Key enabling applications to drive the development of biorefineries

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Waste biorefinery technologies for accelerating sustainable energy processes (WIRE)

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List of acronyms

ABE	Acetone-butanol-ethanol
ACE	Accelerated solvent extraction
AD	Anaerobic digestion
ATJ	Alcohol-to-jet
CAGR	Compound annual growth rate
CBG	Compressed biogás
CHP	Combyned Heat and Power
DTSS	Deep tunnel sewerage system
FAME	Fatty Acid Methyl Ester
FFA	Free fat acid
FT	Fischer-Tropsch
HEFA	Hydroprocessed Esters and Fatty Acids
HFS	Hydroprocessed fermented sugars
HTL	Hydrothermal liquefaction
HVO	Hydrotreated vegetable oil
ICAO	International Civil Aviation Organization
LA	levulinic acid
LBG	Liquid biogas
MSW	Municipal solid waste
NGVs	Natural gas vehicles
ORC	Organic ranking cycle
PHA	Polyhydroxyalkanoates
PHB	Polyhydroxybutyrates
PM	Particulate matter
PVOH	Polyvinyl alcohol
PSE	Pressurized solvent extraction
SAF	Sustainable aviation fuel
SFE	Supercritical fluids extraction
SIP	Synthetic iso-parafins
THF	Tetrahydrofuran
TRL	Technology Readiness Level
VFAs	Volatile fatty acids
WtE	Waste-to-Energy
WWTP	Wastewater treatment plants

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Executive summary

The WIRE COST Action has been established to foster innovation and collaboration in the biorefinery sector, accelerating the transition to a circular economy. The project is structured around four working groups, each addressing a specific aspect of biorefinery development. Working Group 3 (WG3) is dedicated to identifying and promoting industrial applications for biomass-derived products. This report aims to elucidate key enabling applications that drive the development of biorefineries, with a particular focus on the identification, valorization, and market integration of bio-based products and their associated industrial value chains. By doing so, WG3 will contribute to the long-term success of bioeconomy initiatives across the European Union. Furthermore, this report is structured to focus on the most relevant bio-based products and processes that align with Europe's strategic goals in the bioeconomy and circular economy. While the broader spectrum of commercialized bio-products is vast, this report prioritizes biofuels, bioenergy, biochemicals, and biomaterials that hold the greatest potential for addressing key European needs, particularly in reducing dependence on fossil fuels, achieving carbon neutrality, and advancing sustainability in industrial sectors.

1. Introduction

The WIRE COST Action is structured into four Key Working Groups (WG), each of which mobilizes expertise from academia, industry, and technology transfer organizations. These working groups are designed to address specific focus areas: (1) Raw Materials, (2) Biorefinery Conversion Technologies, (3) Biorefinery Applications, and (4) Communication and Dissemination. Collectively, these groups aim to:

i. Promote the transition to a circular economy.
ii. Advance bioenergy and the bioeconomy.
iii. Stimulate research and innovation in biorefineries and related fields.
iv. Foster applied research to support biorefinery implementation.
v. Harmonize scientific and technical approaches across the EU, facilitating engagement with policymakers and industry.
vi. Strengthen links with relevant industrial sectors, attracting their interest and collaboration.

The focus of Working Group 3 (Biorefinery Applications) is to identify key industrial applications of biomass-derived products, thereby creating added value and introducing innovative market solutions. The integration of intermediate stages, along with networking between industrial applications, will be crucial for fostering innovation and collaboration in this domain.

To achieve these goals, identifying market applications for bio-based products will be a central task of WG3. Bio-based industries must drive the production of advanced materials and products in solid, gaseous, and liquid forms, which serve as the foundation for industrial innovation. These value chains encompass end-user products such as biofuels, energy storage materials, electricity, bio-based chemicals, fertilizers, polymers, pharmaceuticals, composites, membranes, electronics, and building materials, among others.

The primary objective of WG3 is to enhance collaboration between research groups working on advanced biorefinery processes and materials, thereby accelerating the development and market deployment of novel solutions. The group will foster an interdisciplinary approach that bridges fundamental research and industrial-scale applications. WG3's activities **are** organized around the following tasks:

- T3.1: Comprehensive identification and survey of biorefinery products, by-products, and their potential applications.

