economic output is crucial in order to optimize the energy balance and increase the sustainability of the process (Garuti et al., 2022).

Generally, the energy requirements of mechanical grinding/shredding depend on the type of mill, initial and final particle sizes, biomass characteristics, i.e., processing amount, composition, and moisture content in biomass. Ball mills, vibratory mills, hammer mills, knife mills, two-roll mills, colloid mills, attrition mills, or extruders can be used for milling of lignocellulosic biomass. The choice of the right grinding or milling machine depends especially on the moisture content in the biomass. Taherzadeh and Karimi (2008) concluded that colloid mills and extruders are suitable only for comminuting of wet materials with moisture contents of more than 15–20% (wet basis), whereas two-roll, attrition, hammer or knife mills are suitable only for milling of dry biomass with moisture contents of up to 10–15% (wet basis). The ball or vibratory ball mills are universal types of disintegrators and can be used for either dry or wet materials.

A) Shredding

Lignocellulosic grinding is a method used to reduce the size of compact, difficult-to-handle feedstocks such as waste paper, grasses, seeds, wood. Knife, hammer, and screw shredders, or combinations of these, are the most commonly used machines for disintegrating compact feedstocks. The design of a shredder depends on various biomass characteristics, such as mechanical properties, size, and moisture content. However, different types of knife shredders exist, generally regarded as universal tools for biomass shredding.

Two of the most used examples of milling devices are:

- ➔ *Knife milling*, usually applied to the treatment of dry biomass with a high moisture content of up to 15% (wet basis) and widely used for disintegration of materials like grasses, straws, seeds or crop wastes. The final particle size depends mainly on the feeding velocity, rotational speed of the rotor, and type of the drum screen. The energy requirement depends especially on the final particle size, rotational speed of the rotor, mounting longitudinal angle of the knife, and bevel angle of the knife (Kratky and Jirou, 2011).
- ➔ *Hammer milling*, commonly used for biomass shredding due to their high size reduction efficiency and ease of particle size adjustment. The mill consists of a rotor equipped with a series of hammers; as the rotor spins, the hammers strike the material against a breaker plate. Hammer mills are cost-effective, simple to operate, and capable of producing particles in a wide size range. The energy required for biomass grinding primarily depends on factors such as the initial and desired particle sizes, moisture content, material characteristics, feed rate, and machine settings like hammer tip speed and screen size (Kratky and Jirou, 2011).

B) Extrusion

Extruders are not conventional size reduction machines, but they have frequently been tested for biomass disintegration due to their unique capabilities of disintegrating fibrous materials through friction and shear. One of the key benefits of this technology is that extrusion is a continuous process, making it practical and easily adaptable for large-scale production. Extruders offer several advantages, such as generating high shear forces, enabling rapid heat transfer, and ensuring efficient mixing. This process significantly abrades cell walls, causing structural changes and so digestibility enhancement. A standard extruder is composed of three zones: the feed, transition, and compression/metering zones. Parameters such as compression ratio, screw speed, and barrel temperature are critical factors affecting sugar recovery from biomass (Kratky and Jirou, 2011).

C) Hydrodynamic Cavitation

Hydrodynamic cavitation machines are effective for disintegrating wet materials with a minimum moisture content of 15–20% (wet basis). The process is typically carried out with particles dispersed in water or other liquids, even manure with high moisture content in case of biomass pretreatment for anaerobic digestion. The device consists of stationary and multiple rotating discs, often perforated. The suspension is typically fed into the machine through a central orifice aligned with the rotation axis, accelerated as it passes between the discs. The process involves the generation, growth, and collapse of imploding cavities. The implosion creates high local density points, leading to the disintegration of the treated material, breaking bonds between material layers, and releasing a large amount of energy as heat. The cavitation process is influenced by factors such as biomass characteristics, rotational speed, and the gap size between discs (Kratky and Jirou, 2011).

3.1.2. Chemical Pretreatment Technologies

Chemical pretreatment methods involve the use of certain chemicals, including oxidizers, acids, alkalis, and organic solvents, to break down the crystalline structure of sources of lignocellulosic biomass. These substances increase surface area, which improves biodegradability (Awogbemi and Von Kallon, 2022; Paudel et al., 2017). The following categories apply to chemical pretreatments (Riseh et al. 2024; Kumar et al. 2009; Batista et al. 2022):

A) Acidic Pretreatment

One of the many benefits of using acids in lignocellulosic biomass is that they can be used to inexpensively and effectively extract lignin and hemicellulose (Seidl and Goulart 2016; Verardi

2012). Acids that break down glycosidic linkages in lignocellulose and degrade cellulose and hemicellulose include HCl, H_2SO_4, H_3PO_4, HNO_3, Na_2CO_3, CH_3COOH, CH_2O_2, and $C_4H_4O_4$. (Rezania et al., 2020). Depending on the kind of waste, different conditions for concentration, temperature, and duration are usually used during this process. In general, yield is increased while cellulose's crystallinity and thermal stability are decreased by high temperatures, extended processes, and high concentrations (Kargarzadeh et al. 2017; Liu et al. 2018). Despite its effectiveness, acid pretreatment can cause the release of toxic compounds like furfural and HMF, as well as the breakdown of sugars and lignin, which can lead to the formation of acids like acetic, formic, levulinic, and phenolic (Seidl and Goulart 2016; Verardi 2012; Rasmussen et al. 2014; Zeng et al. 2014). Concentrated acids are very useful for hydrolyzing cellulose, but they are dangerous, poisonous, and require reactors that are resistant to corrosion, which drives up the process's expense. Moreover, for the procedure to be commercially feasible, the acid needs to be recovered after hydrolysis (Sivers et al. 1995). Sulfuric acid concentrations less than 4% have been shown to be among the most favored options in this research, which has effectively developed diluted acid hydrolysis as a pretreatment for lignocellulosic materials. Commercial furfural synthesis from cellulose has been achieved with the use of diluted H_2SO_4 (Zeitsch et al. 2000). By supplying high reaction rates, the diluted H_2SO_4 pretreatment greatly improves cellulose hydrolysis (Esteghlalian et al. 1997). The majority of the hemicellulose is efficiently removed by diluted acid as dissolved sugars, raising the cellulose's glucose yield to almost 100%. High temperatures facilitate the hydrolysis of cellulose. High xylose yields from xylan have been achieved recently by the preference for less severe conditions in dilute acid hydrolysis procedures (Hinman et al. 1992). These methods use low acid concentrations to produce cellulose with great digestibility and good yields of hemicellulose sugars. However, significant energy is needed for pretreatment and product recovery due to the equipment designs used and the high water-to-solid ratio. Dilute acid pretreatment is often more expensive than physicochemical pretreatments, despite the fact that it enhances cellulose hydrolysis. Prior to enzymatic hydrolysis or fermentation operations, the pH must be neutralized. The enzymatic hydrolysis of biomass is adversely affected by diluted acid pretreatment as well. Consequently, it is important to carefully consider the suitable diluted acid pretreatment for various lignocellulosic biomass types. Acid hydrolyzed materials may contain harmful compounds that complicate fermentation. Moreover, high pressures, costly building materials, and the neutralization and conditioning of the hydrolysate prior to biological stages are all associated with acid pretreatment. This may result in sluggish digestion of cellulose and ineffective enzyme binding to lignin (Wyman et al. 2005).

B) Alkaline Pretreatment

Alkaline reagents decrease cellulose's crystallinity, improve conversion yield, and enable the separation of lignin and hemicellulose in the liquid phase (Woiciechowski et al., 2020). Examples of these reagents are NaOH, KOH, NH_4OH, $NH_3 \cdot H_2O$, and $Ca(OH)_2$. Compared to acidic pretreatments like sulfuric acid, alkaline pretreatments are better because they require fewer aggressive reagents (Kim et al. 2016). Alkaline pretreatments also work well for delignifying biomass without having a big impact on the structure of the cellulose. Reactions like the deesterification of intermolecular ester linkages and the breakdown of lignin and hemicellulose take place during pretreatment. Through this process, hemicellulose's acetyl and uronic acid substitutions are eliminated, which prevents enzymes from accessing cellulose and hemicellulose (Singh and Trivedi 1999). Surface area, porosity, and crystallinity of the treated solids vary as a result of variations in the components' degree of polymerization (Kim and Holtzapple 2006). Pretreatment of lignocellulosic materials can be done using a variety of bases; the amount of lignin in the material determines how well an alkaline pretreatment works (McMillan et al. 1994). Compared to other pretreatment techniques, alkaline pretreatment technologies employ lower temperatures and pressures (Mosier et al. 2005). While alkaline pretreatment can be carried out in ambient circumstances, it may take hours or days as opposed to minutes or seconds. Alkaline techniques yield less deterioration of sugar than acid processes, and many caustic salts can be recovered or regenerated. Alkaline pretreatment treatments such as sodium, potassium, calcium, and ammonium hydroxides are appropriate. Sodium hydroxide has been investigated the most out of these four hydroxides (Elshafei et al. 1991). Slaked lime, or calcium hydroxide, is the least expensive per kilogram and has been demonstrated to be an efficient pretreatment agent. In an aqueous reaction system, calcium can be neutralized with carbon dioxide to recover insoluble calcium carbonate, and calcium hydroxide can be regenerated using well-established lime kiln technology.

C) Oxidative Pretreatment

This method releases soluble chemicals by breaking down lignin and hemicellulose with oxidizing agents like hydrogen peroxide and ozone. By using this technique, inhibitor byproducts are avoided (Putrino et al., 2020; Tan et al., 2021).

D) Ozonolysis

In contrast to other chemical processes, the ozone method does not leave harmful residues behind and increases the digestibility of the processed material by reducing the lignin concentration in lignocellulosic wastes. Several lignocellulosic materials, including green grass, peanut shells, pine (Neely 1984), cotton straw (Ben-Ghedalia and Shefet 1983), poplar wood chips (Vidal and Molinier 1988), and wheat straw (Ben-Ghedalia and Miron 1981), are broken down by ozone. The principal target of degradation is lignin; cellulose is retained and hemicellulose is only marginally impacted. The ability to conduct the reactions at room temperature and standard pressure is one benefit of ozonolysis pretreatment. Furthermore, procedures can be created to reduce environmental pollution because it is simple to break down ozone using a catalytic bed or by raising the temperature (Quesada et al. 1999). But because so much ozone is needed, the ozonolysis process can be expensive.

E) Pretreatment with Organic Solvents

Lignocellulose and lignin's internal linkages are broken by organic solvents such as acetone, methanol, ethanol, tetrahydrofuran, and ethylene glycol. Catalysts such as HCl, H_2SO_4, NaOH, NH_3, and $CaCO_3$ are employed in this process (Kumari and Singh, 2018; Mankar et al., 2021). To separate the solid lignin and the syrup-like carbohydrates, a pretreatment using organic solvents is used (Zhao et al. 2009). Recovering and reusing the organic solvent is the main benefit of this procedure (Ravindran and Jaiswal 2016).

F) Pretreatment with Ionic Liquids

Ionic liquids are made up of different anions and organic heterocyclic cations. These liquids stay liquid across a broad temperature range, usually below 100 °C, and are neither volatile nor flammable. One of the most widely used ionic liquids for pretreatment procedures is imidazole ion salts (Adeleye et al. 2019). Dissolving cellulose is an efficient use of these liquids. Through the breakdown of the hydrogen bonds that crosslink lignocellulose, the process improves the digestion of biomass. Afterwards, solvents such as acetone, ethanol, or water are used to recover cellulose; however, this process is expensive to implement (Meneze et al. 2017).

3.1.3. Physicochemical Pretreatment Methods

This category includes the following technologies: wet oxidation, CO_2 explosion, steam explosion, and ammonia fiber explosion (AFEX).

A) Steam Explosion

One popular and useful pretreatment technique for lignocellulosic biomass (LCB) is a steam explosion. During this procedure, high-pressure steam (0.69–4.83 MPa) is applied to the biomass at temperatures between 160 and 260 °C. Water molecules can penetrate the biomass due to this treatment, and when the pressure is suddenly released, the water vapor explodes, shredding the LCB into fibers. High pressure and temperature combine to destroy hemicellulose-lignin linkages and break glycosidic bonds in cellulose and hemicellulose (Chen and Liu, 2015). Acetic acid is released during the conversion of hemicellulose into the monomers glucose and xylose. The hemicellulose is subsequently further hydrolyzed by this acid via a process called autohydrolysis (Singh et al., 2015). When compared to alternative pretreatment techniques, steam explosion is preferred due to its comprehensive sugar recovery, minimal chemical use, high energy efficiency, and low environmental effect (Pielhop et al., 2016). Steam temperature, residence time, biomass size, and moisture content are some of the variables that affect how effective a steam explosion is (Rabemanolontsoa and Saka, 2016). This process produces phenolic chemicals from the breakdown of lignin, which may have detrimental effects on subsequent processes and necessitate detoxification. It has been demonstrated that steam explosion enhances treated corn stalks' microbial digestion (Zhao et al., 2018). Catalysts like H2SO4, H3PO4, SO_2, or CO_2 can be used to increase process efficiency. By reducing residence time and temperature, these catalysts improve enzymatic hydrolysis and decrease inhibitor production (Neves et al., 2016).

B) Ammonia Fiber Explosion (AFEX)

Liquid ammonia is applied to lignocellulosic biomass (LCB) in a high-pressure, closed vessel for five to thirty minutes at temperatures ranging from sixty to one hundred degrees Celsius as part of the AFEX process. The pressure is then quickly removed after that (Shirkavand et al., 2016). The lignocellulose swells as a result of the high temperature and pressure, and the sudden pressure drop breaks the fibrous structure of the biomass, reduces the crystallinity of the cellulose, and increases the accessibility of enzymes. Temperature, blowing pressure, water loading, and ammonia loading are the four main parameters that can be changed to optimize the AFEX process (El-Naggar et al., 2014). Compared to other procedures, AFEX usually produces higher enzymatic hydrolysis results with lower enzyme dosages, but it also partially eliminates lignin and hemicellulose. With their low lignin concentration, herbaceous plants such as tape grass, rice straw, and maize stalks, as well as agricultural leftovers, are particularly well suited for AFEX. The fact that AFEX produces fewer inhibitors than other pretreatment techniques is one of its main advantages. Nonetheless, efficient recovery and recycling are necessary to save operational costs and lessen the environmental impact of ammonia because of its high cost and volatility. Different LCB kinds have had their ideal AFEX conditions investigated. Zhao et al. (2014) discovered that 170 °C, 70% moisture content, and a 5:1 ammonia-to-biomass ratio were the ideal parameters for improving the enzymatic digestibility of maize stalks. Furthermore, soaking maize stalks before AFEX resulted in higher glucan digestibility (87.78%) and delignification

(15.74% to 24.07%). When Mathew et al. (2016) pretreated corn stalks with AFEX versus diluted acid, they discovered that the ethanol production from AFEX-treated corn stalks was higher than that of the dilute acid-treated stalks.

C) CO_2 Explosion

Due to its reduced energy requirements and advantages for the environment, supercritical CO_2 explosion offers a possible substitute (Bharathiraja et al., 2018). The ability of supercritical CO_2 to function as a "liquid-like" solvent and a "gas-like" mass transfer medium makes it unique and allows for efficient material diffusion and dissolution (Rostagno et al., 2015). High pressure causes CO_2 molecules to seep into the biomass, upsetting the lignin and hemicellulose's intricate structures. Carbonic acid, which is produced when CO_2 reacts with water, accelerates the hydrolysis of hemicellulose, albeit it is less efficient when dry biomass is used. On the other hand, pressure release improves access to cellulose fibers by dissolving the biomass's thick structure (Capolupo and Faraco, 2016). Greater pressure accelerates the rate at which CO_2 permeates cellulose pores, increasing the production of glucose. Furthermore, lignin may be greatly reduced and maize straw's enzymatic hydrolysis can be improved by employing cosolvents such as water-ethanol during supercritical CO_2 treatment (Serna et al., 2016). For example, Benazzi et al. (2013) reported that 60% fermentable sugar yield was obtained from sugarcane bagasse after supercritical CO_2 treatment. According to Narayanaswamy et al. (2011), supercritical CO_2 treatment improved glucose yield by 2.5 times when applied to corn stalks (75% moisture) at 24 MPa and 150 °C for 60 minutes. Yin et al. (2014) reported that the enzymatic hydrolysis of maize cob and stalk treated with ultrasonic pretreatment and supercritical CO_2 increased by 75% and 13.4% at 20 MPa and 170 °C, respectively. However, the high cost of the necessary high-pressure equipment poses a significant challenge for industrial implementation.

D) High-Pressure Hot Water Treatment

Similar to steam explosion, low-pressure hot water (LHW) pretreatment uses water instead of steam at high temperatures (172–230 °C) and pressures (up to 5 MPa). LHW prevents sudden reductions in pressure, which is necessary to prevent water from evaporating, in contrast to steam explosion. This process lowers the amount of lignin and hydrolyzes hemicellulose by releasing acetyl groups, increasing the accessibility of cellulose fibers (Zhuang et al., 2016). Hemicellulose remains in the liquid phase in LHW, and there is usually little production of monomeric sugar. The pH needs to be maintained between 4 and 7 to avoid inhibitor production and sugar breakdown (Li et al., 2014). According to Imman et al. (2014), there was a modification in the physical structure of biomass, a decrease in LHW temperature, and an improvement in enzymatic digestibility as a result of the use of acidic and alkaline promoters during LHW. LHW pretreatment is beneficial since it doesn't require any extra chemicals or catalysts, produces less harmful byproducts, is affordable, and can be used on a big scale. LHW is also feasible for large-scale operations since particle fragmentation occurs regardless of biomass size (Bhutto et al., 2017). However, because so much water is used, the procedure consumes a lot of energy.

3.1.4. General review and evaluation of biomass types that hydrolysis can be effective

A) Sugar-based sources

Energy crops like sugar cane, sugar beet, and sweet sorghum; fruits like grapes, dates, watermelon, and apples; and byproducts from sugar refineries like molasses are common sources of sugar-based feedstocks (Nwufo et al. 2016). The low conversion costs and large sugar yields of sugar-based crops make them ideal for the generation of ethanol. Their seasonal unpredictability is, nevertheless, a major disadvantage (Vohra et al. 2014). A C4 plant with a high carbon absorption rate and economical water use, sweet sorghum is a great option for energy generation. It can be cultivated from seeds in both tropical and temperate climes, and it accumulates significant amounts of extractable sugars in its stems (Daniel et al. 1991). Sugar beet is an important source of sugar in North America and Europe; in France, it is used to produce bioethanol (Vohra et al. 2014). Brazil, South Africa, Kenya, China, India, and the United States are among the tropical nations investigating the production of bioethanol from sugar beet (Marx et al. 2016). Sugar beet's sugar concentration varies according to type and development circumstances (Marx et al. 2016). Another C4 plant that does a great job of turning solar radiation into biomass is sugar cane, which is planted mostly in tropical and subtropical areas. About 79% of the bioethanol generated in Brazil comes from sugar cane juice (Soam et al. 2015; Costa et al. 2015). Depending on the plant variety, maturity, and harvest season, sugar cane juice can have a different amount of sugar. Although it has historically been used as a binder and feed ingredient, molasses—a byproduct of the sugar refining industry—is also a desirable raw material for the synthesis of bioethanol. The original raw material and the extraction techniques determine the molasses' composition and sugar content (Sindhu 2016). Additionally, research has concentrated on utilizing damaged or low-quality fruits that are unfit for human consumption to produce bioethanol from waste fruits. There are issues with using edible fruits for bioethanol, however, these fruits have soluble sugars that yeast may ferment without a lot of pretreatment. It is believed that fruit refinery wastes, such as grape and pineapple pomace, are more suitable for producing bioethanol (Chniti et al. 2014).

B) Starch-based sources

Because starchy plants are widely available, easily converted, have a long shelf life, and produce a large amount of ethanol, they are frequently employed in the manufacture of bioethanol. Cereals (60–80% starch), tubers and roots (60–90%), legumes (25–50%), and green and immature fruits (up to 70% starch) are a few examples of feedstocks high in starch (Santana and Meireles 2014). Maize, grains, sorghum, potatoes, cassava, wheat, and sweet potatoes are among the main crops utilized to produce bioethanol (Balat 2011). Of them, maize has grown in significance for the industrial production of bioethanol. The world's largest producer of corn ethanol was the United States, which produced 14.3 billion gallons of ethanol in 2014 and exported over 825 million gallons to 51 nations (Zabed et al. 2017). Other two important tuber crops that have the potential to produce bioethanol are cassava and potatoes. Originating in South America, cassava is a crop that grows well in tropical and subtropical regions. It ranks sixth in terms of consumption among food crops in developing nations, behind potatoes, wheat, rice, and barley (Thatoi et al. 2014). Typically grown in temperate climates, potatoes are one of the top four food crops worldwide and are mostly produced in China (20%), Russia (12%), India (8%), and the United States (8%), according to research (Thatoi et al. 2014). Native to Central and South America, sweet potatoes rank second in importance among root and tuber crops behind potatoes and are the seventh most eaten food crop in the world. In tropical and subtropical climates, they are cultivated. Varieties with white flesh sweet potatoes typically have a greater starch content (25–40%) and are better suited for the manufacture of bioethanol because of their lesser sweetness (Scott and Maldonado 1997).

C) Lignocellulosic Biomass Sources

Energy crops (including specialized energy crops and perennial grasses), aquatic plants (like water hyacinth), forest products (including hardwood and softwood, sawdust, pruning, and debarking wastes), agricultural residues (including bagasse, straw, and cereal straw), and the organic portion of municipal solid waste are some of the elements that make up lignocellulosic biomass (Saini et al. 2014). The wastes from corn, wheat, rice, and sugarcane are the most common types of agricultural residues (Saini et al. 2014). With an average annual output rate of four tons per acre, corn residue—which consists of the stalks, leaves, cobs, and husks left behind after harvesting—has a substantial potential for bioethanol production (Kim and Dale 2004). For the biomass-based ethanol business to create affordable ethanol, a steady and consistent supply of raw materials is essential. In addition, because of their short growth cycle and low needs for land, water, and fertilizer, energy crops are favorable for ethanol production. These crops are categorized as C3 or C4 plants and include alfalfa, reed canary grass (Phalaris arundinacea, C3), giant reed (Arundo donax, C3), miscanthus (Miscanthus spp., C4), and switchgrass (Panicum virgatum, C4). Hardwood and softwood trees are the main sources of forest biomass, which also includes sawdust, dead branches, debarking residue, and pruning residues. And it can be used for ethanol production. Although its varied composition and potential for microbial contamination frequently limit its applicability for bioethanol production, municipal solid waste (MSW), which includes food waste and paper mill sludge, is a recyclable biomass utilized as a feedstock for bioethanol production (Limayem and Ricke 2012).