- T3.2: Identification and evaluation of market segments at regional, national, and international levels.
- T3.3: Development of a roadmap for bio-based fuels and products across diverse market sectors.
- T3.4: Identification of research gaps and critical areas for enhanced knowledge transfer.
- T3.5: Assessment of the viability and reproducibility of circular economy models within biorefineries.

This report aims to elucidate key enabling applications that drive the development of biorefineries, with a particular focus on the identification, valorization, and market integration of bio-based products and their associated industrial value chains. By doing so, WG3 will contribute to the long-term success of bioeconomy initiatives across the European Union. Furthermore, this report is structured to focus on the most relevant bio-based products and processes that align with Europe's strategic goals in the bioeconomy and circular economy. While the broader spectrum of commercialized bio-products is vast, this report prioritizes biofuels, bioenergy, biochemicals, and biomaterials that hold the greatest potential for addressing key European needs, particularly in reducing dependence on fossil fuels, achieving carbon neutrality, and advancing sustainability in industrial sectors. The focus on advanced biofuels, thermochemical conversion processes, and value-added bioproducts is directly linked to the European Union’s Green Deal and Fit for 55 packages, which emphasize decarbonization of transport, energy, and heavy industries. Moreover, the selected bio-based applications are aligned with Europe’s vision of fostering innovation in sustainable materials, such as bioplastics, bio-composites, and bio-based chemicals, while ensuring the scalability of processes that support regional economic development and a low-carbon circular economy. This targeted approach ensures that the report addresses Europe’s most pressing bioeconomy needs, where the deployment of these technologies can have the most significant environmental, economic, and societal impact.

2. A general profile of added-value products

A biorefinery is a multifaceted and integrated system designed to process biomass into a variety of products, ranging from bioenergy and biofuels to high-value chemicals and specialty compounds that can only be sourced from biological materials. Biorefineries are pivotal to the bio-based circular economy, promoting the sustainable valorization of biomass resources while facilitating the closed-loop use of raw materials, water, minerals, and carbon. As such, biorefining is defined as the sustainable conversion of biomass through advanced processes to generate marketable products and metabolites such as carbohydrates, proteins, lipids, bioactive compounds, and biomaterials (Leong et al., 2021; Agudelo-Patiño et al., 2024). This holistic approach not only addresses global energy demands but also contributes to sustainability by minimizing environmental impact (Jamil et al., 2024).

Bio-based products are formally defined by the U.S. Department of Agriculture (USDA) as products derived from plants and other renewable agricultural, marine, and forestry materials, providing alternatives to conventional fossil-based products. These products are either entirely or partially derived from biological sources, excluding fossil resources, and can be broadly classified into three major categories: (a) bio-based materials, (b) bioenergy/biofuels, and (c) bio-based chemicals. Due to their ability to replace petroleum-derived products, bio-based products have become central to the transition towards a low-carbon economy (Dahiya et al., 2020).

By offering sustainable alternatives with lower environmental footprints, bio-based products are becoming increasingly important in the global economy. Biorefineries produce these bio-based products using one or more of four main processing routes: mechanical (or physical), chemical, biochemical, and thermochemical processes. Biochemical processes, such as anaerobic digestion (AD), fermentation (aerobic/anaerobic), enzymatic conversion, and transesterification, are typically considered "wet processing techniques" and are generally applied to biomass with high moisture content (Lee et al., 2022). Thermochemical processes, including pyrolysis, gasification, and hydrothermal liquefaction, transform biomass into biofuels and bio-based chemicals through high-temperature conversion. Mechanical and chemical processes involve methods like mechanical separation, hydrolysis, and catalytic upgrading, which can produce bio-based chemicals, fuels, and materials from both dry and wet biomass. These diverse technological approaches provide flexible options for converting a wide range of biomass feedstocks into valuable products, emphasizing the adaptability of biorefineries to meet both energy and material needs in a sustainable way.

A variety of feedstocks, including industrial waste (e.g., food waste, pulp and paper industry by-products), agricultural residues, forestry waste, and lignocellulosic materials, can be efficiently valorised to generate high-value bio-based products. For instance, biopolymers like polyhydroxyalkanoates (PHA) and polyhydroxybutyrates (PHB), along with biofuels such as biodiesel, bioethanol, biohydrogen, and biogas, can be sustainably produced from various renewable biomass resources. These biopolymers and biofuels are critical in replacing fossil-based materials and fuels, thus supporting the transition towards a bioeconomy with reduced carbon footprints. In addition to their industrial importance, these value-added bioproducts also contribute to maintaining an ecologically sustainable carbon cycle by promoting waste valorization (Dahiya et al., 2020).