3.1.4.1. Design of Hydrolysis Technology

Within the context of global energy security and environmental protection measures, there is a growing interest in alternative and eco-friendly energy sources. Fossil fuel sources are predicted to run out in the next 40–50 years (Vohra et al. 2014). Furthermore, the necessity for alternative energy sources and conversion technologies becomes evident when one considers the negative environmental effects of using fossil fuels, including sea level rise, biodiversity loss, climate change, and greenhouse gas emissions (Vanhala et al. 2016). One of the most potential substitute energy sources is bioethanol, which may be made from a variety of renewable wastes and sources of biomass high in carbs. Because bioethanol includes 34.7% oxygen, it is an oxygenated fuel that is good for the environment. Compared to gasoline, it has a 15% greater combustion efficiency and emits less nitrogen oxide and particulate matter. Bioethanol further lowers sulfur oxide emissions because it contains very little sulfur (Pickett et al. 2008).

Sugars, starch, lignocellulosic biomass, and algae are the main categories of renewable resources utilized in the manufacturing of bioethanol. Second- and third-generation bioethanol are produced by algae and lignocellulosic biomass, respectively, whereas first-generation bioethanol is made from sugar and starch. Although other types of biomass have shown promise as feedstocks for bioethanol production on a commercial scale, third-generation bioethanol synthesis from algae is still in its early stages and can only be studied in lab settings. There are differences in the three primary feedstock types (sugars, starch, and lignocellulosic biomass) when turning them into bioethanol, particularly when getting fermentable sugar solutions. Whereas starchy crops go through hydrolysis to turn starch into glucose, sugar-based feedstocks just need one extraction procedure. Enzyme accessibility to lignocellulosic biomass requires pretreatment before hydrolysis (Zabed et al. 2017). According to recent research by Chao Liu (2022), hydrogenolysis/hydrolysis can be a effective process for phenolic compounds and furfural (Figure 2).

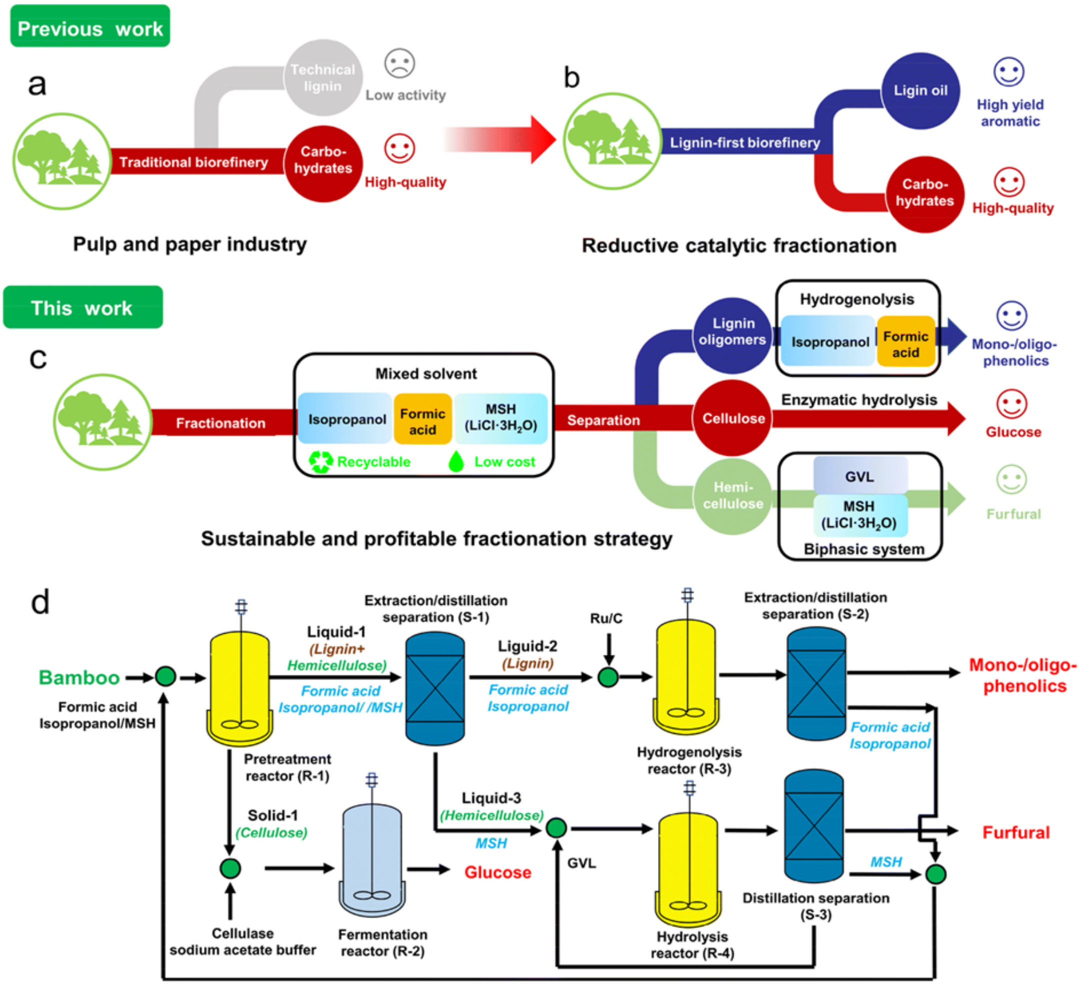

Figure 2. Overview of the biorefinery strategy (Chao Liu, 2022).(a) Traditional biorefinery approaches are heavily carbohydrate-centered and used in the pulp and paper industry. (b) Reductive catalytic fractionation, focused on high yields of lignin derived aromatic compounds and carbohydrates. (c) This work: lignocellulose fractionation and full-component conversion. (d) Proposed comprehensive biorefinery process for furfural, glucose and phenolic compounds.

3.1.4.2. The Technology Status of Hydrolysis Technology

The transition to alternative energy sources has been sparked by the sharp reduction in fossil fuels and the increase in greenhouse gas emissions. In this regard, bioethanol stands out as one of the most environmentally friendly and promising renewable energy sources. Currently, corn and sugar cane are used to make the majority of bioethanol. Nevertheless, the current demand for bioethanol cannot be met by these two primary sources, which makes it difficult to replace fossil fuels. As a result, researchers have focused on other sources, such as lignocellulosic biomass. The use of lignocellulosic biomass in bioethanol production is a focus of technological research and process optimization. However, there are several obstacles to creating a sustainable bioethanol economy. Large-scale ethanol production utilizing lignocellulosic biomass is hampered by costly and energy-intensive pretreatment procedures. Although significant progress has been made in recent years; combining processes and using these technologies on a larger scale will be more beneficial in developing a long-term lignocellulosic ethanol business.

A) Extraction

Extraction refers to processes, which are used to separate and/or purify specific components from a complex matrix. Extraction methods are frequently used in both production and analysis for isolating target compounds from raw materials or complex samples. For instance, in the context of natural products, extraction techniques like solvent extraction, supercritical fluid extraction, and liquid-liquid extraction are commonly used to isolate bioactive compounds from plants (Srinivas et al., 2020; Liao et al., 2019). Similarly, in environmental science, extraction methods are crucial for analyzing pollutants in soil and water samples (Tian et al., 2021). The efficiency and effectiveness of extraction depend on factors such as the choice of solvents, extraction conditions, and the nature of the target compounds (Roh et al., 2022).

Extraction methods play a crucial role in various industrial applications and analytical processes, with each technique offering distinct advantages in terms of efficiency and effectiveness. Solvent extraction, one of the most commonly used methods, leverages the selective solubility of target compounds in different solvents, making it highly effective for isolating a wide range of substances from complex mixtures (Perry et al., 2018). Supercritical fluid extraction (SFE) is another prominent method, employing supercritical fluids like CO_2 to achieve high selectivity and minimal solvent residues, which is particularly beneficial in pharmaceutical and food industries (Bertoli et al., 2020). Additionally, microwave-assisted extraction (MAE) enhances extraction efficiency by using microwave energy to heat solvents rapidly, thus reducing extraction times and improving yield (Feng et al., 2019). Each method's efficiency is influenced by factors such as solvent choice, extraction conditions, and the nature of the matrix being processed, allowing for tailored approaches to meet specific industrial and analytical needs (Kim et al., 2021).

Contemporary extraction methods have evolved to address the limitations of traditional techniques, focusing on enhanced efficiency and reduced environmental impact. Green extraction technologies such as pressurized liquid extraction (PLE) and ultrasound-assisted extraction (UAE) are gaining traction due to their ability to minimize solvent use and energy consumption while maximizing extraction efficiency (Carocho et al., 2021). Pressurized liquid extraction utilizes high pressure to improve solvent penetration and extraction rates, making it suitable for complex matrices like soils and biological tissues (Vardhan et al., 2022). Meanwhile, ultrasound-assisted extraction employs ultrasonic waves to enhance solvent diffusion and extraction efficiency, significantly reducing processing times and energy requirements (Khan et al., 2023). Both methods offer significant advantages in terms of sustainability and efficiency, aligning with the growing emphasis on green chemistry and reducing environmental impact in industrial and analytical applications (Pereira et al., 2022).

Biorefineries, which are designed to convert biomass into valuable products such as biofuels, chemicals, and materials, rely heavily on efficient extraction processes to isolate and purify target compounds from complex biological matrices. These extraction techniques are critical for optimizing the yield and quality of bio-based products. Here, we review several common extraction processes employed in biorefineries, highlighting their applications, efficiencies, and industrial uses.

Table 1. Biomass waste extraction technology readiness levels (TRLs).

Plant Name	Technology Name	Extraction Type	Suitable Feedstock	Capacity (kWh)	TRLs	References
Renewable Energy Group, Inc.	Various (e.g., Transesterification)	Chemical Extraction	Vegetable oils, animal fats	Varies by process	TRL 9	Renewable Energy Group
Neste Corporation	Various (e.g., Hydrotreated Vegetable Oil)	Chemical Extraction	Vegetable oils, animal fats	Varies by process	TRL 9	Neste
Bunge Limited	Various (e.g., Biodiesel Production)	Chemical Extraction	Soybean oil, other vegetable oils	Varies by process	TRL 9	Bunge
Cargill, Inc.	Various (e.g., Biodiesel Production)	Chemical Extraction	Soybean oil, other vegetable oils	Varies by process	TRL 9	Cargill
SABIC	Various (e.g., Bio-based Polymers)	Chemical Extraction	Biomass, waste oils	Varies by process	TRL 8	SABIC
Bioenergy Devco	Anaerobic Digestion	Chemical Extraction	Organic waste, agricultural residues	Varies by process	TRL 7-8	Bioenergy Devco
Green Plains Inc.	Ethanol, Biodiesel Production	Chemical Extraction	Corn, soybeans	Varies by process	TRL 8-9	Green Plains
LanzaTech	Gas Fermentation	Chemical Extraction	Industrial gases, biomass	Varies by process	TRL 8-9	LanzaTech
Velocys	Gas-to-Liquid (GTL)	Chemical Extraction	Biomass, natural gas	Varies by process	TRL 8	Velocys
Advanced Biofuels USA	Various (e.g., Biodiesel Production)	Chemical Extraction	Vegetable oils, waste fats	Varies by process	TRL 7-8	Advanced Biofuels USA
Novozymes	Enzymatic Extraction	Chemical Extraction	Biotechnology and Biodiesel Production	Various vegetable oils	TRL 7-8	Novozymes annual reports and sector analyses
Genomatica	Enzymatic Extraction	Chemical Extraction	Biochemistry and Biodiesel Production	Vegetable oils and biomass	TRL 7-8	Genomatica's technology reports and sector sources
AlgaeTech	Enzymatic Extraction	Chemical Extraction	Algae Biodiesel Production	Microalgae	TRL 6-7	AlgaeTech's technological reports and academic studies

SuSei	Enzymatic Extraction	Chemical Extraction	Waste Oil Biodiesel Production	Waste oils	TRL 6-7	SuSei's sector reports and annual reports

3.1.5. Biopolymers extraction

Aligned with the principles of a circular economy, the recovery/extraction of biopolymers from waste streams or by-products has been an increasing trend that can add economic value to otherwise discarded materials. Biopolymers are biodegradable polymers that can be obtained from waste biomass. This has gained much attention in recent years as it represents a potential solution to overcome problems related to waste management and environmental pollution whilst promoting bioeconomy. Although biopolymers can be obtained from diverse natural sources such as plants, animals or microorganisms, their production using industrial waste/by-products has been an asset of the scientific community and this will be the focus in this report.

Extracellular polymeric substances (EPSs) are the main components of bacterial biofilms playing a significant role in microorganisms' self-attachment and protection. EPSs are mainly composed of polysaccharides and proteins. The extraction of the biopolymers in the form of EPS from surplus biomass formed during wastewater treatment is a great example. Several methods including centrifugation, sonication, ethylenediaminetetraacetic acid (EDTA), formamide with sodium hydroxide (NaOH), formaldehyde with NaOH and sodium carbonate (Na2CO3) with heat and constant mixing were tested to ascertain on the best way to extract such biopolymers (REF[CA1]). In Oliveira et al (2020[CA2]) the potential to recover EPS from granular sludge was assessed in full scale operational settings. Over a 4.-months period, aerobic granular sludge (AGS) from a full-scale WWTP treating urban wastewater was regularly collected and revealed to be an interesting option to obtain EPS which composition varied with time. The study has opened a new scenario on EPS recovery from AGS that represent an opportunity to reduce surplus waste sludge disposal. In October of 2019, the process was scaled-up to the first full-scale installation in Zutphen (the Netherlands) and later, on December of 2020, the second plant in Epe started its operation (Kaumera®, 2024). The EPS biopolymer has been branded as Kaumera® and it looks like a gum. It is considered a profitable material that has been marketed for agricultural and horticultural applications, but many other applications are possible and currently scientists are conducting research on this. The recovery of EPS from sludge has been especially applied to granular sludge, which is a specific type of biofilm process used in wastewater treatment. Nevertheless, more recently the capacity to extract EPS from activated sludge has been explored (REF[CA3]). The yield of the EPS biopolymers extracted from the flocs of activated sludge is low if compared with that extracted from aerobic granular sludge. Nevertheless, it should be taken into account that the amount of the excess sludge in WWTPs that use activated sludge process is much higher than that in granular sludge processes and activated sludge is still the most common process used in full-scale WWTP.

Another promising biodegradable polymers that have emerged are the polyhydroxyalkanoates (PHAs). These biopolymers are synthesized by various bacteria and archaea being accumulated as intracellular granules and further extracted by using appropriate organic solvents (REF[CA4]). In general, PHAs are produced when microbes are cultured in nutrient-limiting concentrations of nitrogen, phosphorus, sulfur, or oxygen but are exposed to an excess of carbon. The PHAs range of applications is wide and each application requires some specific polymer properties. It can be used in agriculture as mulch films, nets and grow bags, in packaging as bottles, laminated foils, fishnets, flowerpots, sanitary goods, disposable cups, in textiles as fibers, in medical applications, such as scaffolds, drug delivery systems, implants and artificial nerve conduits, among others. But the growing interest in the PHAs production is mainly due to their potential to replace some petrochemical-based plastics (REF[CA5]). One of the major constraints in scaling-up PHA production is the cost of the carbon source used as feedstock. Therefore, cheap carbon substrates are currently a major focus of research. That is the case of waste streams as their use not only reduces the production cost for PHAs, but also contributes toward the reduction of environmental pollution.

PHA production coupled to wastewater treatment systems is a process that has been largely explored. It was during the PHARIO pilot project in 2017, that the Dutch regional water authorities successfully produced a PHA variant from sludge and fatty acids in the wastewtaer (as feedstock) (Holland Circular Hotspot©, 2024). It also demonstrated that the produced PHA has a competitive market price.

Biopolymer recovery is a crucial field that supports the development of sustainable materials and promotes environmental conservation. With ongoing research and technological advancements, the efficiency and viability of biopolymer recovery processes are continually improving, paving the way for broader adoption and application of biopolymers in various industries.

3.1.6. Supercritical Processes

Solvent extraction is one of the most ancient separation techniques, with its origins tracing back to the Paleolithic age. Over time, substantial advancements have been made in understanding the principles of solvation and the behavior of liquid mixtures in extraction processes. A pivotal moment in solvent extraction occurred in 1879 when Hannay and Hogarth observed the dissolution of solutes in supercritical fluids (SCF), marking the potential for a new solvent medium. However, it wasn't until the 1960s that significant commercial interest and applications of supercritical fluid extraction (SFE) were thoroughly explored.

The widespread use of organic solvents in global industries poses a severe environmental threat. This led to the establishment of the Montreal Protocol in 1987, which aimed to restrict or eliminate the production and use of harmful ozone-depleting solvents, such as chlorofluorocarbons (CFCs). The protocol has evolved through several amendments—London (1990), Copenhagen (1992), and Beijing (1999)—and now has over 170 signatory nations. Consequently, global industries are increasingly pressured to adopt environmentally sustainable processes that do not rely on harmful organic solvents.

Since the late 1970s, supercritical fluids have been used to isolate natural products. For many years, applications were limited to a few products, but advancements in processes and equipment have sparked increased interest in supercritical techniques. This growing interest is evidenced by the surge in scientific papers on SFE published in recent years and a notable increase in related industrial patents since the 1990s. In 2007, a review was published on the use of compressed fluids, including SCFs, for sample preparation, and since then, numerous new applications have been reported.

The main focus of recent literature is on the use of SFE in food, toxicology, pharmaceuticals, and environmental fields from 2007 to 2009. SFE has been studied both as a sample preparation technique and for analytical-scale process development. Carbon dioxide (CO_2) is the most commonly used supercritical solvent due to its favorable properties: it is inexpensive, environmentally friendly, and generally recognized as safe (GRAS) by regulatory bodies such as the FDA and EFSA. CO_2's critical conditions (30.9°C and 73.8 bar) make it suitable for use as a supercritical fluid in various applications. Its high diffusivity, tunable solvent strength, and gaseous state at room temperature simplify analyte recovery, producing solvent-free results.

One of the major advantages of supercritical CO_2 (SC-CO_2) is that it can operate at low temperatures in a non-oxidizing medium, which is beneficial for extracting thermally labile or easily oxidized compounds. However, SC-CO_2 has a low polarity, limiting its solvation power. This limitation can be addressed by introducing polar co-solvents (modifiers), such as methanol (1-10%), which increase the polarity of SC-CO_2 and broaden its ability to dissolve polar analytes. The addition of these modifiers also enhances analyte-matrix interactions, leading to improved quantitative extraction.

The design and optimization of supercritical solvent processes rely heavily on phase equilibrium engineering, which considers the effects of operating conditions on phase behavior. Phase equilibrium engineering involves the systematic application of thermodynamic data, experimental data, and mathematical models to design supercritical processes. The complex nature of phase behavior near critical conditions makes rigorous simulations necessary for equilibrium stage separations. However, these equilibrium calculations often face convergence difficulties due to the complexity of near-critical conditions.

To address these challenges, techniques such as Michelsen's phase stability criterion, multiple-phase flash algorithms, and global phase computations have been developed. These methods are particularly important for supercritical extraction applications, where precise phase equilibrium calculations are critical for process design and optimization. Brignole's group, along with other researchers, has made significant contributions to the understanding of phase equilibrium in supercritical processes.

Supercritical fluid extraction, particularly with CO_2, has gained considerable attention due to its environmental benefits, low operational costs, and adaptability for various industrial applications. The continued development of phase equilibrium engineering, thermodynamic analysis, and process design methodologies will play a key role in advancing the capabilities and applications of supercritical processes across multiple industries.

Organic solvent extraction is one of the main processes in industrial applications, with the sustainability expectations supercritical carbon dioxide ($scCO_2$) extraction is considered as an alternative to traditional methods, in recent years. A detailed analysis of the extraction of natural waxes and lipids highlights supercritical carbon dioxide ($scCO_2$) as a cleaner, greener alternative to traditional organic solvent extraction methods. Natural waxes are widely used in various industrial applications, and their demand is growing due to increasing petroleum wax costs and supply constraints. Petroleum wax production is decreasing due to shifts in feedstock production and the introduction of catalytic dewaxing technologies. This trend, combined with a projected rise in demand, could lead to a supply shortage by 2020 (Kline, 2015). As a result, there is growing interest in sustainable, natural waxes, with maize stover emerging as a potential feedstock. The United States alone produces approximately 68 million tonnes of maize stover annually, and studies show that two-thirds can be harvested sustainably without affecting soil health.

Traditional extraction methods, such as using hexane, are problematic due to their toxicological and environmental hazards. In contrast, $scCO_2$ is a non-toxic, non-flammable, widely available solvent that offers high mass transfer rates and solvation power at relatively low temperatures. Its properties, which fall between those of a liquid and a gas, allow for enhanced heat and mass transfer. By adjusting the temperature and pressure, the solubility of $scCO_2$ can be fine-tuned, making it an effective solvent for wax extraction. The technique has been commercially applied in various industries for over two decades, including the decaffeination of coffee and the extraction of hops for beer production.

Despite its advantages, $scCO_2$ extraction is often perceived as expensive and energy-intensive, requiring specialized equipment and skilled operators. This perception has hindered its widespread adoption by the chemical industry. However, integrating $scCO_2$ extraction into a holistic biorefinery could mitigate these issues, providing significant environmental and economic benefits. For instance, it has been shown to increase the production efficiency of biofuels, such as ethanol, by improving yields by up to 40% from the residual biomass post-extraction.

The review highlights the potential of $scCO_2$ extraction as a cleaner alternative to traditional solvents, especially in producing sustainable waxes. It also emphasizes the benefits of integrating this technology into a biorefinery, where it could enhance downstream processes, including the production of biofuels and personal care products from post-extraction residues. The text references the work of Herrero et al. (2010) and Attard et al. (2015c), who demonstrated the importance of $scCO_2$ extraction for biomass processing.

While $scCO_2$ extraction has proven useful for high-value applications, such as extracting essential oils, bioactive molecules, and edible oils, its application for waxes remains underexplored. The high costs associated with supercritical fluid extraction (SFE) processes—largely due to the high-pressure equipment required—have limited its use to niche markets. However, recent developments in industrial-scale units have helped reduce these costs. For instance, Turton et al. proposed a methodology to economically assess the production of chemicals using SFE, which has been applied to essential oils and other products. This methodology will be employed in the study to evaluate the cost of extracting waxes from maize stover using $scCO_2$, with the understanding that it would serve as an initial pre-treatment step in a larger biorefinery process.