2.1 List of commercialized bio-based products

The following are examples of commercially viable bio-based products that highlight the breadth and potential of biorefinery outputs (Dahiya et al., 2020; Leong et al., 2021):

- **Bio-based chemicals**: Methanol, Formic acid, Ethylene oxide, Mono-ethylene glycol (MEG), Acetic acid, Propanol, Isopropanol, 1,2-Propanediol, 1,3-Propanediol, Acetone, Epichlorohydrin, Lactic acid, Malonic acid, n-Butanol, iso-Butanol, 1,4-Butanediol, Ethyl acetate, Crotonaldehyde, Succinic acid, Ethyl lactate, Levulinic acid, Xylitol, Furfural, Itaconic acid, Sorbitol, 2,5-Furan-dicarboxylic acid, Lysine, Citric acid.

- **Bio-based materials**: Ethylene (from ethanol), Propylene, Polylactic acid, Polyhydroxyalkanoates (PHA), Acrylic acid derivatives, Tetrahydrofuran (THF), Isoprene, Methyl methacrylate, Adipic acid (for Nylon 6,6), Natural rubber, Cellulosic fibres, Nanocellulose, Biocomposites, Bioadhesives.

- **Bio-based energy**: Bioethanol, Biohydrogen, Biomethane, Biohythane, Syngas, H-CNG, Propane, Biodiesel.

The valorization of waste materials and industrial side-streams through bioprocesses not only contributes to the production of these bio-based products but also reinforces the principles of a circular economy. This paradigm is based on recycling, reusing, remanufacturing, and maintaining a sustainable production cycle that minimizes waste and environmental impact. The integration of waste streams into biorefineries leads to a sustainable flow of carbon and other critical elements, thus ensuring a resource-efficient and eco-friendly approach to manufacturing bio-based products (Leong et al., 2021).

3. Bio-based fuels from biochemical conversion processes

3.1 Anaerobic digestion & biogas

Anaerobic digestion (AD) is a complex biochemical process that involves four stages: hydrolysis, acidogenesis, acetogenesis, and methanogenesis. These stages are carried out by various microorganisms that convert complex organic matter into biogas, which mainly consists of methane (CH_4) and carbon dioxide (CO_2) (Abbas et al., 2021). Methane is biologically produced in the final stage of AD, where organic feedstock is converted. Acidogenesis, a crucial step in AD, results in the production of biohydrogen (H_2) and volatile fatty acids (VFAs), such as acetic acid, propionic acid, butyric acid, and valeric acid (Dahiya et al., 2020).

In biorefinery concepts, all fractions generated during AD can be utilized, with biogas typically being upgraded to biomethane for various applications, such as fuel for vehicles or substitution for natural gas in industrial and domestic uses (Kabeyi & Olanrewaju, 2022). Complex feedstocks often require pretreatment to enhance bioenergy recovery during digestion (Agudelo-Patiño et al., 2024). Additionally, modified AD processes can promote other metabolic pathways to generate valuable compounds under varying operational conditions.

3.1.1 Applications and potential markets

Anaerobic digestion (AD) offers several important applications, presenting significant market potential in various industries (Figure 1).