Therefore the growing need for sustainable processes for extraction of (petroleum)waxes and the potential of $scCO_2$ makes it the green alternative for a biorefinery applications. By integrating $scCO_2$ extraction into a holistic production process, the economic viability of natural wax production could be enhanced, reducing reliance on toxic solvents and increasing the sustainability of industrial wax applications.

One promising use of supercritical extraction process can be in the management of olive mill waste (OMW), a byproduct of olive oil production that poses significant environmental and economic concerns. The global production of olive oil reached 2.9 million metric tons in the 2012–2013 harvest, with the Mediterranean Basin and Middle East accounting for 95.9% of total production. Spain alone contributed nearly 34% of global production. Olive oil production generates four times the amount of waste as oil, creating environmental burdens and wasting potentially valuable byproducts. Most olive mills use a three-phase centrifugation system, which produces two types of waste: olive mill wastewater (OMW) and solid waste known as pomace.

OMW contains high concentrations of biophenols (0.02–10 g kg−1), such as hydroxytyrosol, tyrosol, and caffeic acid, which are known for their antioxidant, anti-inflammatory, and antimicrobial properties.

Biophenols are phytotoxic and bacteriostatic, making the disposal of OMW a challenge. In some regions, OMW is used as fertilizer, with low concentrations improving soil properties like organic carbon and cation-exchange capacity. However, high doses of OMW are toxic to crops and soil microorganisms. On the other hand, biophenols, particularly hydroxytyrosol, are valuable compounds. Hydroxytyrosol retails for around $500 per 100 mg at 98% purity, and nutraceutical products containing it can sell for 100–200 € per 100 mg. Extracting these biophenols from OMW would address disposal challenges while creating a revenue stream for industries such as cosmetics, pharmaceuticals, and health foods.

Additionally, OMW contains unsaturated fatty acids (UFA) and squalene, a compound that can reduce cholesterol and triglyceride levels and protect skin from lipid peroxidation. Squalene is absorbed in the human body and is one of the major components of epidermal lipids. Several methods exist for extracting biophenols, UFA, and squalene from OMW, including micro- and nano-membrane filtrations, ultrasound-assisted extraction, solvent extraction, superheated liquid extraction, and supercritical fluid extraction (SFE). Supercritical carbon dioxide (SCO_2) extraction is particularly attractive due to its non-toxic, non-flammable nature and its moderate critical conditions (31.1 °C and 73.8 MPa), which allow for effective extraction without the use of harsh solvents.

SCO_2 extraction offers several advantages, including tunable solvency power based on temperature and pressure adjustments, which allows for selective extraction of desired compounds. The lower temperatures used in SCO_2 extraction reduce thermal stress on extracts compared to conventional methods. However, the low polarity of CO_2 limits its effectiveness for extracting highly polar compounds, a limitation that can be overcome by using co-solvents such as ethanol or methanol. While methanol is more effective, ethanol is preferred for applications involving human consumption due to its lower toxicity.

OMW's disposal as fertilizer is complicated by the vast quantities produced during the 3–4 month harvest season, making land application insufficient as a sole disposal method. Transporting OMW long distances to agricultural sites would increase costs and the carbon footprint of disposal.

Alternative disposal methods for OMW include combustion and pyrolysis. Combustion is suitable for large-scale olive oil production facilities where land application is not feasible. It reduces waste via oxidation, using the heat for evaporation and other purposes. However, the extent of combustion, volatilized compounds, and ash disposal must be addressed for this method to be viable. Pyrolysis, which involves heating OMW in the absence of oxygen, can produce bio-oil or syngas and carbonaceous char. The bio-oil from raw OMW has a calorific value of 29 MJ kg−1, with maximum oil yield achieved at 550 °C during fast pyrolysis. Syngas produced at 550 °C contains approximately 50% CO_2, 14% CO, 21% H_2, with the remaining balance split between CH_4, C_2H_4, and C_2H_6.

With the use of supercritical extraction in olive waste, a biorefinery approach can be implemented to the olive oil production process. Here a biorefinery use aims to extract high-value antioxidants, biofuels, energy, and sustainable carbon sources for soil, while addressing environmental concerns related to OMW disposal. The development of pyrolysis and other waste treatment methods, in combination with SCO_2 extraction, could further modernize and "green" the ancient practice of olive oil extraction.

Another significantly researched application of supercritical extraction is in its use for plant or wood (lignocellulosic) feedstock processes. Lignin is a complex and robust polymer derived from lignocellulosic raw materials, as an alternative to petroleum-based products. Lignin is also a byproduct of biorefinery processes used to convert biomass into transportation fuels, and this biorefinery byproduct has an opportunity for sustainable use that can reduce global greenhouse gas emissions. However, its complex structure, which varies based on origin and extraction method, makes its utilization challenging.

Lignosulfonates, a type of lignin from sulfite pulping, make up about 90% of commercial lignin with a worldwide annual production of 1.8 million tons. They are water-soluble and have high molecular weight and sulfonate content, important for their use as dispersants in various applications. Controlling the molecular weight of lignosulfonates through techniques like separation, depolymerization, and chemical modification is crucial for their applications. Despite characterization studies, much of their global structure remains unknown.

Environmental concerns are raised about sulfur-based pulping processes, leading to the pursuit of more eco-friendly alternatives, such as supercritical water, which can hydrolyze lignin for potential phenolic chemical production or fuel upgrades. Supercritical water treatment can cleave β-O-4 linkages, with temperature and reaction time influencing the depolymerization pathway. Around 50 million tons of lignin are burned as fuel in pulp mills annually, while only 2% is used commercially, mostly in low-value applications.

Lignin can be valorized in three ways (i) Depolymerizing it into aromatic chemicals, which has significant market potential but remains underdeveloped; (ii) Using it as a macromolecule in applications like additives or polymer blends and (iii) Employing it as a carbon precursor for products like activated carbons and carbon fibers.

Depolymerization of lignin produces aromatic compounds like benzene, toluene, and vanillin, but processes that break C-C bonds (e.g., pyrolysis, supercritical water treatment) are required for more complex lignins. Lignin gasification produces syngas for electricity or hydrogen production. In polymer applications, lignin's chemical and thermal properties determine its effectiveness, with its most advanced application being as a replacement for phenols in adhesives.

Lignin also has potential in carbon fiber production, where it could replace polyacrylonitrile (PAN) and reduce costs. Carbon fibers made from lignin are used in industries such as automotive, aerospace, and sports. Activated carbon produced from lignin is a strong adsorbent for various substances, and lignin is also used in the production of carbon black.

The potential of using supercritical extraction

3.1.7. Transesterification

The world as we know it is facing a rapidly growing global population, along with accelerating urbanization and industrialization. This continuous growth and development significantly increases the demand for energy. Due to rapid industrialization and urban development, a 27% increase in total world energy consumption is projected between 2015 and 2040 (BMWK Newsletter Energiewende - IEA 2024). Currently, traditional energy sources such as coal, petroleum, and natural gas meet most of this demand. Fuels like diesel, gasoline, liquefied petroleum gas, and natural gas are widely used for transportation. However, their environmental impact cannot be ignored, leading to the promotion of natural, clean, and green energy sources.

Although fossil fuels are still produced through subsurface heat and pressure, their depletion rate surpasses their formation rate. Since we cannot replenish these fuels at the same rate we consume them, fossil fuels are considered non-renewable. Additionally, petroleum-based fuel reserves are concentrated in limited regions of the world.

To address the increasing energy demands and the shortage of petrol and diesel fuel, researchers have long focused on biofuels as an alternative to conventional fuels (Demirbas 2009).

Biodiesel is a renewable fuel made from natural sources like vegetable oil or animal fat. It is typically produced through a process called transesterification, where these feedstocks are reacted with an alcohol, typically methanol. In this process, one mole of triglyceride reacts with three moles of alcohol in the presence of an acid or base catalyst, yielding biodiesel and glycerol

(Mahmudul et al. 2017). In other words, biodiesel consists of fatty acid methyl ester (FAME) produced by the reaction of methanol with free fatty acids (FFAs) (Hajjari et al. 2017).

Various feedstocks used in biodiesel production result in varying biodiesel composition, quantity, purity, and yield. However, crude glycerol (CG) is consistently generated as a by-product across all biodiesel production methods. Glycerol is also known as 1,2,3-propanetriol and is a versatile molecule with two primary and one secondary hydroxyl groups that can easily form other derivatives and can be converted into thousands of other chemicals through oxidation, dehydration, esterification, etherification, acetalization, carboxylation, hydrolysis, pyrolysis, polymerization, and other reactions (Wang et al. 2024a). Pure glycerol, usually close to 100 %, is a colorless, sweet-tasting, viscous liquid derived from synthetic feedstocks with a density of 1.26 g/cm3 and is commonly used in foods, pharmaceuticals, and cosmetics (Kaur et al. 2020). In turn, CG is the main by-product of biodiesel production, with circa 1 kg of CG being generated per 10 kg of biodiesel produced (G Quispe et al. 2013; Ardi et al. 2015). Typically, CG contains various impurities, including fatty acids, alkoxide salts, inorganic salts, "matter organic, non-glycerol" (MONG), water and unreacted methanol. Although high-purity glycerol holds significant market value (G Quispe et al. 2013; Ardi et al. 2015), impurities in CG restrict its use in traditional applications. However, CG can undergo purification steps or be utilized directly, without treatment, in the production of other products such as polymers.

Polymers, commonly referred to as plastics, find extensive applications across diverse sectors such as household appliances, packaging, construction, electronics, automotive, and more. Their adaptability in processing and the capacity to tailor their properties make them primary substitutes for metals, wood, and glass. However, a major drawback lies in the fact that polymers are mainly derived from petroleum feedstocks. Yet, many polymers are produced using alcohol, hence CG represents a good candidate for the substitution of the fossil raw materials.

In general, CG is used as substitute or partially substitute of the fossil-based materials to produce poly(glycerol-co-diacids) polyesters, polyhydroxyalkanoates (PHA) polyglycerols, and others (Hejna et al. 2016; Goyal et al. 2021; Wang et al. 2024b). Yet, the most commonly polymer produced using CG is polyurethane (PU).

PU is one of the main types of polymers. It is widely used in various applications due to its versatility, durability, and resilience (Gama et al. 2018a). PU ranks among the most adaptable polymers due to its versatility in various applications, including elastomers, adhesives, paints, and foams. The synthesis of this polymer occurs through the creation of urethane linkages, which result from the reaction between the OH groups of a polyol and the NCO groups of an isocyanate (Gama et al. 2018a). Due to its wide range of uses, the production of PU has seen significant growth in recent decades, primarily in the form of foam (PUF). Indeed, in 2023, the global PU market size reached USD 75.19 billion and is projected to experience a compound annual growth rate (CAGR) of 4.4% from 2023 to 2030 (Plastics 2023).

Like other polymers, PUs rely on petroleum feedstocks and the increasing concern over the environmental impact and scarcity of petroleum, has motivated the development of PUs from bio-based and renewable raw materials (Tan et al. 2011). For example, lignin (Vieira et al. 2023), cork (Gama et al. 2015), starch (Kwon et al. 2006), soybean (Hu et al. 2012), sugar beet pulp (Pavier and Gandini 2000) or date seeds (Briones et al. 2011) have been used to replace conventional polyols in the synthesis of PU. However, the processes used to obtain polyols from this type of resources generally require glycerol (or similar chemicals) as reactant. Hence, CG being itself a polyol, it has been used as an alternative raw material for the production of PU (Luo et al. 2013; Ferreira et al. 2014). Furthermore, a couple of processes regarding the treatment of CG and subsequent use in the production of PUs have been patented (Yebo Li and Yuguang Zhou 2009; Yebo Li et al. 2010). Li et al (Li et al. 2014) have reported the preparation of biopolyols, from CG, via a one-pot thermochemical process and subsequently used them in the production of PUs. They have concluded that the presence of branched fatty acid ester chains in biopolyols helps reduce the degree of microphase separation and stabilize the bubbles during the foaming process.

As mentioned, CG composition may vary depending on the biodiesel production conditions. In that sense, the impact of CG composition on the properties of the ensuing PU foams was evaluated (Gama et al. 2018c). Foams were prepared using CG samples with different composition, pure glycerol and GC subject to a purification process. From the results obtained it was concluded that the impurities present in unrefined CG seem to positively affect the foaming process, the crosslinking density and can have some plasticizing effect. As a result, the mechanical properties of the ensuing foams were lower than those obtained for PU foam derived from pretreated CG. However, a judicious control of the percentage of this type of impurities, reaction parameters and even inorganic fillers can be explored to tune these properties. Moreover, the thermal stability and thermal conductivity are not significantly affected by the presence of fatty acids and esters. Indeed, all CG derived PU foams were thermally stable up to 180 ºC and exhibited low densities and low thermal conductivities hence CG, without any purification step or pre-treatment is a suitable material for the production of PU. Additionally, the evaluation of the impact of the use of these ecofriendly polyols towards sustainability of foam production yielded promising results.

Next, the effect of the main components of the formulation used for the preparation of PU foams derived from unrefined CG was systematically studied (Gama et al. 2016). A series of PU foams were prepared using formulations with judicious variations of the percentage of each component. The physical properties of the resulting materials were measured, and the data collected were statically treated using a four-way functional ANOVA method. From the ANOVA results, the paramount importance that the blowing agent and the surfactant have on the regulation of density and thermal conductivity of the foams was recognized. Regarding the mechanical properties, the isocyanate content presented a dominant influence on the increase of mechanical properties of foams. Overall, it was demonstrated that independent of the foam population, a series of PU materials can be produced using CG, being their properties easily adjustable.

Being this type of foams mainly used for thermal insulation, to enhance the thermal comfort properties of CG derived PU foams using phase change materials (PCMs) (2.5–10.0% (wt/wt)) (Gama et al. 2018d). The main challenge in incorporating PCMs into PU foams is to balance the low conductivity of such materials with the heat released or absorbed by PCMs for efficient thermal regulation. To address this challenge, expandable graphite (EG) was considered as a solution (0.50–1.50% (wt/wt)). Results indicate that the use of PCMs increased the heterogeneity of the foam cellular structure, and the incorporation of PCMs and EG increased the stiffness of the resulting composite PU foams by acting as filler-reinforcing materials. Furthermore, numerical simulations were conducted using a single-layer panel and measured thermal and physical properties to evaluate the behavior of composite PU panels with different compositions. These simulations aimed to guide future formulations for achieving more effective results in terms of temperature buffering and delay of temperature peaks. In conclusion, it was demonstrated that CG is a suitable precursor to produce high value materials.

Similarly, the sound absorption properties of foams produced using CG and/or liquefied coffee grounds derived polyol (POL) was evaluated (Gama et al. 2017). The lignin content of POL was found to significantly influence the structure and mechanical properties of the foams. Specifically, the POL content increased the cell size and stiffness of the foams, subsequently impacting the sound absorption coefficients. Foams derived from POL exhibited slightly higher sound absorption coefficient values at lower frequencies, whereas CG-based foams demonstrated higher values at higher frequencies. Foams prepared using a 50/50 mixture of polyols exhibited slightly higher sound absorption coefficient values in the medium frequency range due to a balance between cell structure and mechanical properties. These results suggest that the sound absorption mechanisms depend on the foam formulation used. Additionally, higher POL contents improved the thermal stability and mechanical properties of PU foams. Overall, it was demonstrated the suitability of CG and/or POL-derived foams as sound-absorbing materials.

The reaction to fire performance of PU foams derived from CG was also enhanced using EG (Gama et al. 2018b). The impact of different loadings of EG on the physical and mechanical properties of composite foams was assessed, showing significant influence. Furthermore, the reaction to fire of the foams and composites was investigated, revealing that the fire behavior of composite foams containing as little as 5 wt% of EG was significantly improved. Notably, a dramatic reduction in the rate of heat release, mass loss rate, effective heat of combustion, and specific extinction area was observed even with relatively low amounts of EG. Similarly, the use of infrared thermography over time indicated that when EG was incorporated, combustion halted suddenly, and the temperature dropped sharply compared to unfilled PU samples, suggesting that EG acted as a flame extinguisher.

Finally, PU scraps derived from GC where recycled via acidolysis (Quinteiro et al. 2022). In this process, succinic acid was used as cleavage agent, using a reaction solvent (CG, conventional polyol or using an inert solvent i.e. paraffin. The function of the cleavage agent is to react with the carbamic group of PU, as well as with ureas, allophanates, biurets or amides network, which will gradually depolymerize into a polyol (CG) and/or other oligomers and small molecules. The viscous liquid obtained can be used as partial or total substitute of the conventional polyols in the production of a wide range of applications including, but not limited to, the production of PU elastomers, adhesives, paints or foams.

The studies presented in literature illustrate the suitability of CG as a valuable resource for producing new materials through a cost-effective process. Rather than disposing of or burning this biodiesel by-product for energy, these works highlight the potential to add value to CG by utilizing it in various applications. This not only addresses environmental concerns associated with CG disposal but also contributes to the development of sustainable materials and processes.

Conclusion

Physicochemical treatment operations or processes include the vast majority of pretreatment technologies such as mechanical processing, extraction, hydrolysis, transesterification, supercritical extraction, steam pretreatment (or steam explosion), liquid hot water pretreatment, wet oxidation pretreatment, ammonia fiber/freeze explosion, ammonia recycle percolation, aqueous ammonia pretreatment, and organosolv pretreatment. Recently, the use of ionic liquids and cellulose solvent-based lignocellulose fractionation has been proposed (Zhu et al., 2006; Zhu et al., 2009). These forms of pretreatment exploit the use of conditions and compounds that affect the physical and chemical properties of biomass. Physicochemical processes can be grouped but are not limited to steam pretreatment (SP), liquid hot pretreatment, ammonia fiber/freeze explosion (AFEX), ammonia recycle percolation (ARP), soaking aqueous ammonia (SAA), dilute acid treatment, lime pretreatment (LP) + wet oxidative pretreatment (WOP), organosolv treatment, ionic liquid treatment, and carbon dioxide (CO_2) explosion pretreatment (CDE). Selected processes from these categories are evaluated in this chapter. Scientific research on physicochemical biorefinery processes is very dynamic. Based on the current knowledge, the following Technology Readiness Level (TRL) evaluation table may lead to a technology comparison among the processes.

Table 2. Biomass waste physicochemical processes readiness levels (TRLs)

Biorefinery Process	TRL	Description
Steam Pretreatment (SP)	7-8	Demonstration to early commercial stage; widely used for biofuel production, scaling up across industries.
Liquid Hot Water Pretreatment	5-6	Pilot scale, showing potential for scalability, but not widely commercialized yet.
Ammonia Fiber/Fiber Explosion (AFEX)	4-5	Lab-scale to pilot studies, effective for certain feedstocks, but not yet commercially implemented.
Ammonia Recycle Percolation (ARP)	4-5	Mostly in lab and pilot stages, effective for lignin removal but requires more optimization.
Soaking Aqueous Ammonia (SAA)	4-5	Lab to pilot scale, showing potential for lignocellulosic biomass but still in developmental stages.
Dilute Acid Treatment	7-8	Well-established in commercial biorefineries; used at industrial scale for ethanol production.
Lime Pretreatment (LP) + Wet Oxidative Pretreatment (WOP)	5-6	Tested at pilot and demonstration scales, with potential for commercialization.
Organosolv Treatment	5-6	Pilot scale; promising technology but faces economic and scalability challenges for full commercialization.
Ionic Liquid Treatment	3-4	Early-stage research and lab-scale experiments; high cost and recovery issues hamper commercial progress.
Carbon Dioxide (CO2) Explosion Pretreatment (CDE)	3-4	Lab scale; effective for specific feedstocks, but further research needed for commercial viability.
Mechanical Treatment	5-6	Commonly used in biomass processing; effective for size reduction and enhancement of biomass accessibility.
Supercritical Extraction	4-5	Pilot scale; shows promise for extraction of bioactive compounds, but not widely commercialized yet.

Transesterification	7-8	Well-established process for biodiesel production; widely used and commercialized.
Hydrolysis	6-7	Established at pilot to commercial scale, often used in conjunction with other processes for biofuel production.
Extraction	5-6	Various methods at pilot scale for bioactive compounds; established but dependent on target compounds.

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KEY ENABLING TECHNOLOGIES ACCORDING TO FEEDSTOCK TYPE

Part IV

Emerging Conversion Technologies

CA 20127

Waste biorefinery technologies for accelerating sustainable energy processes (WIRE)

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Table of contents

List of acronyms

AD	Anaerobic digestion
AEM	Anion exchange membrane
BESs	Bioelectrochemical systems
CDH	Cellobiose dehydrogenase
CEM	Cation exchange membranes
COD	Chemical oxygen demand
DET	Direct electron transfer
EFC	Enzymatic fuel cells
EM	Electromethanogenesis
EPS	Extracellular polymeric substances
FAD	Flavin adenine dinucleotide
GDH	Glucose dehydrogenase
GOx	Glucose oxidase
GSB	Green sulfur bacteria
HC	Hydrodynamic cavitation
ICT	Immobilized cell technologies
MDCs	Microbial desalination cells
MEC	Microbial Electrolysis Cell
MES	Microbial electrochemical systems
MET	Mediated electron transfer
MFC	Microbial Fuel Cell
MSCs	Microbial solar cells
NAD	Nicotinamide adenine dinucleotide
PEM	Proton exchange membranes
PNSB	Purple non-sulfur bacteria
PPBs	Purple phototrophic bacteria
PSB	Purple sulfur bacteria
RO	Reverse osmosis
SCW	Supercritical water
SCWG	Supercritical water gasification
SCWO	Supercritical water oxidation
VSEP	Vibratory shear enhanced process

List of figures

List of tables

Executive summary

Novel technologies in waste refineries are gaining attraction as the need to address resource depletion and environmental pollution. Thermochemical, physicochemical, biological, and other emerging processes provide sophisticated, environmentally acceptable ways to transform waste into useful sources like energy, biochemicals, and biofuels. These processes, when harmonized, can drive the development of integrated biorefineries, which are critical for promoting sustainability and a circular bioeconomy. This executive summary explains the emerging processes within each domain and highlights the importance of their approach in optimizing waste refinery. Biological and biochemical waste refinery processes leverage the natural capabilities of microorganisms and enzymes to degrade, metabolize, and convert organic matter into energy and valuable byproducts. Microbial Fuel Cells (MFCs) and Microbial Electrolysis Cells (MECs) are examples of bioelectrochemical systems that generate electricity or hydrogen while simultaneously treating wastewater. Additionally, microbial electrosynthesis (MES) utilizes microbes to convert carbon dioxide and electricity into bio-based chemicals. These processes not only help in resource recovery but also offer solutions for energy generation from waste streams. In parallel, technologies that use purple phototrophic bacteria (PPB) are being explored for their ability to treat wastewater while recovering nutrients like nitrogen and phosphorus, essential for agriculture. Another emerging biochemical method is Bokashi fermentation, a low-energy anaerobic composting process that breaks down organic waste into nutrient-rich compost, reducing landfill contributions and enhancing soil health.