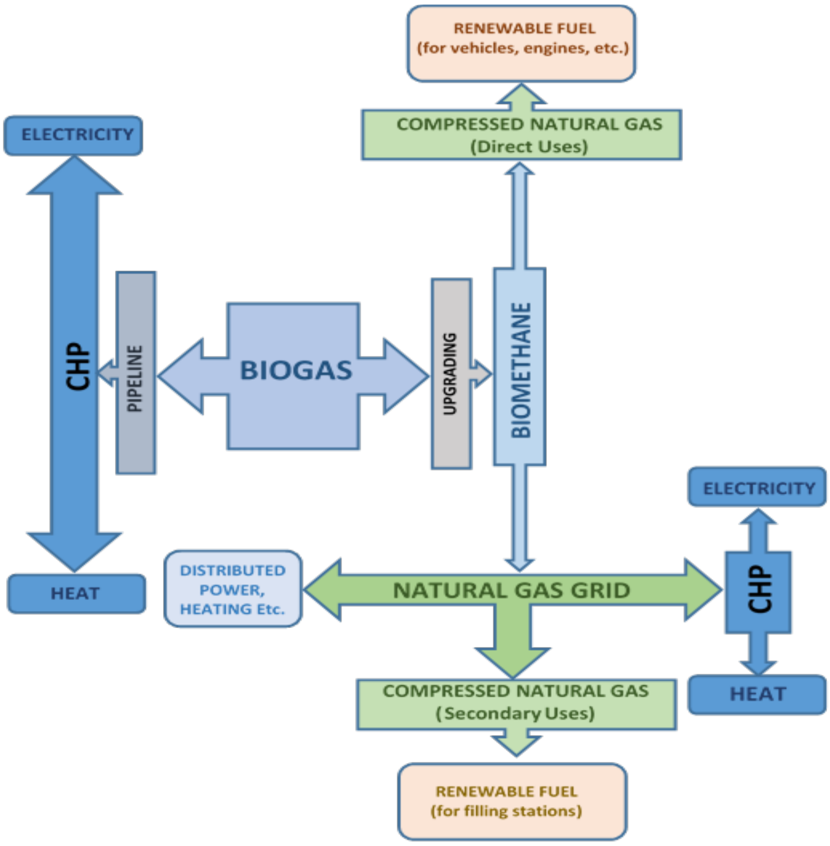


Figure 1. The applications of biogas (adapted from Capodaglio et al. 2016)

The first application of biogas from AD is heating, where biogas is combusted in specially modified or purpose-built boilers. The heat generated warms water (vapor), which is used to heat the digester and nearby buildings or is distributed through local district heating networks (Capodaglio et al., 2016).

The second significant application is the use of biogas for heat and power generation. In this process, biogas is used as a fuel in special stationary engines, modified for biogas combustion, to co-generate electrical, mechanical, and thermal energy. The third major application is as motor fuel for natural gas vehicles (NGVs), including cars, buses, and trucks. Biogas must be upgraded to biomethane, which meets automotive standards (Capodaglio et al., 2016).

In the future, biogas is expected to play an increasingly important role in local energy distribution, contributing efficiently to electricity, heat, cooling, and fuel production (Yousuf et al., 2017). Moreover, biogas production and use are growing globally and are positioned to become a leading economical alternative for producing renewable bioenergy. Biogas can be processed into various fuels for transportation and other applications, including compressed biogas (CBG), liquid biogas (LBG), methanol, hydrogen, dimethyl ether, and Fischer-Tropsch (FT) fuels. Biogas has wide applications for cooking, lighting, cooling, engine combustion fuel, and gas supply for both domestic and industrial use (Kabeyi & Olanrewaju, 2022).

Biomethane, derived from upgrading biogas, can directly replace natural gas in many domestic and industrial applications, offering a technically feasible and sustainable alternative to fossil fuels. In addition to being used for cooking and lighting, biogas can be used for power generation or to produce Fischer-Tropsch (FT) fuels. Upgraded biogas/biomethane can also be converted into methanol fuel. Compressed biogas (CBG) and liquid biogas (LBG) are versatile fuel forms made from biomethane and can be used for various direct and indirect applications, such as fuels and power generation (Kabeyi & Olanrewaju, 2022).

Biogas can also be utilized in combined heat and power (CHP) generation, compressed into bio-CNG or bio-LPG, and used as a clean, renewable alternative to conventional fossil fuels. In more advanced applications, biogas can be purified and reformed into syngas, which is then partially oxidized to produce methanol, a key component in the production of gasoline. Syngas can further be utilized to produce alcohols, jet fuels, diesel, and gasoline through the Fischer-Tropsch process, providing additional market opportunities for biogas in the transportation and energy sectors (Kabeyi & Olanrewaju, 2022).

In addition to biofuels, AD also produces valuable bioproducts such as VFAs and polyhydroxyalkanoates (PHAs), which are precursors for bioplastics. The digestate, a by-product of AD, can be applied as a fertilizer or soil improver.

3.1.2 Environmental benefits and biogas market

AD offers multiple environmental advantages, including waste reduction, renewable energy generation, and nutrient recycling. The process can treat a wide range of organic wastes, transforming them into biofuels and valuable biobased products, contributing to circular economy goals. From a life-cycle perspective, biogas-based electricity shows over 90% resource savings compared to conventional electricity (De Meester et al., 2012). This makes AD a highly sustainable technology, especially when it is integrated into biorefinery systems that valorise multiple by-products.

The use of digestate as a fertilizer offers a sustainable solution for nutrient recycling, reducing the need for synthetic fertilizers and enhancing soil health providing further economic and environmental benefits by closing the nutrient loop in agricultural systems (Agudelo-Patiño et al., 2024).

Economically, biogas production is growing globally and promises to be a cost-competitive alternative to fossil fuels, particularly for transportation and industrial applications (Yousuf et al., 2017). The diverse uses of biogas and biomethane, along with the production of high-value biochemicals, ensure that AD-based biorefineries are not only environmentally beneficial but also economically viable.

The demand and prospect of biogas technology as a renewable energy source in terms of market value should be adequately addressed. The global Biogas Plant market looks promising in the next 5 years which is anticipated to reach more than USD 29000 million in 2028, with a compound annual growth rate (CAGR) of about 11% during the forecast years. The largest Biogas Plant market share in 2023 is as follows: Agricultural waste, energy crops, industrial waste, and sewage sludge. Although energy crops were the primary choice of feedstock for the available biogas industry, the policy has recently shifted more towards the use of crop residues and livestock waste. Major emerging markets for biogas are the "clean" (i.e., non-fossil-fuel derived) hydrogen market and the sustainable aviation fuel market (Pratson et al., 2023). On the other hand, North America (United States, Canada, and Mexico), Europe (Germany, UK, France, Italy, Russia, and Turkey, etc.), Asia-Pacific (China, Japan, Korea, India, Australia, Indonesia, Thailand, Philippines, Malaysia and Vietnam), South America (Brazil, Argentina, Columbia etc.), and Middle East and Africa (Saudi Arabia, UAE, Egypt, Nigeria and South Africa) are the regions which are leading this market. Currently, Europe is the largest producer of biogas and Germany is by far the largest market with two-thirds of Europe's biogas plant capacity. The installed power generation capacity from biogas is around 18 GW whereas about 3.5 Mtoe of biomethane are produced worldwide today. Capacity increased on average by 4% per year between 2010 and 2018. In Germany, the overall renewable energy share would be increased to about 40–45%, 55–60%, and 80% by 2025 2035, and 2050, respectively (Farghali et al., 2022) Although most of this capacity is running in Germany, the United States and the United Kingdom; other countries such as Denmark, Sweden, France, Italy and the Netherlands also actively encourage biogas production. Among them, countries such as Denmark and Sweden have been boasting more than 10% shares of biogas/biomethane in total gas sales and the number of upgrading facilities in Brazil, China, and India has been tripling since 2015. Biogas production through anaerobic digestion in Portugal has substantial potential, estimated at around 83 MW (Inegi, 2024), particularly when utilizing the organic fraction of municipal solid waste (MSW) and sludge from wastewater treatment plants (WWTP). In 2021, approximately 5 million tons of MSW were generated, with 1.78 million tons (45.48%) of biowaste collected from mixed waste streams. To process these materials into biogas, 12 organic recovery plants are currently in operation. Additionally, WWTP sludge serves as another significant resource. By 2020, 32 wastewater treatment plants with anaerobic digestion units had been identified for biogas production from sewage sludge (RCM, 2024). The first generation of biogas plants began in 1999, adopting a business model centered on electricity and/or heat production for self-consumption or grid injection, benefiting from the favorable conditions of the special regime production. However, many of these plants are now transitioning to standard market conditions, prompting the need to explore new business models. As a result, there is a recognized opportunity to convert these units for biomethane production, positioning them as key players in the development of this value chain and exploring potential synergies with the gas sector.

The biogas market in Turkey has also started to grow recently due to changes in policy support with the largest enterprises to produce second-generation biogas and bioethanol located in Izmir (i.e., DB Tarimsal Enerji with an installed capacity of 80,000 t per year and Konya Seker with a capacity of 84 million L/y). The largest biogas plant in the country is the Bagfas Bandirma Fertilizer Biogas plant with an installed capacity of 9.9 MW. in the U.S., the most valuable market for biogas-to-energy projects is currently the transportation fuel market. Sweden is also facing an increase in the demand for biogas to be used as a fuel for vehicles. Other countries (i.e., Germany, Austria, and France) are also making progress toward the production and utilization of biogas as a potential fuel for automobiles because the purified biogas has various potential uses, including the production of heat, the injection of the gas into natural gas grids, and fuelling automobiles (Jamil et al., 2024).