Large-scale thermochemical processes such as pyrolysis, gasification, and hydrothermal liquefaction (HTL) involve the application of heat and pressure to decompose organic materials. These processes are critical for converting complex organic waste into energy-dense products and offer a complementary pathway to biological methods for addressing waste that is not easily biodegradable. They have been applied for decades now. On the other hand, emerging thermochemical technologies such as supercritical water oxidation (SCWO) and supercritical water gasification (SCWG) offer advanced methods for breaking down waste at high temperatures and pressures. SCWO, in particular, excels in treating hazardous and complex waste, producing clean water and energy. These processes are invaluable for handling waste that cannot be treated biologically or physically, expanding the range of waste refinery capabilities.

While each of these processes—biological, biochemical, thermochemical, and physicochemical—have their strengths, harmonizing them within integrated biorefineries is key to maximizing their potential. An integrated biorefinery combines multiple processes to handle different waste streams efficiently, creating a system where each technology complements the other. For instance, biological processes can be used for initial waste treatment and energy generation, while thermochemical methods can refine the residual waste into biofuels or chemicals. Physicochemical processes can manage difficult-to-treat waste and recover additional resources like clean water or syngas.

This harmonization also allows for flexibility in handling diverse types of waste, ensuring that nearly all components are converted into useful products. Such integration reduces the need for external inputs, lowers waste management costs, and enhances resource recovery. Moreover, combining these processes improves the overall energy efficiency of the system, minimizes greenhouse gas emissions, and promotes a circular economy by ensuring that waste is treated as a valuable resource rather than a disposal problem.

Emerging biological, biochemical, thermochemical, and physicochemical processes represent the future of sustainable waste refineries. By harmonizing these diverse technologies within integrated biorefineries, industries can not only optimize waste-to-resource conversion but also reduce environmental impacts and contribute to the global shift toward renewable energy and materials. The convergence of these technologies is essential for developing comprehensive waste refinery systems that are scalable, energy-efficient, and environmentally sustainable. Through continued research and investment, harmonized biorefinery systems hold the potential to revolutionize waste management and drive the circular bioeconomy forward.

4. Introduction

The word "emerge" comes from the Latin verb *emergere*, which is defined as “rising out of or coming forth from” something. In its modern usage, it means to come out into view, to become apparent from a difficult or uncertain situation (OED, 2024). Conventional technologies come across difficulties such as resource depletion, water and environmental pollution, effects on global climate change, and the obligation to use renewable and cleaner energy for the last decades (Jain, 2024). Emerging technologies offer new solutions to these problems. They facilitate the conversion of waste streams into valuable products such as biofuels, value-added materials and chemicals, and energy, thereby reducing waste and lowering carbon emissions (Kong et al., 2023). The integration of such technologies with the current technologies is essential for industries aiming to meet stricter environmental regulations and achieve long-term sustainability goals while maintaining economic viability (Lobato-Peralta et al., 2021; Jain, 2024). They have a critical role in transforming current industrial applications by promoting innovative methods that improve efficiency, sustainability, and competitiveness (Wilberforce et al., 2021).

Wastes and waste streams can be defined as a material, substance, or by-product eliminated or discarded as no longer useful or required after the completion of a process. They are derived from all kinds of modern world activities, such as housing and transportation industries, agricultural, livestock, and nutrition processes (Kataya et al., 2023). However, nowadays a new concept is being prioritized regarding waste and waste streams. The approach of the European Environment Agency and the United Nations to waste materials can be summarized as the circular and sustainable management strategy that has been promoted recently. In their waste management strategy, wastes are referred to as valuable resources that are used to produce sustainable benefits and end products as long as the resource can be converted (EEA, 2023). Therefore, the organic wastes and waste streams (biomass, waste/waste stream, including biosolids) derived from human activities can be called prominent resources for the current and developing conversion technologies. In this regard, emerging conversion technologies can potentially be a new approach for the treatment of the waste/waste streams that have been treated by conventional biological, physical, and thermochemical technologies, which sometimes are not efficient enough or at the desired level. Hence, the studies focus on the alternative treatment technologies or the new insights to the current technologies, such as integration, new designs, etc. Emerging conversion technologies can be categorized under four different groups according to their driving forces and mechanisms, as illustrated in Figure 1.

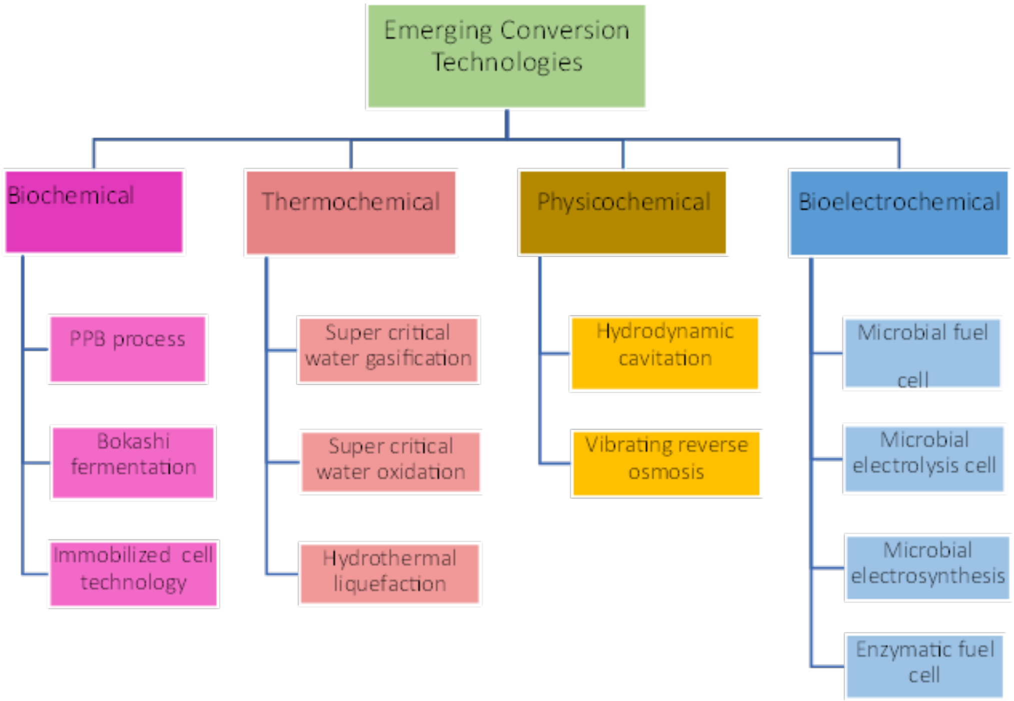

Figure 1. Emerging conversion technologies according to their mechanisms.

A biochemical process is the conversion of biomass and wastes into value-added or non-hazardous products (biogas, fertilizer, chemicals, sludge, and compost) via biological catalysts such as enzymes and/or microorganisms in certain and organized conditions (Velvizhi et al., 2023; Tshikovhi and Motaung, 2023). Biochemical processes are the well-known processes such as waste-activated sludge process, anaerobic digestion, fermentation, composting, and hydrolysis (Ambaye et al., 2023). These processes can be integrated and/or applied in series as in pretreatment according to the waste type and targeted end product. Other than these biochemical processes, there are emerging biochemical technologies such as the phototrophic purple bacteria process, bokashi fermentation, immobilized cell technology, and microalgae cultivation process that are promising methods to present an alternative and sustainable way to treat biomass and wastes. These biochemical emerging technologies are detailed in the following sections. Bioelectrochemical technologies are the recent technologies among other conversion technologies that utilize many kinds of waste and waste streams as feedstock and produce electricity, hydrogen, methane, fertilizer, value-added chemicals, clean water, etc. and provide nutrient recovery as well as CO_2 recovery and CO_2 removal (Bhattacharya et al., 2023; Annie Modestra et al., 2022; Wilberforce et al., 2021). BES are derived from the conventional electrochemical cells and the microbial biochemical processes such as anaerobic digestion and aerobic digestion (Wang and Zhou, 2024). The first discovered BES is the Microbial Fuel Cell (MFC), which harvests electrical current from the degradation of organic substances via an electrogenic microbial consortium (Wang and Zhou, 2024; Zheng et al., 2020). They produce electrons, protons, and CO_2 at the anode electrode using organic material, and electrons flow from the anode to the cathode electrode, producing current.

Meanwhile, reduction of protons at the cathode via O_2 produces water (Wilberforce, et al., 2021). In contrast to MFC, the Microbial Electrolysis Cell (MEC) is an electrical current-consuming (0.2-1.2 V) system where electrons are combined in the cathode chamber and produce hydrogen, methane, or value-added biochemicals such as ethanol, hydrogen peroxide, etc. from organic matters in an anaerobic environment (Escapa et al., 2016). The micobial desalination cell (MDC), which has a similar working mechanism to MFC, is operated with two membranes to separate anions and cations from the stream, respectively, and produces desalinated water and power at the same time (Wang et al., 2022). The MDC is proposed to serve as a pre-desalination unit for the subsequent reverse osmosis (RO) desalination process. One of the latest emerging bioelectrochemical technologies is the microbial electrosynthesis cell (MES), which is used to produce biochemicals including ethanol, short/medium chains of volatile fatty acids, H_2O_2, and polyhydroxybutyrate (PHB) using CO_2 as the feedstock under voltage application (Wang et al., 2022; Modestra et al., 2022).

One of the most used biomass conversion technologies is the thermochemical process, which relies on high-rate heating and high-temperature application at pressurized or ambient air conditions with/without a catalytic gas such as oxygen (Afraz et al., 2024). Many kinds of biomass and waste can be used in thermochemical processes as feedstock to produce valuable products such as heat, bio-oil, bio-char, and syngas (H_2, CH_4, CO_2, etc.), which may need an extra purification step before usage (Velvizhi et al., 2023). The main industrialized thermochemical conversion techniques are pyrolysis, gasification, combustion, and hydrothermal carbonization. All have modified sub-methods according to their process parameters, such as, residence time, heating rate, process temperature, medium, catalyst, etc. (Tshikovhi and Motaung, 2023). As a result of the difficulties encountered during the thermochemical processes, new approaches are provided as emerging technologies. These are the supercritical water gasification and oxidation, hydrothermal liquefaction, microwave pyrolysis, etc., some of which are detailed in the following sections.

Physicochemical conversion technologies are mostly applied as the pretreatment phase for further biochemical or thermochemical processes. General physicochemical technologies include milling, extrusion, ultrasonication, heating, and microwave radiation (Gallego-García, et al., 2023). Physicochemical conversion technologies such as hydrodynamic cavitation and vibrating reverse osmosis are the recent ones that are being developed for the physical treatment and conversion of the feedstocks. There are hydrodynamic and ultrasonic cavitations that can be applied to form products from waste streams.

Cavitation occurs when the transient pressure in a liquid flow changes suddenly, causing microbubbles to form, grow, and implode under intense energy bursts. Hydrodynamic cavitation is created in a flow system by forcing liquid through constriction zones, where rapid changes to low pressure can be realized (Ranade, 2022; Ranade et al., 2022). On the other hand, vibrating reverse osmosis, also known as vibratory shear enhanced process (VSEP), is a phase separation process driven by pressure and a selective membrane. The membrane separation technology process consists of a synthetic barrier with the capacity to selectively prevent the passage of certain components across it. The limitations of conventional membrane systems, such as rapid fouling, clogging of the membrane pores, and short periods of usage, led the way to VSEP, which is a promising technology also for wastewater treatment.

4.1. Emerging Biochemical and Bioelectrochemical Technologies

Emerging biochemical and bioelectrochemical processes represent a rapidly advancing frontier in the fields of biotechnology and environmental engineering. These processes harness the metabolic activities of microorganisms, enzymes, and bio-based catalysts to convert organic and inorganic substances into valuable products, such as biofuels, biochemicals, and electricity. Notably, bioelectrochemical systems (BESs) integrate biology with electrochemical systems to facilitate energy-efficient waste treatment, resource recovery, and renewable energy generation. On the other hand, emerging biochemical technologies like the use of purple phototrophic bacteria (PPBs) and bokashi fermentation are opening new pathways in sustainable agriculture, waste management, and environmental biotechnology. PPBs, known for their ability to capture light energy and utilize organic waste as a carbon source, offer innovative solutions in wastewater treatment, biofuel production, and nutrient recycling. Similarly, bokashi fermentation, a method of composting using anaerobic fermentation with beneficial microorganisms, provides an efficient way to manage organic waste while enhancing soil health and carbon sequestration. Innovations in these processes are gaining attention for their potential to address global challenges in energy sustainability, environmental remediation, and circular bioeconomy. As research progresses, these technologies hold promise for more sustainable, eco-friendly industrial applications.

4.1.1. Purple Phototrophic Bacteria (PPB)

The ability to grow using energy from light without evolving oxygen characterizes a diverse collection of organisms known as anoxygenic phototrophic bacteria, of which the four main groups are purple sulfur bacteria, purple nonsulfur bacteria, green sulfur bacteria, and green and red filamentous anoxygenic phototrophic bacteria (Frigaard, 2016). One of the main groups of phototrophic microorganisms that live in terrestrial and aquatic habitats is anoxygenic phototrophic purple bacteria. "Aerobic anoxygenic phototrophs" are purple bacteria that only perform photosynthesis aerobically and live in hazardous environments. Anoxygenic photosynthesis is the process by which purple bacteria, which are gram-negative prokaryotes, transform light energy into chemical energy. Purple bacteria can grow autotrophically using CO_2 as their only carbon source and possess photosynthetic pigments called carotenoids and bacteriochlorophylls. Purple bacteria are classified into numerous genera, and they are similar to their nonphototrophic counterparts in many fundamental ways. The capacity to store energy through photophosphorylation is an ability that oxygenic phototrophic prokaryotes, or cyanobacteria, share with purple bacteria. Purple bacteria can only photosynthesise in anoxic (O_2-free) environments, in contrast to cyanobacteria and aerobic anoxygenic phototrophs. The heliobacteria, green nonsulfur bacteria, and green sulfur bacteria are examples of other classical anoxygenic phototrophs that have this property. For purple bacteria to thrive phototrophically, anoxic conditions are necessary since molecular oxygen inhibits the synthesis of pigments in these creatures. Therefore, both light and anoxic conditions are necessary for purple bacteria to succeed in competition in nature. This combination is most frequently observed in lakes, ponds, estuaries, and other aquatic settings where H_2S is abundant (Madigan and Jung, 2009).

Purple Phototrophic Bacteria (PPB) is made up of two types of bacteria that frequently coexist in the same environment: purple non-sulfur bacteria (PNSB) and purple sulfur bacteria (PSB). With reduced sulfur compounds acting as an electron donor to lower inorganic carbon, PSBs are mostly photoautotrophic. PSB are mostly sulfur-dependent organisms with restricted photoheterotrophic and dark metabolic capacities. On the other hand, PNSBs are widely distributed photoheterotrophs that possess both photoautotrophic and varied capacity for dark chemotrophy, both anaerobic and aerobic (Capson-Tojo et al., 2020).

4.1.1.1. Current technology status

Compared to their aerobic and anaerobic counterparts, PPBs can assimilate a higher fraction of the carbon, nitrogen, and phosphorus present in wastewater. PPBs use infrared radiation (IR) as a source of energy, which lowers the power required by photon emission and allows a deeper light penetration into the cultivation broth (thus reducing the footprint of the process). PPBs have emerged as a promising technology platform for wastewater treatment. PPBs are also very resistant to temperature changes, which makes them the perfect microorganisms to support wastewater treatment in a variety of weather scenarios. PPB's adaptable metabolism may eventually enable an affordable biogas upgrade since it may use the organic matter in wastewater or the H_2S in biogas as an electron donor to reduce CO_2 from biogas without producing O_2 (Marin et al., 2019). PPBs grow at yields almost equal to unity in the photo-heterotrophic mode, allowing for the one-step recovery of nutrients and organics inside the PPBs biomass (Segura et al., 2023). Anaerobic phototrophic energy generation (by photophosphorylation) provides various advantages over chemoheterotrophic growth, with a focus on carbon and resource recovery. The advantages of using biomass as a value-added product include: (i) higher biomass yields that are nearly unified in terms of chemical oxygen demand (COD) basis (one g COD biomass formed per g COD taken up), leading to higher resource recovery efficiency; (ii) no need for aeration; and (iii) efficient PPB selection and enrichment in non-sterile environments (Capson-Tojo et al., 2020). It has also been noted that phototrophic bacteria have strong tolerance to heavy metals. Typically, trace elements serve as cofactors for vital cell reactions. According to reports, when molybdenum is present, *Rhodobacter sphaeroides* produces the most hydrogen, zinc and cadmium are poisonous to *Rb. sphaeroides*, whilst nickel and cobalt were found to reduce the cellular content of the light harvesting complexes. Yet, *Rhodobacter sphaeroides* exhibited a high degree of metal tolerance, particularly with regard to cobalt, iron, and molybdenum (Merugu et al., 2012).

4.1.1.2. The challenges and prospects

One of the main disadvantages of phototrophic processes is their need for light, as microalgae-based technology has extensively shown. The rates at which biomass is produced and the capacity for nutrient removal are determined by the availability of sufficient light. Next, the reactor needs to be built with efficient light delivery in mind. The great majority of PPBs research conducted to date has been in systems with artificial lighting. Due to the numerous lamps needed and the challenges associated with providing light to biomass growth regions, particularly on a large scale (which is necessary for practical implementation), this alternative has high capital costs and significant energy consumption. If treatment goals are the only consideration, phototrophic technologies are not cost-effective when compared to current treatment technologies (Capson-Tojo et al., 2020).

One of the primary pollutants found in biogas is hydrogen sulfide (H_2S), whose presence is undesirable because of its corrosive and poisonous character. H_2S quickly oxidizes to sulfuric acid in the presence of water, which degrades metals and damages engines, storage tanks, reactors, compressors, and pipelines. Both biological and physicochemical techniques can be used to desulfurize biogas. However, in comparison to biological approaches, physicochemical methods consume more energy and produce more waste. Because of their potential for sulfur recovery and environmental friendliness, biological technologies can overcome these disadvantages and provide extra benefits. High removal efficiency photosynthetic and chemolithotrophic bacteria can be used for biological biogas desulfurization (Struk et al., 2023).

A class of microorganisms known as chemolithotrophic bacteria uses inorganic sulfur compounds, such as sulfide, elemental sulfur, thiosulfate, or organic sulfur compounds, as a source of energy. Chemolithotrophic bacteria employ oxygen as an electron acceptor for the aerobic biodegradation of sulfide, however, under anoxic circumstances, certain species can use other electron acceptors, such as nitrate or nitrite. Chemolithotrophs are employed in biogas desulfurization technologies as well as full-scale biofilters, biotrickling filters, and bioscrubbers in traditional reactor designs. Even though these biotechnologies have inherent benefits for desulfurizing biogas, oxygen dosing needs to be carefully regulated at ideal levels to minimize O_2 levels in biomethane and avoid the formation of elemental sulfur, which can clog packed beds. Another unresolved operational issue with conventional biotechnologies is the development of biofilms and biofouling in packed bed bioreactors as a result of excessive biomass growth (Struk et al., 2023).

Alternative biological biogas desulfurization processes need to be researched in light of these constraints. Green sulfur bacteria (GSB) and purple sulfur bacteria (PSB) are two members of the broad group of prokaryotic organisms known as phototrophic sulfur bacteria. These bacteria were first identified by their distinctive colors, high sulfide tolerance, and utilization of sulfur. These microbial communities use different sulfur compounds as electron donors and carry out anoxygenic photosynthesis. Compared to microalgae or chemolithotrophs, their metabolism is distinct and advantageous, minimizing the possibility of O_2 and N_2 pollution. Sulfide can be oxidized to sulfur when light is scarce or to sulfate when light is abundant, depending on the intensity of the light (Struk et al., 2023). An oxygen-free, one-step desulfurization process that eliminates the possibility of oxygen contamination is offered by anaerobic phototrophic H_2S removal systems powered by anoxygenic photosynthesis (Egger et al., 2023).

4.1.2. Immobilized Cell Technologies

Immobilized cell technologies (ICT) confine microorganisms within a support or matrix, allowing for reuse and easy separation from products (Chacón-Navarrete et al., 2021). ICTs are used in biorefinery applications such as biofuel and bioplastic production (Lapponi et al., 2022). They offer advantages (Figure 2) over free cell systems, including higher cell concentrations, increased productivity, and easier separation (Obradovic et al., 2004). These systems can operate continuously at higher dilution rates without cell washout and allow for co-immobilizing different cell types. Additionally, immobilized cells create unique microenvironments affecting cell physiology and mobility (Karel et al., 1985).

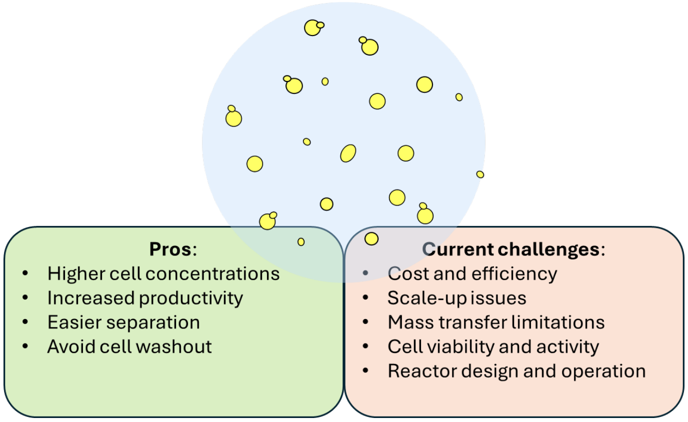

Figure 2. Cell Immobilization Technologies Applied in Biorefinery.