The consumption of biogas is estimated to double over the next several years from 14.5 to 29.5 GW. The combustion or burning of fossil fuels for energy purposes results in various environmental concerns due to the generation and release of greenhouse gasses in the atmosphere which is demanding renewable energy sources for power generation. However, biogas is not competitive in the market because its production and utilization is still not cheaper than other bio-based products. For example, biogas is expected to be at least 20 to 30% less expensive in comparison to bioethanol and biodiesel. The major barrier to their adoption and spread across the globe is the limited number of gas stations which also leads to an increased infrastructure cost (Jamil et al., 2024).

The “biogas road” has a Technology Readiness Level (TRL) that already reached a value equivalent to the market availability, that is the maximum level of development of a technology and the “biogas road” and the “syngas road” for biomethane production was compared to demonstrate the high potentials in terms of energy efficiency and carbon utilization of the syngas road. The latter, on the other hand, still suffers from its low TRL and, above all, from economic feasibility obtainable only with large-scale plants. In the last decades, novel reactor designs based on alternative sludge retention strategies have been developed up to technology readiness levels (TRL) of 8-9, which are able to deal with the main problems associated to AD of biomass (Ardolino et al., 2021).

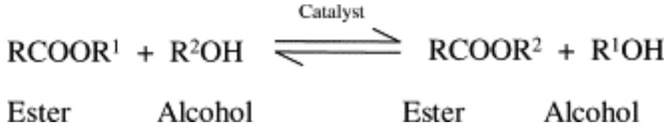
There are currently more than 18,000 AD units in operation in the EU, 80% of which are used in the agricultural sector. Due to the need for sustainable production of bio-based products from agricultural waste and the rapidly approaching end of tariff programs in many countries, there is an urgent need to restructure these facilities. These can be turned into biorefineries that can convert agricultural waste into valuable bio-based products (Bolzonella et al., 2023).

The future use of biomass should be focused more on enhancing biogas production (e.g., pretreatment/co-digestion applications) and the local market. Because the market is one of the barriers to biogas technology. First, the high price of biogas and the lower price of fossil fuels is critical, as is the low-priced electricity produced from coal and natural gas-fired power plants. Then, the electricity from other renewable sources, such as solar, hydro, and wind, are also cheaper than AD-based power generation; the operation and maintenance costs of biogas-based power plants are quite high. (Kasinath et al., 2021).

4. Bio-based fuels from chemical processes

4.1 Transesterification & biodiesel

For an in-depth analysis of the chemical process needed to produce biofuel, biodiesel (Fatty Acid Methyl Ester or FAME) is used as an illustrative example. The conversion of vegetable oils or animal fats to biodiesel primarily involves the transesterification process (Figure 2), also known as alcoholysis:



$$\underset{\text{Ester}}{\mathrm{RCOOR^1}} + \underset{\text{Alcohol}}{\mathrm{R^2OH}} \xrightleftharpoons{\text{Catalyst}} \underset{\text{Ester}}{\mathrm{RCOOR^2}} + \underset{\text{Alcohol}}{\mathrm{R^1OH}}$$

Figure 2.General equation of catalysed transesterification (Meher et al., 2006).

The term "lysis" refers to the process of breaking apart the esters. While hydrolysis uses water (hydro) to cleave esters, alcoholysis uses alcohol in the presence of a catalyst to replace one ester with another through the exchange of an OR group. The general reaction for triglycerides, which are the main constituents of vegetable oils and animal fats, can be represented as follows (Figure 3):

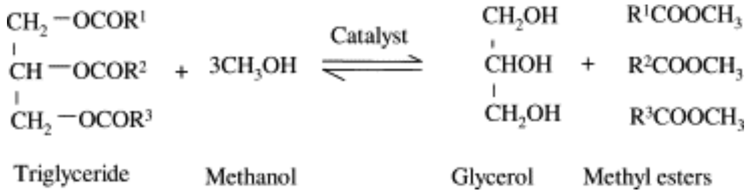


Figure 3. General equation of catalysed transesterification of triglycerides (Meher et al., 2006).

One mole of triglyceride interacts with three moles of alcohol to generate three moles of ester (biodiesel) and one mole of glycerol. The efficiency of this reaction is typically influenced by several factors, including the type of alcohol, the molar ratio of alcohol to oil, the levels of free fatty acid (FFA) and water content, reaction temperature, reaction time, and the type of catalyst (Issariyakul and Dalai, 2014).