4.1.2.1. Current technology status

ICT in biorefinery processes can enhance cost efficiency and tolerance to high substrate concentrations, but challenges such as the need for advanced recycling technologies, mass transfer limitations, and maintaining cell viability over time are significant (Champagne, 1996; Liu et al., 2021). There are several types of immobilization matrices. Synthetic polymers such as polyacrylamide, polyvinyl alcohol, or polyurethane have been widely used as immobilization matrices due to their controllable physical and chemical properties. More recently, the interest in natural polymers as immobilization matrices has been growing mostly due to their biocompatibility and biodegradability. Alginate, chitosan, and extracellular polymeric substances (EPS) are some natural polymers that have been used to immobilize microorganisms. Interestingly, this latter is also an example of a biorefinery process, as EPS can be recovered from waste sludge produced in wastewater treatment plants (Oliveira et al., 2020).

The scale-up introduces further complexities to the immobilization process, affecting microbial and enzymatic activities, particularly when dealing with toxic by-products. Additionally, reactor design plays a critical role in optimizing these systems, requiring careful consideration of factors like mass transfer and shear stress to ensure overall process efficiency and sustainability (Chacón-Navarrete et al., 2021).

Nowadays, ICTs are being used as biochemical conversion technologies transforming waste biomass, both at commercial scale and in experimental phases (Table 1).

Table 1. Immobilized Cell Technologies applications in biorefineries, including the cell carrier, microbial species, application, phase (experimental or commercial), and respective references.

Cell Carrier	Microbial Species	Application	Phase	Reference
Alginate	Yeast (*Saccharomyces cerevisiae*)	Bioethanol production from lignocellulosic biomass	Commercial	(Edwards and Heitkamp, 1992; Ramos et al., 2023)
Membrane modules	Yeast (*S. cerevisiae*)	Biofuel production with simultaneous detoxification of inhibitors	Experimental	(Lu et al., 2020; Ramos et al., 2023)
Biomass-derived materials	Various microbes	Bioremediation, biochemicals production, agriculture applications	Experimental	(Willaert, 2018; Lu et al., 2020)
Chitosan, alginate	Bacteria (Clostridium, Zymomonas)	Consolidated bioprocessing for biofuel production	Experimental	(Lu et al., 2020; Ramos et al., 2023)
Alginate, silica	Microalgae	Biofuel (biodiesel) production from microalgal biomass	Experimental	(Willaert, 2018)
Extracellular polymeric substances	Bacteria (*Rhodococcus* sp.)	Bioremediation (treatment of wastewater with fluorophenol)	Experimental	(Oliveira et al., 2021)
Polyurethane foam, polyvinyl alcohol	Microbial consortia	Bioconversion of waste biomass to biochemicals	Experimental	(Willaert, 2018; Lu et al., 2020)

4.1.2.2. The challenges and prospects

The initial capital costs for implementing ICTs in biorefineries can be high due to the need for specialized equipment, materials for cell immobilization, and the design of reactors to accommodate these systems (Nedović et al., 2011). However, these upfront expenses may be offset by long-term benefits such as increased process stability, reduced downtime, and lower operating costs. ICTs can decrease the need for frequent cell replacement, reduce byproduct production, and allow for operation at higher substrate concentrations and extreme conditions, leading to cost savings in cell maintenance, process inputs, and energy consumption (Nedović et al., 2011).

The future of ICTs in biorefinery processes is promising, driven by advancements in bioprocessing integration, novel carrier development, and enhanced process stability (Champagne, 1996; Gaur et al., 2024). These technologies can improve efficiency and yield in bioconversion processes, optimize mass transfer, and support microbial growth, contributing to more efficient and sustainable biorefineries. Continued research and innovation are crucial to fully realize these benefits.

4.1.3. Microbial Fuel Cell

Microbial fuel cell (MFC) is a promising technology for harvesting bioenergy as in electricity along with waste and wastewater treatment (Du et al., 2007). An MFC is generally composed of an anode (anode chamber) and a cathode unit (chamber or a solid material) optionally separated by special membranes such as proton exchange membranes (PEM), cation exchange membranes (CEM), or j-cloths (Virdis et al., 2011). At the anode chamber, degradation of organic materials by biofilm microorganisms for metabolic activities leads to electron and proton production as a result (Du et al., 2007). Electrons flow from the anode electrode to the cathode electrode through an external circuit, producing electric current. Meanwhile, protons (H^+) that are generated in the anode, selectively migrate to the cathode through a membrane and then react with oxygen as an electron acceptor to form water or any other reduced compound (Du et al, 2007). An illustration of an MFC is shown in Figure 3.

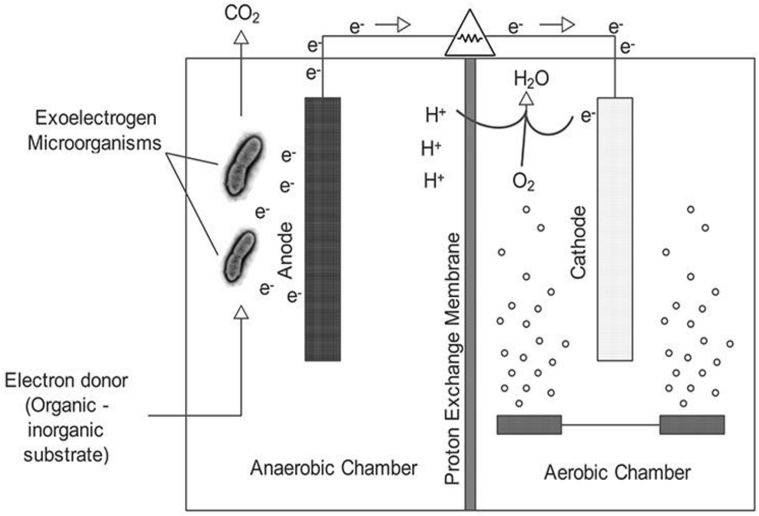

Figure 3. Scheme of a two-chamber MFC (Ucar et al., 2017).

What actually happens in MFCs is that biofilms as catalysts convert chemical energy stored in the carbonaceous material and fatty acids and other organic materials through extracellular electron transport chains into electrical energy (Virdis et al., 2011; Choi, 2015).

4.1.3.1. Current technology status

MFC technology is still in its infancy period due to the low current production and high construction cost. It is well known that membranes and the cathode materials, amongst the other MFC components, constitute the most part of the expenses, which is around 85% (Escapa, et al., 2016). In addition to the cost, membranes tend to biofoul, and if this is the case, they need to be renewed, which will increase the operational costs (Du et al., 2007; Zhou et al., 2013). Beside the membrane cost, cathode electrodes such as platinum, steel, and other precious metals, as well as platinum catalysts used on cathode electrodes, increase the construction costs (Virdis et al., 2011; Oliveira et al., 2013; Zhou et al., 2013). In order to turn high-cost MFCs into more cost-effective MFCs, studies focused on the structural changes such as membrane-less MFCs or using simple separators (j-cloth, ceramic) other than membranes, using bacteria as catalysts in biocathode MFCs, and combining two chambers in a single chamber (Virdis et al., 2011; Oliveira et al., 2013; Zhou et al., 2013). Although these changes reduce the constructional and operational costs, it should be noted that coulombic efficiencies of the MFCs and, in some cases, power density of the MFCs may decline due to diffusion of oxygen or any other e-acceptor to the anode and distortion of the anodic bacteria activity (Virdis e al., Xing et al., 2013). Similarly, ions and other components in the substrate/wastewater other than protons can easily pass to the cathode and form biofilm on the cathode electrode and reduce oxygen diffusion on cathode electrodes associated with metal catalysts, resulting in poor operation performance (Xing et al., 2013).

4.1.3.2. The challenges and prospects

At the cathode of an MFC, generally a catalyst is used to increase the reduction rate of oxygen since oxygen has a very slow reduction rate without a catalyst (Gude, 2016). It is also stated that microbial biofilm in the cathode chamber of biocathode MFCs can consume electrons coming from electrodes and hence reduce oxygen instead of inorganic catalysts (Hong et al., 2015). Biocathode applications in MFC studies are reportedly increasing due to the cost of the cathode electrode materials and catalysts as well as the biocathode MFCs being able to treat wastewater and nutrients (Zhou et al., 2014). In MFC, wastewater with high organic pollution (>1000 mg COD/L) can be treated while energy can be obtained, in addition to wastewater with low organic pollution, such as domestic wastewater. These wastewaters can be listed as composite fruit-vegetable and food wastewater rich in carbohydrates, food industry wastewater, acidic food waste leachate, beverage industry, yeast and fermented beverage wastewater, fruit juice wastewater and cheese wastewater, agricultural and animal industries, slaughterhouse wastewater, milk and dairy product wastewater, pig farming wastewater, biorefinery wastewater from the petroleum and petroleum products industry, petrochemical industry wastewater, and pharmaceutical industry wastewater (Zhou et al., 2013).

4.1.4. Microbial Electrolysis Cell

Bioelectrochemical systems (BESs) can be regarded as electrochemical systems, in which at least one of the electrode reactions involves electrochemical interactions with microorganisms.

More often than not, the anodic reaction necessitates the presence of certain microorganisms, commonly known as anode-respiring bacteria, that can move electrons from a biodegradable substrate to a solid electrode (Escapa et al., 2016). Microbial electrochemical systems (MES) are a very desirable energy generation option due to their sustainable and eco-friendly nature. MES uses biological catalysts to convert the chemical energy from wastewater and waste lignocellulosic biomass into electrical energy through a reduction-oxidation reaction. In MES, water is oxidized at the anode, producing protons and electrons that are then transferred to the cathode in the presence of an external electric potential. Redox reactions occur in the cathode area when electroactive microorganisms are present. Microbial fuel cells (MFCs), microbial electrolysis cells (MECs), microbial desalination cells (MDCs), and microbial solar cells (MSCs) are further classifications for MESs. While MECs need an electricity supply to make hydrogen from organic waste streams, MFCs are known to produce power from organic waste streams (Pawar et al., 2022).

The method known as MECs is derived from MES and involves applying an external voltage to accelerate metabolic reactions by breaking down the thermodynamic energy barrier. Methane can be produced through two different processes called electromethanogenesis (EM): direct EM, which involves directly absorbing electrons from the electrode, and mediated EM, which involves producing hydrogen and other compounds like formate and acetate and combining them with carbon dioxide to form methane (Pawar et al., 2022). MEC is made up of a cathode chamber, an anode chamber, and a power supply. The anode and cathode electrodes are separated to form a distinct unit by a separator (Hua et al., 2019). Organic molecules in MECs are converted to protons, CO_2, and electrons by electrochemically active microorganisms, which are the predominant populations at the anode. By means of an electrical circuit that produces hydrogen, the electrons produced by these microbes are moved from the anode to the cathode. Similar to those found in water electrolyzers, there are two types of ion-selective membranes: anion exchange membrane (AEM) and cation exchange membrane. Their primary function is to stop the reaction between oxygen and hydrogen being produced. Since the AEM has less internal resistance than the other membrane type, it is thought to be more effective in facilitating ion transport through the membrane (Yu et al., 2018).

Using microbial biofilms in an anodic chamber, MECs oxidize organic matter electrochemically to produce protons and electrons that are then employed in a reduction reaction to produce value-added products like hydrogen and methane. The anodic reaction is accelerated by the electrogenic biofilm on the anode, which functions as a biocatalyst. Via an external electrical current, electrons given to the anode by the anodic biofilm are transferred to the cathode, where they convert H_2O and proton to create OH- and H_2, which are then discharged from the cathode compartment. Since the linked redox reaction is thermodynamically unfavorable, an externally supplied voltage is necessary. The breakdown of organic carbon in a MEC provides part of the energy required for the process; therefore, less power is required than in water electrolysis. If something other than a proton or water is reduced on the cathode, additional products, such as methane, can also be produced in addition to biohydrogen (Zhou et al., 2013).

4.1.4.1. Current technology status

MEC should be combined with other mainstream processes to provide high-quality effluent for reuse or release (Katuri et al., 2019). Waste has been treated using conventional anaerobic digestion (AD), which consists of the four main processes of hydrolysis, acidogenesis, acetogenesis, and methanogenesis. Exoelectrogens (attached to anode) and hydrogenotrophic methanogens activity (attached to cathode) can be enhanced by integrating AD with BES. Recalcitrant compound degradation rates in wastewater are higher in the combined MEC-AD system, and the effluent's organic and ammonium content are found to be low (Hua et al., 2019). While methane can be created in AD, the purpose of employing MECs is to enhance the creation of hydrogen. Utilizing MECs during fermentation enables the breakdown of the substrate, which produces hydrogen. Therefore, a number of tactics, such as exposing MEC-AD to oxygen to produce hydrogen, have been proposed to inhibit methanogens in MEC-AD (Yu et al., 2018). Several substrates, such as acetic acid, butyric acid, lactic acid, glucose, cellulose, and other wastewater types, can be used to create electrosynthesis chemicals in MECs (Kadier et al., 2014). Figure 4 classifies the various substrates that are being used in MECs.

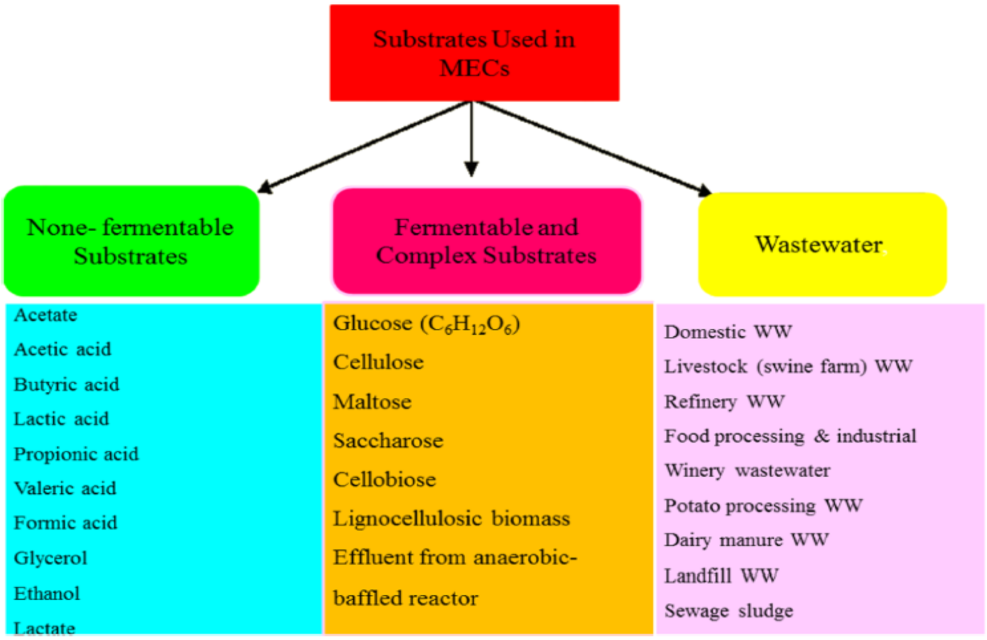

Figure 4. Classification of different substrates used in MECs (Kadier et al., 2016).

Furthermore, resistant pollutants including organic pollutants like nitrobenzene and 4-chlorophenol and inorganic pollutants like sulfate, perchlorate, and nitrate can be eliminated at the cathode of MECs by controlling the cathode potential of MECs through the supply of electricity. By far, MECs require far less energy for the elimination of these contaminants than traditional electrochemical reduction. Recent research has shown that MECs can recover Cu, Pb, Cd, and Zn from a simulated municipal solid waste incinerator ash leachate in addition to removing other pollutants (Zhang and Angelidaki, 2014). In addition to recovery of metals and removal of pollutants, MECs can be converted into microbial electrosynthesis reactors, used for value-added chemical production.

Hydrogen Peroxide production: By electron-reducing O_2 in the cathodic compartment, MFCs and MECs can produce hydrogen peroxide from wastewater (Radhika et al., 2022).

Methane production: Methane makes up between 50 and 90 percent of natural gas and is utilized in all applications that use natural gas. A newly developed MEC allows non-degradable organic material, toxic chemicals, and supersaturated organic wastes to break down more quickly through bioelectrochemical reactions, increasing the production of biogas in a power plant. Exoelectrogenic bacteria break down organic compounds in the reactor at a low electrode potential of 0.2 V to 0.8 V, producing electrons at the anode. After that, in a closed circuit, these electrons move to the cathode, where they produce CH_4 (Radhika et al., 2022).

Hydrogen production: One sustainable and environmentally beneficial energy source that can be used as green fuel in cars is hydrogen. With the use of innovative technology, MECs can create sustainable hydrogen from a variety of biomass sources. Organic materials are broken down by bacteria at the anode. To create hydrogen at the cathode, protons and electrons are discharged to the anode (Radhika et al., 2022).

Ethanol production: Electron mediators like methyl viologen help convert acetate to ethanol in a two-chamber MEC (Zhang and Angelidaki, 2014).

Formic acid production: Formic acid synthesis is based on organic matter oxidation in the anode and CO_2 reduction in the cathode. Formic acid is an essential chemical utilized in pharmaceutical syntheses as well as in the manufacturing of paper and pulp (Zhang and Angelidaki, 2014).

4.1.4.2. The challenges and prospects

MECs technology could generate energy and fuel from organic matter, including renewable resources and wastewater. MECs assist in the removal of organic compounds from wastewater in addition to promising the creation of value-added goods and renewable hydrogen (Pawar et al., 2022). MEC has several advantages over other traditional processes (such as water biophotolysis, dark fermentation, and photofermentation) when it comes to producing hydrogen from organic wastes. First of all, creating H_2 at comparatively modest energy inputs is theoretically possible with MECs. Second, because microbial biocatalysts (electrochemically active microorganisms) are self-sustaining, precious metals are not required on the anode of MEC. Thirdly, MEC can achieve high conversion efficiency to hydrogen. Fourthly, the cathode chamber produces relatively pure hydrogen, negating the need for costly gas purification procedures. Since MEC requires very little energy input and can transform organic waste into hydrogen and other value-added compounds, it is a very promising technology (Kadier et al., 2016). In summary, MECs offer several advantages, including low energy consumption, high conversion efficiency, self-sustaining microbial biocatalysts, low cost, and pollution inhibition. Moreover, two distinct processes in MECs that result in a high methane content in biogas are methane generation and the oxidation of organic materials. MECs also have the benefit of producing methane when exposed to ambient temperature, which eliminates the need for heating and demonstrates MECs' energy efficiency. The acceptance of electrons straight from cathodes, which makes the process resistant to hazardous materials like ammonia, is a further benefit of employing MECs. While MECs produce CH_4 even in lower concentrations of organic molecules, anaerobic digestion requires a high organic content to produce methane (Pawar et al., 2022).

When developing MEC for the generation of biohydrogen, there are numerous obstacles to overcome. It is still a major challenge to find affordable materials, such as anode, cathode, and membrane materials, and use them in large-scale applications (Murugaiyan et al., 2022; Hua et al., 2019). MEC technology's primary issue is increasing H_2 production rate with low energy input. Additional difficulties with employing a MEC include the removal of sulfate and nitrogen in terms of system scalability, microbiological process, long-term operational stability, capital investment and operating cost, and assessment of the environmental and economic impacts (Hua et al., 2019).

Challenges and requirements for the creation of useful MEC technology (Kadier et al., 2016):

- High capital cost: Without a doubt, the biggest obstacle to the widespread use of MEC is its reduced capital cost, which is mostly caused by the costly construction materials.
- Cathode limitations: One of the main factors preventing cathode materials from being used more widely is their expense.
- Scalability of MEC reactors: Another important consideration for MEC upscaling is reactor design.
- Long-term stability: Improving the MEC system's long-term stability is critical to its energy balance and financial viability.
- Operational mode: The MEC system's operation mode is another factor limiting its use in the production of hydrogen.
- Application: Other MEC application opportunities, such as chemical synthesis, pollution elimination, and metal recovery, are still in the laboratory.
- Power Sources: The utilization of sustainable and renewable power sources is imperative to enhance the overall process's cost-effectiveness and sustainability.

4.1.5. Enzymatic Fuel Cell

Conventional fuel cells transform chemical energy into electrical energy by oxidizing fuel (substrate) at the anode and reducing oxidant at the cathode (Xiao et al., 2019). The reactivity of the chemicals is converted into electrical current using noble metal catalysts (e.g., platinum, ruthenium, palladium, etc.) or their alloys in the presence of fuel and oxidant (Leech et al., 2012; Xiao et al., 2019). This oxidation and reduction process takes place in an optimized basic and/or acid electrolyte, resulting in a very high efficiency (Xiao et al., 2019). In this regard, a biofuel cell can be expressed as the fuel cell that can produce electrical energy from the chemical conversion of the organic material/feedstock through biological oxidation and reduction reactions that occur at anode and cathode electrodes, respectively (Choi et al., 2020; Leech et al., 2012). Being one type of biofuel cell, enzymatic fuel cells (EFC) drive biological catalysts for the oxidation of the fuel, and those biological catalysts are extracted from the cells that we call enzymes and enzyme cascades (Leech et al., 2012; Mazurenko et al., 2017). It is an emerging electrochemical system that projects the natural oxidation-reduction reactions inside the cells to produce energy (Shi et al., 2022). Although the first proto-type EFCs were meant to produce electrical energy for utilization, the low current production diverted the studies to electrochemical device powering. In EFCs, enzymes can be used at both anode and cathode or one of the chambers (Leech et al., 2012). Optionally, the anode and cathode electrodes are separated with a PEM or a proton-conducting medium (Xiao et al., 2019). At the anode electrode (chamber), the fuel is oxidized by an appropriate enzyme (biocatalyst), then electrons, protons, and an end product are formed at the anode. The electrons flow to the cathode electrode through an external circuit, and protons are released to the electrolyte medium and move to the cathode. At the cathode, oxidants (O_2, peroxides) are reduced to water by the combination of electrons and protons that were transferred from the anode (Leech et al., 2012; Xiao et al., 2019). The Figure 5 presents enzymatic fuel cell operation, fuel degradation, electron flow, and reduction of the oxidant at the cathode.

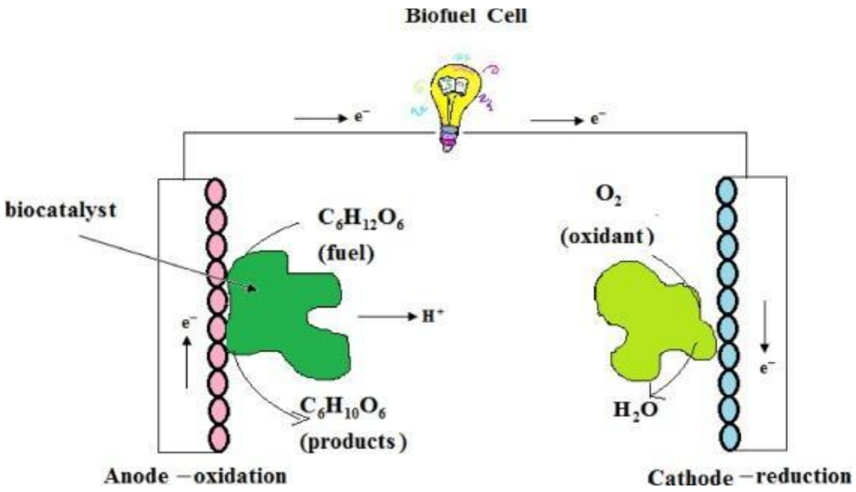

Figure 5. Schematic illustration of Enzymatic Fuel Cell (Rajendran et al., 2017).

The enzymes used in EFCs are the macrobiomolecules, which are at the size of several nanometers, and their redox sites are mainly located at the electrically inert protein matrix (Cai et al., 2024). The redox enzymes are generally made up of apoenzymes (the protein component) and cofactors (nonproteinaceous electroactive particles), which transfer the electrons between the enzyme and substrate (fuel) (Leech et al., 2012). The main cofactors that are in glucose-oxidising enzymes are flavin adenine dinucleotide (FAD), nicotinamide adenine dinucleotide (NAD), and pyrroloquinoline, which can be tightly attached to the enzyme structure and freed from the enzyme redox sites during the reaction (Gonzalez-Solino and Lorenzo, 2018; Leech et al., 2012). The enzymes that have been used in EFCs are specific to the fuels, such as glucose oxidase (GOx) or other sugar-oxidizing enzymes, such as glucose dehydrogenase (GDH) and fructose dehydrogenase, alcohol dehydrogenase, formate dehydrogenase, and hydrogenase (Mazurenko et al., 2017; Rewatkar et al., 2019). The other mostly used enzymes are cellobiose dehydrogenase (CDH), hexose oxidase, and glucooligosaccharide oxidase (Choi et al., 2020). On the other hand, the most widely used oxidants in EFCs are pure O_2 (or O_2 from air) and peroxides, whereas the substrate/fuel that is available can vary among the glucose, fructose, pyruvate, sucrose, glycerol, hydrogen, lactate, methanol, ethanol, and starch (Cosnier et al., 2018; Mazurenko et al., 2017). The substrates used in EFCs include a high amount of energy, potentially when oxidized fully by the EFC, which can be as high as more than 80 times higher energy (3500 Amp.hours/kg) than that of a 1 kg lithium-ion battery (Shi et al., 2022). There are other feedstocks that can be used in EFCs, which are the hydrolysates of biomass such as lignocellulosic waste and algal biomass that includes glucose and xylose (Kim et al., 2016; Lee et al., 2018; Shi et al., 2022).

4.1.5.1. Current technology status

The general performance of an EFC is dependent on the electron transfer efficiency from the enzyme to the electrode. There are two types of electron transfer mechanisms from enzyme to electrode surface: direct electron transfer (DET) and mediated electron transfer (MET). If the distance between the enzyme and electrode is more than 15 angstroms, natural or synthetic mediators such as neutral red, methylene green, ferricyanide, etc. are needed for the transfer (Leech et al., 2012; Xiao et al., 2019). Because of the disadvantages of the mediators, such as cost, poor biocompatibility, and leaching from electrode to electrolyte in the process, recently, nanostructured materials have been employed to enhance the electron transfer (Pankratov et al., 2015; Xiao et al., 2019). These nanostructured materials are single and multi-walled carbon nanotubes, nano- and meso-porous materials, carbon fibers, and graphene that are used for enzyme hosting (Haque et al., 2021; Mazurenko et al., 2017). EFC has the potential to use a wide range of catalysts derived from sustainable processes under moderate pH and temperature conditions. Thanks to recent developments on enzyme electrochemistry and modified electrodes, higher and stable current production in EFCs enabled the manufacture of microelectronics and smaller and lower-energy-consuming devices (Leech et al., 2012). These devices (bioelectronics) are artificial devices that can be either implantable within or worn on the body to operate using body fluids such as sweat, saliva, or blood. They offer novel opportunities for personalized medicine with respect to sensing, diagnosis, and treatment (Xiao, 2022).

There are many potential applications that EFC devices have been used for trials so far. Since glucose is an essential and relatively abundant source of energy in living organisms, implantable EFC has been tried and operated as medical devices powered by body fluids (Cosnier et al., 2018; Monsalve et al., 2015). In addition to this, EFCs have the potential to supply electrical energy for portable electronic devices such as mobile phones, sensors/biosensors, digital music players, laptops, GPS systems, environmental monitoring sensors, and wearable smart sensors (Mazurenko et al., 2017; Pankratov et al., 2015). They have the ability to power themselves and measure the intended parameters, as in self-powered biosensing, pulse generators, and therapeutic systems (Xiao, 2022). There was an attempt to use an EFC as a power supply unit to the cardiac pacemaker for a lifetime period. A successful experiment focusing on determining the lactate concentration in body fluids such as tears, saliva, and sweat was reported by researchers, and it was stated that the lactate concentration was in correlation with the lactate concentration in blood (Gonzalez-Solino and Lorenzo, 2018). Cholesterol, metabolites, such as ketone bodies, uric acid, sarcosine, creatinine, etc. are the other parameters that can be detected from the physiological fluids using EFC equipped with appropriate enzymes and electrodes (Gonzalez-Solino and Lorenzo, 2018; Wang et al., 2021). Table 2 presents the potential biomarkers and related health issues that can be detected with an EFC-powered wearable/implantable biosensor.

Table 2. Potential biomarkers and associated diseases that can be detected with an EFC biosensor (Gonzalez-Solino & Lorenzo, 2018).

Biomarker/ Analyte	Enzymes	Application	Biofluid	Type of Sensor
Glucose	GOx, DH, CDH	Diabetes	Blood, saliva, sweat	Wearable
Lactate	LOx, LDH	Hypoxia	Blood, saliva, sweat	Wearable
Cholesterol	ChOx, ChDH	Heart Failure	Blood	Implantable
Alcohol	ADH, AOx	Alcohol abuse	Blood	Wearable
Uric Acid	Uricase	Reanl syndrome	Blood, saliva	Wearable
Creatinine	SOx	Chronic kidney disease	Blood, saliva	Wearable
Ketone bodies	3-HBDH	Diabetes	Blood	Implantable
Levodopa	Tyrosinae	Parkinson treatment	Blood	Implantable
Glutamate	GlOx	Neurodegenerative diseases	Blood	Implantable
Sarcosine	SOx	Prostate Cancer	Blood, urine	Implantable

GOx: glucose oxidase; GDH: glucose dehydrogenase; CDH: cellobiose dehydrogenase; LOx: lactate oxidase; LDH: lactate dehydrogenase; ChOx: cholesterol oxidase; ChDH: cholesterol oxidase; 3-HBDH: 3-hydroxybutyrate dehydrogenase; SOx: sarcosine oxidase; GlOx: glutamate dehydrogenase; ADH: alcohol dehydrogenase; AOx: alcohol oxidase.

4.1.5.2. The challenges and prospects

The recent studies have focused on the enhancement of the EFC performance in terms of current production, in other words, electron transfer. The electron transfer is dependent on various factors such as enzyme type, electrode material, and type, electrolyte, fuel, regeneration of enzymes, and whether or not using membrane. In order to develop and commercialize EFCs, the challenges derived from EFC components must be addressed. Fundamentals of electron transfer mechanisms and understanding of electron transfer metabolic chains must be detailed to determine alternative and low-cost enzymes, mediators, and electrodes (Mazurenko et al., 2017; Xiao et al., 2019). Focusing on the electrode materials and high-surface electrode materials for enhanced enzyme catalysis and electron transfer will also help to achieve these objectives (Mazurenko et al., 2017). The shape and the origin of the electrodes are important parameters for the current production and its lasting period. Fabric, yarn, and fiber types of electrodes can be classified for the usage area (wearable/implantable) of the electrode (Cai et al., 2024). It was reported by several researchers that nanometals, nano-structured carbon materials, and also conducting redox polymers applied on the electrode materials as in doping, coating, or covering, can increase electron transfer efficiency (Haque et al., 2021; Xiao et al., 2019).

The two important technical obstacles that EFCs face and must be overcome to make them developed and ready for large scale production are their short lifetime, stability, and weak power output (Leech et al., 2012; Xiao et al., 2019). The efforts that have been made so far are to enhance the electron transfer and to tackle the weak power output of the EFCs. The studies on the development of the new mediators or mediatorless EFCs, new and cost-effective electrode and membrane materials, and smart and reusable catalysts are moving forward. For the stability and long duration of the EFCs, cheap, effective, and compatible electron transfer materials as in electrodes are needed. These materials must be compatible with the enzymes that are being used in the EFCs.

4.1.6. Biomass Electrolysis (Biological Electrolysis)

Biological electrolysis is an emerging technology for producing hydrogen from biomass and biowaste, attracting growing interest from researchers (Ito et al., 2018). The basic concept is to extract the hydrogen in biomass, replacing water's oxygen evolution reaction with the oxidation of biomass-derived fuels at the anode (Liu et al., 2016). The advantage is the lower electricity required by the process and the possibility of using non-noble catalysts, compared to water electrolysis. Biomass electrolysis consumes, on average, between 17% and 60% of the electricity needed by water electrolysis (Liu et al., 2016; Du et al., 2017; Xu et al., 2023). Reactions happen at a voltage between 0.8 to 1.2 V, below the minimum voltage required by water electrolysis of 1.6 V (Carmo et al., 2013). However, unlike water, biomass and biowaste cannot be treated directly; a catalyst must first degrade the feedstock.

The extraction of hydrogen from biomass, therefore, happens in two phases: a pre-treatment phase that allows biomass to be degraded and requires a catalyst and energy in the form of heat or light (Liu et al., 2016) and a second phase where the electrolysis process happens, and voltage is provided. In the electrolysis phase, the reduced solution is oxidised at the anode, releasing positive hydrogen ions (H^+) that cross the electrolyte and are reduced into hydrogen at the cathode.

Examples of catalysts currently used in biological electrolysis are iron chloride (Wang et al., 2021) and polyoxometalate, which can act as catalysts and charge carriers. They can facilitate hydrolytic and oxidative processes, helping convert more complex organic material into organic acids and alcohols (Evtushok et al., 2022). Polyoxometalate offers higher selectivity in the oxidation reaction, limiting the creation of unwanted products and, therefore, is currently the preferred catalyst used in biogenic electrolysis (Zhong et al., 2021). Another critical characteristic required by the catalysts used in the process is their ability to be recovered and reused, which is crucial to making biological electrolysis cost-effective.

Figure 6 shows a schematic of the process, assuming using POM as a catalyst and energy carrier. In the same picture, the general reactions that describe the process are reported. It is worth noting that CO_2 is emitted during the pre-treatment process that can be directly captured and used.

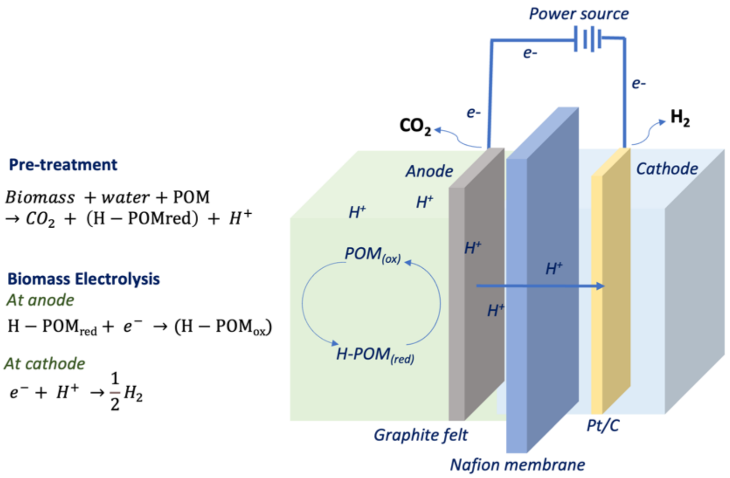

Figure 6. Schematic of biological electrolysis (adapted from Liu et al. (2016).

Once the hydrogen is extracted, the residue is still rich in carbon. Umer et al. (2024a) showed that 3% to 13% of the carbon contained in the biomass leaves the solution as CO_2 (in the case of cellulose, starch, lignin, and glucose as feedstock). For this reason, it is essential to look at technologies that can be combined with biological electrolysis to valorise the residue, especially if the starting feedstock is pure biomass rather than biowaste.

4.1.6.1. Current technology status

The concept has been experimentally proven, and ongoing laboratory work is occurring. The technology is, therefore, between TRL 3 and 4. Table 1 shows examples of critical parameters of the conversion process. Feedstocks range from biomass components (e.g., cellulose, hemicellulose, glucose) to natural biomass (fresh algae) and biowaste (e.g., cypress sawdust, bread residue, banana peel). Electrolytic cells with different architectures have been used. They range from H-type cells to Membrane Electrode Assembly, MEA, and flow-based cell systems that reduce the ohmic losses and minimise the cell voltage, improving energy efficiency. Cationic membranes, like Nafion, have been widely applied since they result in a high acidic pH on the cathode that favours the hydrogen evolution reaction (Liu and Li, 2021).

The process is relatively low temperature. The pre-treatment temperature ranges from 80°C to 175°C. Once the biomass is degraded at temperatures between 80°C and 150°C, the electrolysis process may happen at ambient temperature. However, higher temperatures in the electrolysis process (about 80°C) show a higher density current and a higher volume of hydrogen (Liu et al., 2016). If heat is provided to the electrolysis cell, the pre-treatment is carried out at the anode side with the biomass oxidation reaction (Xu et al., 2023), and pre-treatment and electrolysis happen simultaneously.

The applied potential ranges from 0.12V to 1.2V, with an onset potential that depends on the electrolysis operating temperature and the feedstock, and it is influenced by the pre-treatment process. Current densities range from 100 to 500 mA cm^{-2}. The hydrogen production is generally reported after 1 hour of reaction, with few publications showing the output per gram of biomass (Table 3).

4.1.6.2. Challenges and Prospects

The main advantages of biomass electrolysis are: i) good hydrogen yield, ii) the possibility of producing pure hydrogen, iii) the possibility of dealing with biomass with a high moisture rate since the electrolyte solution is an aqueous solution, iv) low-temperature of the process (below 150°C), v) low voltage required (below 1.2 V) and v) low electrical energy consumption.

Although the process shows several strengths, there are still challenges to overcome. The current density is still low, requiring a bulky system compared to water electrolysis (Liu and Li, 2021). To improve the current density, researchers should focus on a better degradation of the biomass to increase the hydrogen extracted that is currently below 20% of the hydrogen content *(*Umer et al., 2024b). To make the process economically viable, it is mandatory to recycle the catalyst fully. Researchers have already shown that it is possible with POMx (Li et al., 2022). However, more studies are needed to understand how this can work continuously. The residue is still rich in carbon, and the reduced volume is limited, so it is worth studying the combination with different systems, like pyrolysis.

Table 3. Some examples of key performance parameters of biological electrolysis.

Feedstock	Cell Type	Electrolyte	Current density (mAcm^2)	Applied potential (V)	Temperature	Electrodes	Hydrogen produced	Power consumption (kWh/Nm^{-3} H_2)	Authors
Alcohols, starch, cellulose, lignin, wood powder	PEMEC Cell	Aqueous POM	100 200 500	0.15-0.7 0.28-0.8 0.6-1.2	Ambient to 80°C	Graphite felt anode and carbon cathode Pt-coated	24 mL H_2 within 1 hour	0.36-1.27 0.67-1.91 1.44-2.87	Liu et al., 2016
Cellulose, starch, lignin, protein, bread residue, cypress sawdust, rice chaff	H-type and Flow-type EC	Aqueous H_3PO_4	<20	<1	150°C	Metal free meesoporous carbon anode, PTFE membrane, Pt/C cathode	0.00008 mole/ mincm^{-2} 0.000032 mole/mincm^{-2} 0.1-0.2 mg of H_2/gram of waste	>0.8	Hibino et al., 2018
Lignin	H-type	Aqueous H_3PO_4	<20	<1	100-200°C	Pt/C anode and cathode	<16 μmole per minute	1.4 kWh Nm^{-3}	Hibino et al., 2017
Corn Straw	H-type cell	Aqueous POM	20-50	0.5-1.23	80°C-110°C pretreatment 80°C electrolysis	Anode – carbon rod Cathode- Pt mesh Membrane Nafion 117	5-20 mL H_2 within 1 hour	1.50-2.09 kWh Nm^{-3}	Li et al., 2022
Glucose, starch, lignin hemicellulose	H-type cell	Aqueous $FeCl_3$	<16	<1.2	100°C pretreatment – ambient to 80°C electrolysis	Graphite felt anode and carbon cathode Pt-coated. Nafion membrane	6-12 mL H_2 within 1 hour	30.99-151.54 kWh/kg	Umer et al. 2024 a)
Banana peel, Cucumber peel	H-type cell	Aqueous POM	<16	<1.2	100°C pretreatment – ambient to 80°C electrolysis	Graphite felt anode and carbon cathode Pt-coated. Nafion membrane	49.2 mL per 1 g 39.2 mL per 1 g	35.35 kWh/kg 42.17 kWh/kg	Umer et al. 2024 b)

4.1.7.Current Status and Future Prospects of Emerging Biochemical and Bioelectrochemical Technologies

Bioelectrochemical conversion technologies (generally known as Bioelectrochemical Systems (BES) are a promising and growing area of research with a great possibility of finding solutions to recent and crucial environmental and energy problems (Al-Sahari et al., 2021). These technologies integrate biological, chemical, and electrochemical fundamentals and process designs (Baek and Lee, 2024; Khanthong et al., 2023). BES offers new and more enhanced methods to treat waste streams, harvest energy, and manage resources (Khanthong et al., 2023; Kong et al., 2023). The future of BES looks promising due to the developments in reactor design, operational procedure, equipment with modified materials, and a better understanding of the microbes involved (Baek and Lee, 2024; Jiang et al., 2024).

There are various BES, namely microbial fuel cells (MFC), microbial electrolysis cells (MEC), and microbial electrosynthesis cells (MES), that can be applied to treat different types of waste streams, such as domestic wastewater, industrial effluents, manures, sludges, etc. (Al-Sahari et al., 2021). It can be stated that BES has been applied for treating a wide range of waste streams with or without pretreatment, such as agricultural, agro-industrial, and other biodegradable biomasses. Therefore, BES can be very advantageous for sustainable development. As overviewed by Wilberforce et al. (2021), these systems can treat waste streams while also harvesting energy, which is an attractive method for the circular economy. Additionally, BES can also produce valuable products like biochemicals and biofuels, making them even more desirable (Kong et al., 2023; Wang et al., 2022). Figure 7 presents the common bioelectrochemical systems and their role in sustainability, economy, and current technology.

Even though BESs are very promising technologies, there are significant barriers that must be overcome for BESs to become full-scale operational and replace conventional technologies such as activated sludge processes for wastewater treatment, anaerobic digestion for biogas production, thermochemical processes for electricity and syngas production, electrochemical systems, and so on (Baek and Lee, 2024; Bhattacharya et al., 2023; Ning et al., 2021). Recent improvements on materials science are helping to overcome some of the technical problems of BES encountered during the development, design, and operational stages (Kong et al., 2023; Noori and Min, 2022). These findings especially resulted in the enhancement of the efficiency and stability of electrodes, which are prominent parts of the BES. It is stated that new materials used for electrode preparation, including nanomaterials and algae-derived electrodes, have significantly improved the performance of BES in terms of bioenergy and biochemical production (Kong et al., 2023; Ning et al., 2021). These recent discoveries are crucial for expanding the BES from the laboratory to the industrial scale, as discussed by Zhao et al. (2024), who point out the requirement for durable and affordable materials.

Scaling up BES is also being tackled by developing better reactor designs that improve efficiency and reduce costs. Noori & Min (2022) and Wang et al. (2022) emphasize new reactor designs that can be easily combined with current conventional technology to make BES readily available and adaptable for various applications. In addition, the implementation of membrane technologies improves the separation of the processes within BES and leads to increasing the quality of recovered products and reducing energy use (Bakonyi et al., 2018; Zhu et al., 2022). However, some challenges still need to be overcome for BES to reach its full potential. Jiang et al. (2024) and Thengumthottathil et al. (2024) state that the complexity of the microbial communities, their relationship with each other, and their interactions with electrodes make it even harder to understand the mechanism completely. As a result, it becomes a major obstacle in front of enhanced performance and stability. More research is needed to optimize these microbial communities and find ways to control and divert the microbial community dominance (Thengumthottathil et al., 2024). There are also other challenges, such as the high costs of electrodes and system maintenance, that still need to be addressed. Baek and Lee (2024) suggest that ongoing efforts to reduce material costs and improve system durability are key factors that will make BES more competitive and propelling in the future.

There are other recent BES technologies aside from the most known methods utilizing microbial communities for harvesting hydrogen, methane, electricity, and value-added chemicals from the highly mild waste streams. One of them is the Enzymatic Fuel Cell, in which organic fuels such as glucose, fructose, pyruvate, sucrose, glycerol, hydrogen, lactate, methanol, ethanol, and starch can be oxidized and converted into electrons and protons by a group of specific enzymes/enzyme cascades (glucose oxidase, glucose dehydrogenase, fructose dehydrogenase, alcohol dehydrogenase, formate dehydrogenase, and hydrogenase) called biocatalysts (Leech et al., 2012; Mazurenko et al., 2017). The reduction of the electrons at the cathode following the electron flow from the anode to the cathode generates electricity in EFCs (Shi et al., 2022).

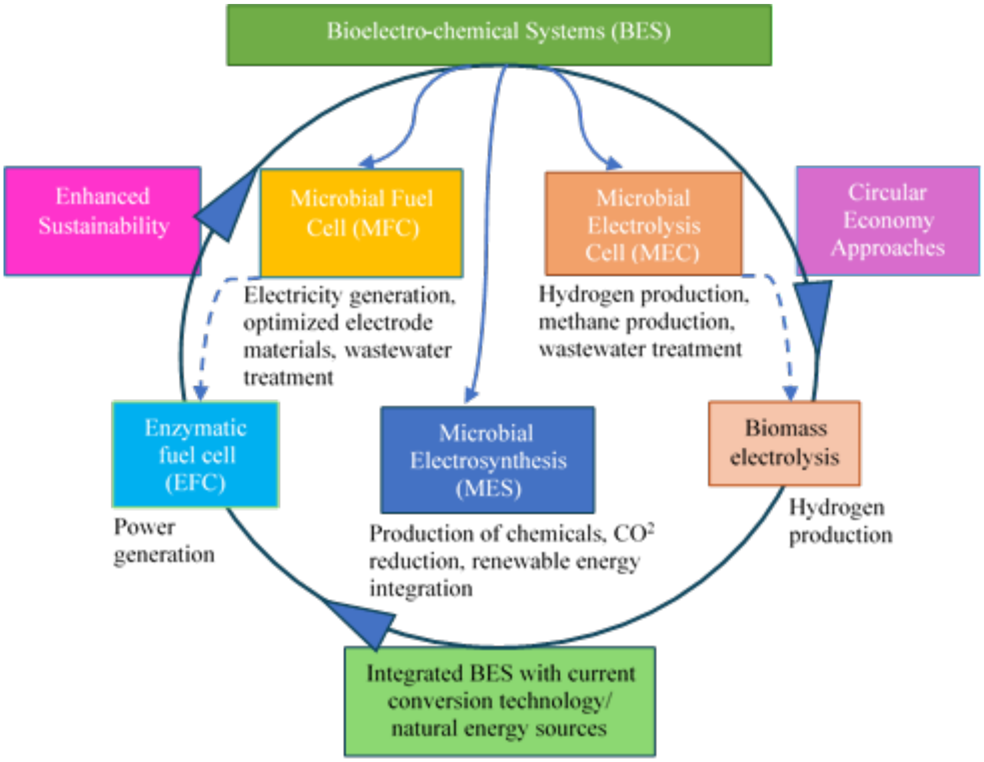

Figure 7.Common bioelectrochemical systems and their role in sustainability, economy, and current technology.

Due to the low current production in EFCs, the studies focused on the electrochemical device powering, which is shown to apply to biosensors, microelectronics, and lower energy-consuming devices (Leech et al., 2012). These devices are artificial devices that can be either implantable within or worn on the body to operate using body fluids such as sweat, saliva, or blood (Xiao, 2022). They can power themselves and measure the intended parameters, as in self-powered biosensing, pulse generators, GPS systems, and environmental monitoring sensors (Xiao, 2022, Mazurenko et al., 2017; Pankratov et al., 2015). As in generally known BES technologies, some barriers must be overcome for the EFCs to become commercially available. Therefore, studies are focusing on the electron transfer metabolic chains to find alternative and low-cost enzymes, mediators, and electrode materials for enhanced current production, stability, and long duration (Mazurenko et al., 2017; Xiao et al., 2019).

Biomass electrolysis is another developing technology that has been under observation for the last decade. Similar to the MEC technology, biomass electrolysis is used to harvest hydrogen gas from low-mild biowaste and biomass under lower energy application of 0.8 to 1.2 V compared to conventional electrolysis cells (H. Liu and Li, 2021; W. Liu et al., 2016; Xu et al., 2023). In contrast to water electrolysis, lower electricity, and non-noble catalysts can be used in biomass electrolysis for energy generation, which makes it an environmentally and cost-effective method. One of the main challenges that biomass electrolysis poses is the pretreatment requirement of the biomass, before electrolysis due to the structure of the biomass such as cellulosic and hemicellulosic biomass, sawdust, banana peel, etc. (Liu and Li, 2021). Even though the process can take place at ambient temperature, moderately high temperatures over 75 °C present higher current and hydrogen production (Liu et al., 2016). Recovery of the catalysts used in the system, enhancement of the current production, and carbon-rich and high-volume residues are the challenges that should be overcome before the full application of the process (Xu et al., 2023).

Environmental sustainability is another important factor driving the adoption of BES. These systems can help reduce greenhouse gas emissions, prevent pollution, and recover resources, which have parallel aims with global climate change policy and reduction of environmental impact. It is emphasized that BES can play a vital role in lowering the carbon footprint of wastewater treatment and industrial processes by its feature of lower energy consumption in the process (Khanthong et al., 2023). Additionally, Ning et al. (2021) discuss the potential of integrating BES with other renewable energy systems, like solar and wind, to create hybrid systems that maximize energy efficiency and resource recovery.

Looking ahead, the future of bioelectrochemical conversion technologies is very bright, with great potential for innovation and impact. Continuous improvements in system efficiency, materials, and microbial understanding will likely lead to the commercialization of BES for various applications, from wastewater treatment to bioenergy production. As noted by Wang et al. (2022), integrating BES into circular economy models will further enhance their role in sustainable development by turning waste into valuable resources and reducing environmental impact. In conclusion, while there are still some obstacles, the future of bioelectrochemical conversion technologies is encouraging. Ongoing research, technological innovation, and the growing demand for sustainable solutions will drive the development and adoption of BES in the long view. With continued progress, these technologies have the potential to become a key part of sustainable energy and waste management strategies worldwide.

4.2. Emerging Thermochemical Technologies

Thermochemical technologies are processes that use heat and chemical reactions to convert organic materials into energy, fuel, or chemical products. These technologies are increasingly recognized for their potential to transform biomass and waste into valuable resources, contributing to the circular economy and reducing reliance on fossil fuels (Okolie et al., 2020). This section explores the design and development of emerging thermochemical technologies, with a particular focus on the latest advancements in supercritical water gasification and oxidation.

Water is a polar solvent that, under normal conditions, can dissolve the majority of inorganic salts. However, it is either weakly soluble in or insoluble in gases and the majority of organic materials. Its density, dissolution performance, diffusion coefficient, thermal conductivity, viscosity, ion product, and dielectric constant change significantly at the supercritical state ($P > 22.1$ MPa, $T > 374°C$) (Ding et al., 2014; Gökkaya et al., 2015; Huelsman and Savage, 2012), as shown in Figure 8. Supercritical water (SCW) is characterized by a low dielectric constant akin to a polar organic solvent, a high diffusion coefficient, low viscosity, and minimal quantities of hydrogen bonds (Akizuki et al., 2014). Because of its strong dissolving capacity, SCW becomes mutually soluble with organic matter and oxygen, significantly lowering mass transfer resistance and making it an excellent reaction medium. Conversely, inorganic materials, particularly salts, are readily removed from SCW due to their very poor solubility. Furthermore, SCW's temperature and pressure may be altered to regulate the catalyst's selective activity, coordinate the pace of reaction and chemical balance, and manage the reaction environment (Chakinala et al., 2013). Supercritical water oxidation (SCWO) and supercritical water gasification (SCWG) are now the two most common uses of SCW.

Many publications have now been published discussing the impacts of various operational parameters on the rate of organic matter degradation in SCWO and the ability to produce hydrogen in SCWG. These factors include the oxidation coefficient, catalyst, residence time, temperature of the reaction, and reactant concentration. They have significantly advanced our knowledge of the processes involved in the conversion of organic materials in SCW. Furthermore, numerous articles state that the conversion of organic compounds in SCW involves a variety of reactions, such as pyrolysis, dehydration, hydrogenation, polymerization, isomerization, and others. These reactions lead to the formation of numerous different intermediate products during the oxidation/gasification process (Wei et al., 2021).

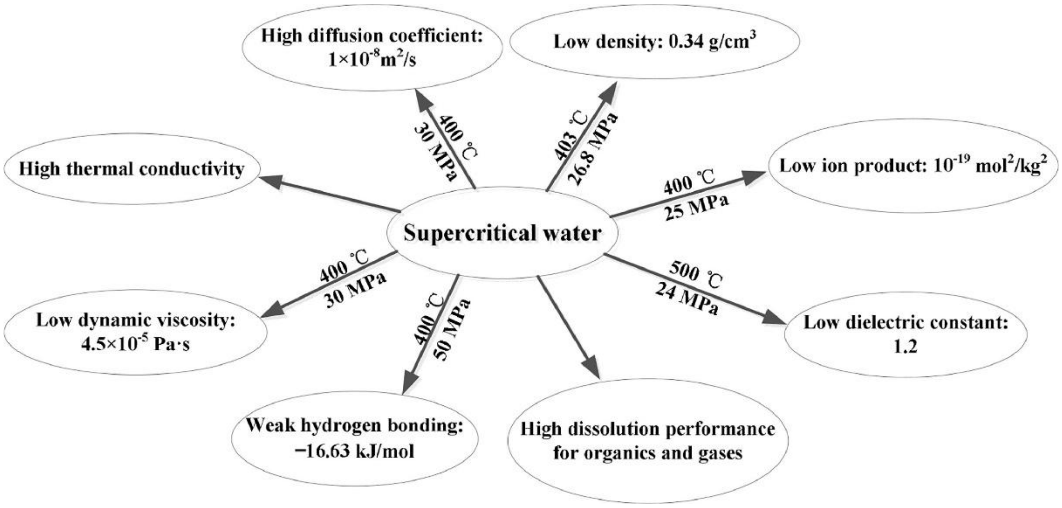

Figure 8. Supercritical water's primary characteristics (Wei et al., 2021).

4.2.1. Supercritical water gasification

The term "gasification" describes the reaction of organic compounds with steam or water to produce light gases, namely carbon dioxide, methane, and hydrogen. The use of biomass as an organic material is now quite popular because it addresses both global warming and energy security. Similar to SCWO, the special qualities of SCW provide a number of potentially beneficial characteristics to its employment as a gasification medium, specifically:

- High response rates at a certain temperature are supported by high transport rates.
- Compact gasifiers with little heat loss are associated with high operating pressure.
- High solvation of organic compounds helps lower the amount of tar and char that develop as condensation products with a greater molecular weight.
- Elevated water density stimulates the gasification processes.
- A high density environment that is good for heat recovery.
- Works well with feeds that have a high-water content, such as biomass and sludge; it minimizes or does away with the requirement for feedstock drying, which is necessary for traditional gasifiers.
- The water condenses during the cool-down process, resulting in an inherent scrubbing action that lessens or eliminates the requirement for gas cleaning before utilization or further processing.
- Compact storage is made possible by product gases that are accessible at high pressure.
- Elevated pressure allows CO_2 to be extracted and stored.

The use of SCWG may present some technological challenges, such as corrosion, solids buildup, and high pressure operation (Marrone & Hong, 2008).

Supercritical water gasification (SCWG) is the process of transforming organic compounds into gaseous substances by subjecting them to water at temperatures and pressures higher than its critical point (374 °C and 22.1 MPa) (Correa & Kruse, 2018). Water is suitable for high moisture feeds due to its usage as the reaction medium, and the thermophysical features of supercritical water (SCW) provide further benefits. After beyond the critical point, the density and viscosity decrease, leading to an increase in diffusivity. This decrease in transport limits results in higher reaction rates (Akiya and Savage, 2002). In the supercritical state, water exhibits unique properties, including the ability to act as both a solvent and a reactant, which significantly enhances the efficiency of the gasification process. SCWG is particularly advantageous for treating wet biomass and waste, as it eliminates the need for energy-intensive drying processes required by conventional gasification methods (Kruse, 2008).

4.2.1.1. Current technology status

The use of SCWG enhances the production of hydrogen, minimizes the creation of tar, and eliminates the need for drying, distinguishing it from other thermochemical techniques. SCWG, in contrast to traditional gasification processes, requires much lower reaction temperatures in order to get equivalent H_2 production (Zhang et al., 2014). The primary gaseous byproducts in this process are hydrogen (H_2), carbon dioxide (CO_2), methane (CH_4), small quantities of carbon monoxide (CO), and other hydrocarbons, which vary depending on the specific working conditions and catalyst used. Considering the data obtained from the experiments, it was concluded that the gas created with the SCWG method comprises 40-60% H_2; 30-70% CO_2; 15-25% CH_4 and 5-30% CO (Afif et al., 2011). In this approach, total oxidation of most organic compounds, including lignin, is achieved in a relatively short period. Since SCWG takes place at temperatures below 700 °C, it makes it possible to utilize waste heat from other processes to produce the required energy. Considering the CO_2 emissions, SCWG has been claimed to be a highly efficient approach for the disposal of wet biomass (Yoshida et al., 2004). One of the most noteworthy benefits of the SCWG process is that high solids conversion is accomplished, and extremely minimal levels of coke and tar are seen. While syngas is generated over 800 °C in traditional gasification, hydrogen and carbon dioxide are created at 500 °C or higher in SCWG. Thanks to the tunable solubility of supercritical water, separating the phases created as a consequence of gasification enables the products to be separated from one another and to be purer (Kurt, 2009).

4.2.1.2. The challenges and prospects

While SCWG offers significant advantages, several challenges must be addressed to enhance its commercial viability:

- Corrosion and Material Degradation: The harsh operating conditions in SCWG reactors pose a challenge in terms of material degradation and corrosion. Ongoing research focuses on developing advanced materials and coatings that can withstand supercritical conditions over prolonged periods (Calzavara et al., 2005; Elliott and Sealock Jr, 1996).
- Catalyst Development: Catalysts are often employed in SCWG to enhance reaction rates and selectivity. However, catalyst deactivation due to fouling and sintering remains a significant issue. The development of robust and long-lasting catalysts is a key area of research (Sato et al., 2003).
- Process Optimization: Optimizing process parameters, such as temperature, pressure, and feedstock composition, is essential for maximizing gas yield and improving the overall efficiency of the SCWG process. Advanced modeling and simulation tools are increasingly being used to optimize reactor design and process conditions (Macrì et al., 2020).

4.2.2. Supercritical water oxidation

The optimum conditions for oxidation in SCW are provided by the high solubility of oxygen and most nonpolar organic molecules, the naturally high temperature, and the comparatively dense, single-phase environment. Aqueous or pure organic feed, oxidant (such as oxygen, air, or peroxide), water, and auxiliary fuel (if needed) are heated and compressed to a range of 550–650 °C and 23–25 MPa in the standard SCWO process. Under these conditions, the organic meal quickly oxidizes to CO_2 and H_2O. Complete feed degradation usually requires less than one minute of residence time. The comparatively lower temperature and higher density of SCWO compared to air incineration provide a cleaner reaction without the development of unwanted byproducts such as CO, dioxins, NO_x, and SO_2, despite the reaction's numerous similarities to a combustion reaction. If there is any nitrogen, it oxidizes mostly to N_2 or N_2O. Mineral acids (e.g., HCl, H_2SO_4, H_3PO_4) are produced from other heteroatoms, including phosphorus, sulfur, and halogens. These acids have the potential to cause corrosion if they are not neutralized, especially downstream of the reactor where subcritical conditions exist (Marrone and Hong, 2008).

The annihilation of hazardous organic wastes, especially those in diluted aqueous solutions (i.e., 1-20 weight percent organic), is the most prevalent use of SCWO. Over the last three decades, a great deal of work has been done in both the scientific and commercial domains to comprehend and create a workable SCWO process, especially in the areas of corrosion and salt precipitation management. Many full-scale commercial SCWO facilities are now in use worldwide, processing a range of foods (Kutz, 2007). Several review articles (Bermejo and Cocero, 2006; Gloyna, 1998; Kritzer and Dinjus, 2001; Kutz, 2007; Schmieder and Abeln, 1999) provide further in-depth details regarding the SCWO method and technology. The present state of SCWO is examined in a more recent study by Brunner (2009) using information. Full-scale SCWO facilities have been created, constructed, and made available globally by a number of commercial companies, including General Atomics (GA), Chematur AB, Organo, SRI International, Mitsubishi Heavy Industries, and Hanwha Chemical (Marrone and Hong, 2008).

After experiments for the conversion of carbohydrates in supercritical water media by M. Modell and S. Amin at the Massachusetts Institute of Technology in the mid-1970s, the potential of supercritical water oxidation (SCWO) was discovered. In the 1980s, chemical and engineering research began very actively in national laboratories and universities, especially in the USA (Schmieder and Abeln, 1999).

SCWO is a process that operates in the supercritical phase of water, where water's properties as a solvent are significantly altered. At temperatures above 374°C and pressures above 22.1 MPa, water becomes supercritical, exhibiting both liquid- and gas-like properties that enable the effective oxidation of organic materials. SCWO has gained attention for its ability to completely mineralize organic compounds into carbon dioxide, water, and inorganic salts, making it a promising technology for treating hazardous waste and complex industrial effluents (Jiang et al., 2020; Yan et al., 2020). Figure 9 shows the typical SCWO process flow diagram (Tang et al., 2021).

Supercritical water oxidation is a closed-system process that efficiently eliminates organic contaminants in wastewater within a matter of seconds, without generating any detrimental by-products. The supercritical water environment is well-suited for the oxidation of organic contaminants. Employing elevated temperatures enhances the rate of reaction. Under supercritical conditions, nonpolar organic substances dissolve in water and form a single phase where they come into close molecular contact with each other. This occurs with an equal distribution of the substances in the presence of oxygen. Due to the absence of mass transfer limitations in the intermediate phase, organic pollutants undergo rapid oxidation and transform into end products such as carbon dioxide (CO_2) and water (H_2O). Phosphorus undergoes a transformation in the organic structure and becomes phosphate, sulfur transforms into sulfate, and nitrogen-containing molecules are converted into N_2 and NO_2. Precipitation of inorganic compounds in wastewater occurs due to their limited solubility in supercritical water (Vadillo et al., 2018).

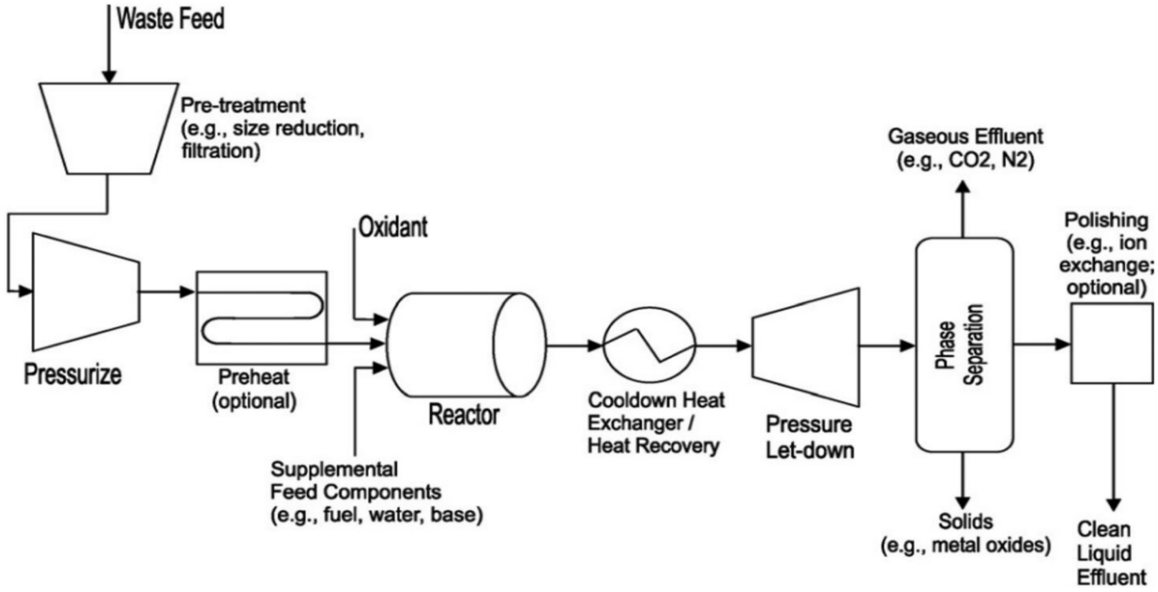

Figure 9. The standard SCWO process flow diagram.

4.2.2.1. Current technology status

SCWO leverages the unique properties of supercritical water to oxidize organic compounds:

Reaction Mechanism: The reactor has to be built to withstand the severe working environment and oxidative atmosphere. Reaction temperature, residence time, oxidant concentration, and pressure are the primary operational parameters (Bermejo and Cocero, 2006).

Oxidation Kinetics: The kinetics of SCWO are influenced by temperature, pressure, and the concentration of organic compounds and oxygen. High temperatures and pressures accelerate the oxidation reactions, leading to rapid and efficient destruction of organic materials (Jiang et al., 2020).

Designing an effective SCWO system involves several critical aspects:

Reactor Design: SCWO reactors are typically tubular, designed to withstand high pressures and temperatures. Materials of construction, such as Hastelloy, titanium, or ceramic-lined steel, are chosen for their corrosion resistance in the supercritical environment. Continuous-flow reactors are preferred for their scalability and consistent operation (Guo et al., 2022; Yan et al., 2023).

Feedstock Handling: The feedstock, often a liquid waste stream, must be preheated and pressurized before entering the reactor. The design of preheating systems and high-pressure pumps is crucial to ensure efficient energy use and reliable operation (Zhang et al., 2022).

Heat Recovery and Management: SCWO is an exothermic process, generating significant amounts of heat. Effective heat recovery systems, such as heat exchangers, are essential for maintaining energy efficiency. Managing the thermal environment within the reactor is also critical to prevent hot spots and ensure uniform reaction conditions (Vahed Qaramaleki, 2022).

Effluent Treatment: Post-reaction, the effluent contains water, carbon dioxide, and inorganic salts. The design of separation systems for salt removal and effluent cooling is integral to the overall process. The treated water can often be reused or safely discharged, while the salts can be recovered or disposed of (Barnes, 1994).

4.2.2.2. The challenges and prospects

While SCWO offers numerous advantages, several challenges remain:

Corrosion and Materials Degradation: The aggressive conditions within a SCWO reactor, particularly the presence of high concentrations of inorganic salts and acids, pose significant corrosion challenges. Developing and selecting materials that can withstand these conditions over long periods is an ongoing area of research (Marrone and Hong, 2008; Xu et al., 2012).

Salt Precipitation: Inorganic salts can precipitate out of solution under supercritical conditions, leading to potential blockages and fouling within the reactor. Designing systems that can handle or mitigate salt precipitation is essential for maintaining continuous operation (Fauvel et al., 2004; Xu et al., 2010).

Energy Consumption: Although SCWO is highly effective at destroying organic waste, the high energy input required to reach supercritical conditions can be a drawback. Energy recovery systems and the integration of SCWO with other processes, such as waste heat recovery, are critical for improving the energy efficiency of SCWO systems (Vadillo et al., 2013).

4.2.3.Current status and prospects of emerging thermochemical technologies

SCWG has several potential applications, particularly in the field of renewable energy and waste management. It is an efficient method for producing hydrogen from wet biomass, making it a promising technology for the hydrogen economy (Adar et al., 2020; Su et al., 2022). SCWG offers an effective solution for the treatment and valorization of organic waste streams, including industrial effluents, sewage sludge, and agricultural residues (Adar et al., 2020; Okolie et al., 2020; Su et al., 2020). Methane produced through SCWG can be upgraded to renewable natural gas, which can be used as a fuel for heating, electricity generation, or as a transportation fuel (Bian et al., 2020).

SCWO has a wide range of applications, particularly in industries that generate complex or hazardous waste streams. It is highly effective at destroying toxic organic compounds, such as PCBs, dioxins, and organic solvents, making it an attractive option for hazardous waste management (Chen et al., 2021). SCWO can also be used to treat sewage sludge, converting it into clean water, carbon dioxide, and a small amount of inert ash. This application is particularly relevant in urban areas with limited space for traditional sludge disposal methods (Yan et al., 2020). The chemical industry produces a variety of waste streams that contain refractory organic compounds. SCWO can effectively treat these effluents, reducing their environmental impact and enabling the recovery of valuable byproducts (Tang et al., 2021).

The future of SCWG lies in addressing the current challenges and scaling up the technology for commercial applications. The integration of SCWG with other renewable energy systems, such as biorefineries and waste-to-energy plants, could enhance the overall sustainability and economic viability of these technologies. Additionally, advancements in reactor design, catalyst development, and process optimization are expected to drive the commercialization of SCWG in the coming years (Guo et al., 2010; Kruse, 2009; Matsumura et al., 2005; Peterson et al., 2008). On the other hand, recent advancements in SCWO technology have focused on improving reactor design, enhancing material durability, and optimizing process efficiency. Innovations include the development of new corrosion-resistant materials, improved heat recovery systems, and the integration of SCWO with other waste treatment technologies. The future of SCWO lies in its ability to scale up for industrial applications while maintaining cost-effectiveness and energy efficiency (Zhang et al., 2017).

4.3. Emerging Physicochemical Technologies

Physicochemical technologies like hydrodynamic cavitation and vibrating reverse osmosis are innovative methods used in the valorization of waste streams, from various sectors to produce valuable products in biorefineries. Physicochemical technologies like hydrodynamic cavitation and vibrating reverse osmosis are advanced processes that utilize waste streams from various sectors to produce valuable products in biorefineries. Hydrodynamic cavitation harnesses the power of high-energy microbubbles generated by pressure fluctuations in liquid media. These microbubbles implode, releasing intense localized energy that breaks down complex organic molecules. The driving force behind this process is the rapid pressure change, which enhances mass transfer and chemical reactions. This technology is effective in treating agricultural waste, wastewater, and sludge, breaking down lignocellulosic biomass or extracting bioactive compounds for biofuels and biochemicals. Vibrating reverse osmosis, in contrast, applies oscillating forces to traditional reverse osmosis membranes, improving permeation and filtration efficiency while reducing membrane fouling. The driving force here is the combination of mechanical vibration and pressure, which allows for better separation of water and dissolved solids from waste streams. This technology is ideal for concentrating nutrients, proteins, and valuable organics from food industry waste, dairy effluents, or wastewater. The key specifications of vibrating reverse osmosis include its ability to operate at lower pressures with enhanced flux rates, reducing energy consumption. Together, these technologies promote the efficient conversion of industrial and agricultural waste streams into high-value bio-based products, contributing to the sustainability of biorefineries.

4.3.1. Hydrodynamic cavitation (HC)

Cavitation occurs when the transient pressure in a liquid flow changes suddenly, causing microbubbles to form, grow, and implode under intense energy bursts. Small particles or dissolved gasses can provide nucleation sites for bubbles in most liquids. The gas bubbles or vapor cavities emerge when the local static pressure drops below the vapor pressure of the liquid. The gas formation is analogous to opening a bottle of sparkling water and releasing the pressure, accompanied by a stream of bubbles expanding and bursting, sometimes overflowing the bottle. In cavitation, on the other hand, the pressure drop in the flowing liquid is transient. When the liquid's static pressure is reestablished, i.e., exceeding the vapor pressure, the cavities or voids formed will implode instead of exploding.

The implosion or collapse of the vapor-filled bubbles can cause an intense energy release. Under certain conditions, the collapse can reach extreme temperatures (>2000 K) and pressures (>100 MPa). The violent collapse also creates local supersonic microjets (100 m/s) propagating high-pressure shock waves. The jets can cause damage to solid surfaces. Thus, metal corrosion by cavitation has been a century-long challenge to marine propeller technology.

Of the four types of cavitation processes (incl. particle and optic), only acoustic and hydrodynamic cavitation have practical application to bulk solutions. Acoustic cavitation uses high-frequency ultrasound (20 kHz–200 MHz) to create imploding microbubbles and local shockwaves in a liquid. Ultrasonic cavitation, among many practical applications, is a well-known cell disruption method in the laboratory. The downside of ultrasonic cavitation is the low energy efficiency and inability to distribute the cavitational effect in larger volumes.

Hydrodynamic cavitation is created in a flow system by forcing liquid through constriction zones, where rapid changes to low pressure can be realized. Cavities form in the low-pressure zone, travel briefly with the turbulent flow, and eventually implode. The cavitation effect depends on flow rate, temperature, and constriction design. Thus, hydrodynamic cavitation is more feasible to scale up for use in industrial processes. Cavitation theory is well understood and described with sufficient models. However, the extension of the theory into practical uses is still under development (Ranade, 2022; Ranade et al., 2022).

4.3.1.1. Current technology status

Devices for HC are of two types; with and without moving parts (Wu et al., 2019; Bimestre et al., 2022). HC with moving parts consists of a rotor-stator principle where the rotor has small indents suitable for creating local low-pressure zones. The effect of rotor-stator devices depends on rotor speed and flow rate, are complicated in design, and, thus, are energy and capital-intensive.

HC without moving parts consists of linear flow and swirling flow devices. Linear or axial flow devices are constructed with flow path constrictions. These can be orifice plates (OP), venturi channels, or similar narrow hindrances along the flow direction. When a non-compressible fluid like water passes a constriction, the throat speed increases, reducing the local static pressure enough to create vapor cavities. In swirling flow devices, on the other hand, the liquid enters a circular chamber tangentially, vortexing freely before exiting axially through a center port into a forced vortex. The abrupt change in flow pattern creates the necessary low-pressure zone for cavitation at the exit point. Swirling flow devices have some benefits over linear flow, the latter being prone to clogging the narrow constrictions and orifices with suspended particles.

Various full-scale versions of the HC designs above are available commercially (i.e., BioBang/Cavimax, HyCaTechnologies, VIVIRA Process Technologies, ROTOCAV, and others). The applications vary from wastewater treatment to biogas boosting (Garuti et al., 2018) to biomass pretreatment (Hilares et al., 2017). A comprehensive review is provided by Panda et al. (2020).

Besides the design, the process depends on various physical (density, viscosity, surface tension) and operating parameters (temperature, pH, load, particle sizes, flow rate) (Ranade et al., 2022). Thus, applying HC to practical use depends on the main cavitation effect exerted by the device, considering that in the case of (1) intense shear and high-velocity jets, this will be efficient in biomass pretreatment. In scenarios where (2) transient high pressure and temperature and (3) strongly oxidizing radicals are generated, wastewater treatment and acceleration of chemical processes benefit from HC. For the scope of this report dealing with biomass, applications of HC exploiting the effect (1) with the synergetic effect exerted by (3) are relevant.

Delignification can enhance the depolymerization of recalcitrant lignocellulose. In the presence of alkali, the hydroxyl radical formation by HC from the splitting of H_2O into •OH and H• can cause lignin to depolymerize. Holding the biomass load stationary in the cavitation zone in an OP-type cavitator, a 50-60 % lignin removal from sugarcane bagasse by radical oxidation has been investigated in detail (Bimestre et al., 2022; Hilares et al., 2019; Hilares et al., 2020; Prado et al., 2022; Prado et al., 2024). Furthermore, the radical-assisted splitting of glycosidic bonds resulted in extensive saccharification of the celluloses (Prado et al., 2024). Another process with OP-cavitation, but with circulating biomass, is described for corn cob in combination with enzymatic treatment, with 47% lignin removal demonstrated with laccase (Thangavelu et al., 2018). Other examples of HC biomass pretreatment are the extraction of antioxidants from dried olive leaves and cocoa bean shells (Grillo et al., 2019). Lipid extraction was obtained from microalgae using OP-type HC, which provided a better yield than ultrasonication (Lee and Han, 2015).

4.3.1.2. The challenges and prospects

The benefits offered by HC can broadly be termed process intensification. The physicochemical effects can improve or boost purity, yield, rates of transport, and chemical reactions (Ranade, 2022). HC has a relatively lower energy input per unit biomass than sonication, pressurized, and steam-heated processes. Most reported ultrasound-assisted processes can be performed with HC at a lower cost and higher productivity. The main energy consumption is the pumping of the feedstock, while only moderate heating (50-70 °C) is required, if at all.

However, investment and operating costs vary with the design and complexity of the device. Linear flow devices may also suffer from wall corrosion and frequent maintenance. Milling and desizing the dried biomass to particle sizes < 1-2 mm is a prerequisite for OP-type cavitation. Depending on the biomass toughness and water content, this preparatory step may be energy and time consuming.

HC, as described, is typically a water-based phenomenon that can work under ambient conditions. Thus, solvent systems other than water are limited due to vapor pressure incompatibility. However, a hexane/ethanol/water mixture was used for antioxidant extraction (Grillo et al., 2019). With closed-loop systems, higher pressures can be applied to the process, facilitating organosolv and higher processing temperatures.

A lack of fundamental understanding of the physicochemical processes in HC seems to hinder optimal exploitation (Ranade et al., 2022). Thus, developing predictive models for the process output is challenging without quantitative insight into what happens around the implosion phenomenon. One such measure could be to harness suitable sensors to detect molecular-level changes in the process flow close to the cavitation zone.

Although commercialized, the availability of robust devices with effective performance is lacking. Swirling flow devices appear to have the best potential to meet these requirements.

4.3.2. Vibrating Reverse Osmosis Technology

In today's modern world, agriculture constantly faces increasing water quality deterioration and a growing scarcity of fresh irrigation water. Concurrently, the trend to centralise livestock production in large operations housing huge herds is creating significant challenges in implementing sustainable slurry management systems. The problem causing huge challenges is that the local agri-landscape used for the dispersal of manure slurry is fixed in size and has limited capacity to absorb the fertilising nutrients. The risk of nutrient overload, pathogen release, and excessive odour emissions, are potential threats when operating a production unit at or near the limits of the land are of real concern. The high density of livestock in these areas has resulted in excessive manure production for the available regional land base. To comply with land application legislations, part of the manure slurry has to be transported over relatively long distances and at great costs given the high-water content and low nutrient concentration in liquid manure, moreover, crop producers are sometimes reluctant to apply manure in their land because of the poorly balanced nutrient concentrations. Environmental problems have given a bad reputation to manure, which should be considered as a valuable fertiliser resource that is part of a sustainable agriculture, not as a disposable waste.

Alternatively, animal wastes have also been identified as one of the most energy-efficient and environmentally beneficial technologies for bio-energy production (Fehrenbach et al. 2008). In both cases, an important issue complicating the development of bio-digestion in high-nutrient regions is that a by-product of this technology is the production of digestate may not be returned to arable land as a fertiliser in its crude, unprocessed form (Lemmens et al. 2007). The underlying reason for this technical prerequisite is that intensive industrial animal production is confronted with an overproduction of animal manure in comparison to the available arable land on which it can be spread. To avoid overfertilization, the EU Nitrate

Directive (91/676/EEC) obliges local administrators and government to enforce more stringent regulations regarding manure and digestates. This legislation limits the land application of manure and any of its by-products based on the nitrogen load.

Technologies for the dewatering of liquid manure and digestate involve the use of separation and/or dewatering processes resulting in a dry fraction and a liquid fraction that would still contain most of the inorganic nitrogen. This excess nitrogen can be processed in nitrification–denitrification bioreactors, converting valuable nitrogen into nitrogen gas (N_2) thereby eliminating a valuable nutrient from the agricultural system. The wastage of manure nitrogen means that additional inorganic fertilisers must be produced, using an energy-intensive and greenhouse-emitting process, as nearly 1 m^3 of natural gas is required per kg of anhydrous ammonia (Noble Foundation, 2001). In addition, aerobic and nitrification–denitrification technologies can lead to significant emissions of nitrous oxide (Béline & Martinez, 2002; Melse & Verdoes, 2005; Yamagishi et al., 2001), an important greenhouse gas that can travel great distances and contributes to the destruction of the ozone layer (Choi et al., 2004; Lansing and Downey, 2011). In today's reality, where due to geopolitical volatility prices for mineral fertilizers are increasing, it has therefore become an important challenge to recycle valuable nutrients in waste streams in a sustainable and environmentally friendly manner. In this context, membrane filtration technologies are of increasing interest.

The membrane separation technology process consists of a synthetic barrier with the capacity to selectively prevent the passage of certain components across it. Different membrane characteristics are determined by the Pore size or Molecular Weight cut-off enabling a variety of separation performances ranging from reverse osmosis to microfiltration. The limitations of conventional membrane systems is their tendency of rapid fouling due to the colloidal scale formation, thereby obstructing or clogging the membrane pores, thereby compromising throughput and increasing the frequency and amount of cleaning required. These limitations have hindered their widespread application for wastewater treatment. During the 1980s, a system known as the vibratory shear enhanced process (VSEP) was developed to overcome these limitations and utilized to filter practically any type of wastewater, including landfill leachate and municipal sludge. This VSEP technology is now past its experimental phase and can be considered to have a proven track record of performance. Following its application in handling industrial wastewater, the first installation to treat swine wastewater was installed in Korea in May 2000. Depending on the physical nature of the manure slurry, the VSEP process concept can either provide a complete manure treatment solution or be used in conjunction with other technologies. Despite its benefits, there is still a chronic lack of awareness of this technology and its potential application to treat livestock waste.

4.3.2.1. Current technology status

Recently, Wanga et at 2022, described the VSEP technology as consisting of multiple modules, each having a filter pack, motor shaft, and membrane. The filter pack is fitted with a stack of ring-shaped membranes, and a motor shaft drives the movement of the filter pack. The membrane is made up of flat-disk modules having an effective filtration area of 1.54 m^2. The system is usually operated at a constant feed pressure of 38 bar with a constant inflow of 0.6 m^3 /h, and a rotation frequency of ~55 Hz. The process employs torsional vibration at the membrane surface, creating very high shearing energy on the membrane surface and near the pores, thereby reducing the probable occurrence of colloidal fouling and polarization of the membrane. The sinusoidal shear waves propagating from the membrane surface act to hold suspended particles above the membrane surface, thus allowing for the free passage of the liquid fraction across the membrane. The solids at the membrane surface are removed by the shear allowing for higher operating pressures and increased permeate rates. Feed pressure is provided by a pump, which consistently circulates new fluid to the filter. The water recovery rate of the VSEP system is estimated to be 70%.

Various configurations involving the VSEP have been installed on livestock farms. Since the technology is compact, modular, and versatile, it can be custom fitted to the requirements on the farm. It is operational over a large temperature range (5°C to 60°C) and can withstand large fluctuations in pH, solids loading, and changes in chemical composition of the wastewater. The VSEP works automatically and produces results immediately without reaction time or waiting for biological activity to develop. The only pre-treatment required for the VSEP is a coarse mechanical screen to prevent beach sand sized particles from entering the system. It is not necessary to completely remove suspended solids, only the ones large enough to act as projectiles and possibly do damage to the membrane. Normally, 60 to 100 mesh screen size is sufficient.

VSEP can have the following applications:

1. As a single treatment method with just a mechanical screen to make clean water for reuse and a concentrated nutrient slurry for composting, land application, or portable slurry for off-site fertilization from a spray truck

2. As pre-treatment to either an aerobic or anaerobic digester. The clean water is produced ahead of the digester for reuse. The concentrate from the VSEP is then sent to the digester at a greatly reduced volume. This means a smaller digester system that is working on more concentrated material, thus improving efficiency.

3. As post-treatment for a digester to treat the effluent produced. VSEP polishes the water to make it suitable for reuse or discharge. The reject from the VSEP can be either returned to the digester or blended with digester sludge or blended with screen reject composting.

4.3.2.2. The challenges and prospects

Membrane fouling and the flux decline are common problems of the membrane technology. They increase the operational costs and decrease the overall performance. VSEP is introduced to prevent the accumulation of long-chain molecules and phenolic compounds in the surface boundary of the membranes employed. Thus, alternative membrane designs and materials that avoid membrane fouling and polarization phenomena or the use of NF modules instead of RO are necessary to improve the performance of the integrated membrane systems (Contreras-Jácquez, et al., 2022). Most of the studies on VSEP technology focused on the evaluation of the technology to treat different wastes and recover nutrients. However, there is very little information about the agronomic assessment of the obtained concentrated products to be used as bio-based fertilizers in agriculture (Subramani et al., 2012). Operational conditions and recovery yields for the VSEP process are required to be evaluated. On the other hand, even if the VSEP-concentrated products are characterized by significant nutrient contents and show an agronomic value similar to mineral fertilizer, the salinity of the concentrate was identified as a key factor which may limit high application rates. There are other limitations, such as insufficient information gathered from a continuous pilot scale process. Chemical consumption for the cleaning of the membranes is another disadvantage to be emphasized (Subramani et al., 2012).

4.3.4.Current status and future prospects of emerging physicochemical technologies

Emerging physicochemical technologies for waste and wastewater treatment are transforming traditional approaches to resource recovery and environmental protection. These innovative methods focus on using chemical, physical, and electrochemical processes to remove contaminants, recover valuable materials, and produce clean water. Technologies such as hydrodynamic cavitation and membrane filtration systems are gaining attraction and are at the forefront of wastewater treatment and resource recovery (Gogate and Pandit, 2011; Nagarajan et al., 2022).

VSEP technology uses high-frequency vibrations to prevent membrane fouling during filtration, allowing for more efficient separation of contaminants from water (Pall, 2015). This technology is particularly effective for treating highly concentrated waste streams, enabling the recovery of clean water and valuable biomaterials such as nutrients and organic compounds (Stoller and Bravi, 2010). However, VSEP technology faces challenges related to energy consumption and the complexity of handling certain types of wastewater. While it reduces fouling, the mechanical vibrations used in the process require substantial energy input, which can increase operational costs (Stark, 2021). Additionally, the membrane lifespan and performance in highly viscous or heavily polluted wastewater streams may degrade over time. Scaling the technology for large-scale applications, along with ensuring long-term membrane stability and efficiency, is another significant hurdle (Pall, 2015).

Hydrodynamic cavitation, on the other hand, involves the generation of vapor bubbles that collapse, creating localized high-pressure zones. This process enhances the breakdown of pollutants and accelerates chemical reactions without the need for chemical additives (Nagarajan et al., 2022). Hydrodynamic cavitation is used to degrade organic pollutants, improve sludge digestion, and enhance the recovery of bioenergy and other valuable materials from wastewater (Capocelli et al., 2014). The challenges faced in this technology are primarily related to optimizing operational parameters such as cavitation intensity and flow conditions (Gogate and Pandit, 2011). Inconsistent cavitation bubble formation can affect the efficiency of pollutant degradation. Another limitation is the potential wear and tear on equipment due to high-pressure conditions, which can lead to increased maintenance costs. Moreover, hydrodynamic cavitation may require the addition of catalysts or post-treatment processes in some cases to fully remove certain complex contaminants (Capocelli et al., 2020).

Both technologies offer significant advancements in reducing energy consumption and operational costs, while promoting sustainability by maximizing the recovery of clean water and valuable by-products (Pradhan, et al., 2019). VSEP holds promise in becoming a key solution for high-strength industrial wastewater and complex waste streams due to its enhanced filtration capabilities (Stoller and Bravi, 2010). As the membrane materials improve their durability and fouling resistance, the technology is expected to become more energy-efficient and scalable, and integrated into biological and chemical treatment processes (Pall, 2015). Hydrodynamic cavitation has the potential to become a versatile and low-cost method for enhancing chemical and biological wastewater treatment processes. Research is focused on refining cavitation conditions to improve the efficiency of pollutant degradation without the need for chemical additives and integration of the technology into bioreactors (Capocelli et al., 2020).

Conclusion

The emerging technologies mentioned above that convert biomass, biowaste, wastewater, and other waste streams into electricity, hydrogen, methane, and value-added chemicals have a significant importance to move forward to a more sustainable future and circular economy. These technologies offer solutions for waste treatment and a cleaner environment and also contribute to the production of renewable energy and chemicals, helping to mitigate the environmental impact of waste, fossil fuel emissions, and carbon footprints derived from human activities. Continued research and development are essential to keep up research and development to tackle the challenges related to these technologies, such as scaling up, cost reduction, and process optimization, to make them expansively available for implementation or integration into existing industrial infrastructures.

The future of bioelectrochemical technologies is very promising, with great potential for innovation due to its continuous improvements in system efficiency, materials, and microbial understanding. It has the capability of leading to various commercialization applications such as wastewater treatment, biomaterial production, and bioenergy generation. Integrating BES into conventional technology is inevitable since it offers a circular economy and enhancement in sustainable development by turning waste into valuable resources and reducing environmental pollution. It seems that ongoing research, technological innovation, and the growing demand for sustainable solutions will lead the way to the adoption of BES in the long term. They have the potential to become a key part of sustainable energy and waste management strategies worldwide. Finally, while there are still some obstacles, the future of bioelectrochemical conversion technologies is promising.

Further improvements of supercritical water gasification (SCWG) and oxidation (SCWO) lie in addressing the current challenges and scaling up the technology for commercial applications. The integration of SCWG with other renewable energy systems could enhance the overall sustainability and economic viability of these technologies. Improvements in reactor design, catalyst development, and process optimization are expected to commercialize the SCWG in the future. Also, for the advancement of the SCWO technology, research has focused on improving reactor design, enhancing material durability (corrosion-resistant materials), optimizing process efficiency, improved heat recovery systems, and the integration of SCWO with other waste treatment technologies. Maintaining cost-effectiveness and energy efficiency will scale-up the SCWO technology for industrial applications.

VSEP and hydrodynamic cavitation technologies offer significant advancements in reducing energy consumption and operational costs while promoting sustainability by maximizing the recovery of clean water and valuable by-products. VSEP holds promise in becoming a key solution for high-strength industrial wastewater and complex waste streams due to its enhanced filtration capabilities. As the membrane materials improve their durability and fouling resistance, the technology is expected to become more energy-efficient, scalable, and integrated into biological and chemical treatment processes. Hydrodynamic cavitation has the potential to become a versatile and low-cost method for enhancing chemical and biological wastewater treatment processes. Research is focused on refining cavitation conditions to improve the efficiency of pollutant degradation without the need for chemical additives and integration of the technology into bioreactors.

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