The choice of catalyst is crucial for both efficiency and cost-effectiveness and is typically classified into chemical and biological categories. Chemical-based catalytic systems include heterogeneous catalysts, nano-catalysts, and the use of supercritical fluids (SFC). In the biological category, the use of enzymes, such as lipases, is gaining considerable interest, though it has not yet reached full commercial scale. Enzymatic catalysis offers several advantages over traditional chemical methods; it is generally simpler and more efficient, requires less stringent feedstock quality, and produces little to no glycerol as a byproduct. However, the use of enzymes can significantly impact production costs, primarily due to their limited reusability. To address this challenge, various solutions have been proposed, including traditional immobilization techniques and the use of enzymes immobilized on magnetic nanoparticles (Thangaraj et al., 2019, Hoogendoorn and van Kasteren, 2020). Extremophilic lipases are versatile enzymes with potential applications across diverse industrial sectors, from textiles to biomedical fields. While they have demonstrated robustness as industrial biocatalysts, they do not completely resolve all challenges. Effective industrial application requires further advancements, including protein engineering, enzyme immobilization, and optimization of production media (Vivek et al., 2022).

Currently, the most common commercial route to produce biodiesel is the transesterification of triglycerides using homogeneous alkaline catalysts. This process involves reacting high purity vegetable oils or animal fats with alcohol, typically methanol or ethanol. A significant challenge in biodiesel production is its competition with fossil fuels, which impacts its economic feasibility. To overcome this challenge, alternative feedstocks and technologies are being explored to enhance the economic viability and competitiveness of biodiesel (Gebremariam and Marchetti, 2018).

The two-step hydro esterification process offers an alternative to the standard biodiesel production method. It involves first hydrolyzing oils to produce free fatty acids and glycerol, followed by esterification of the free fatty acids to produce biodiesel. This method is advantageous for producing high-purity glycerol and biodiesel in a sequential process, distinguishing it from traditional transesterification methods that include energy-intensive unit operations of drying and lipid extraction (Chen et al., 2006). Alternative processes are visualized in Figure 4. This study uses microalgae as feedstock and performs a techno-economic analysis of the hydro-esterification process, demonstrating it as a favorable route in terms of energy consumption (Song et al., 2016).

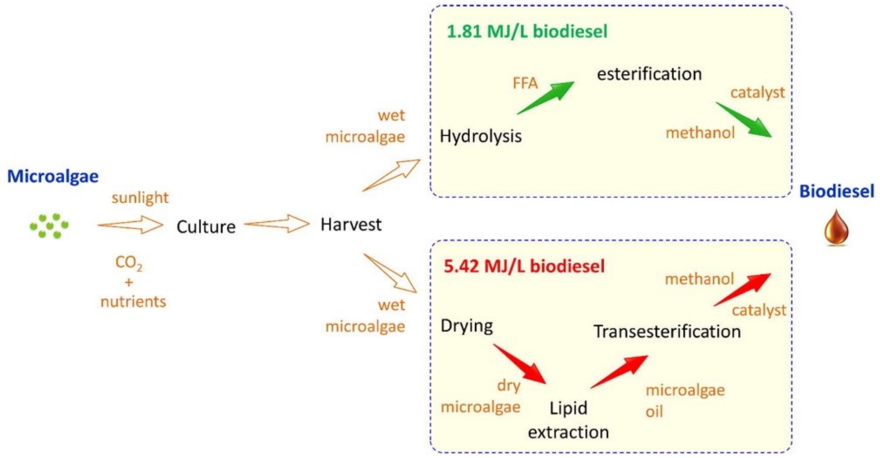


Figure 4. Alternative routes for biodiesel production from microalgae (Song et al., 2016).

Microalgae are increasingly recognized as a valuable oil source due to their high lipid content, rapid growth rates, and ability to be cultivated without competing with food crops for arable land. They fall into the category of second-generation biomass feedstocks, which also includes non-edible oil seeds, animal fats, and waste materials such as used cooking oil. The flip side is that there have been dozens of companies over the last decades that failed to scale and/or commercialize fuels based on microalgae oil.

For non-edible oil seeds, Figure 5 provides a detailed representation of the stages involved in biodiesel production.

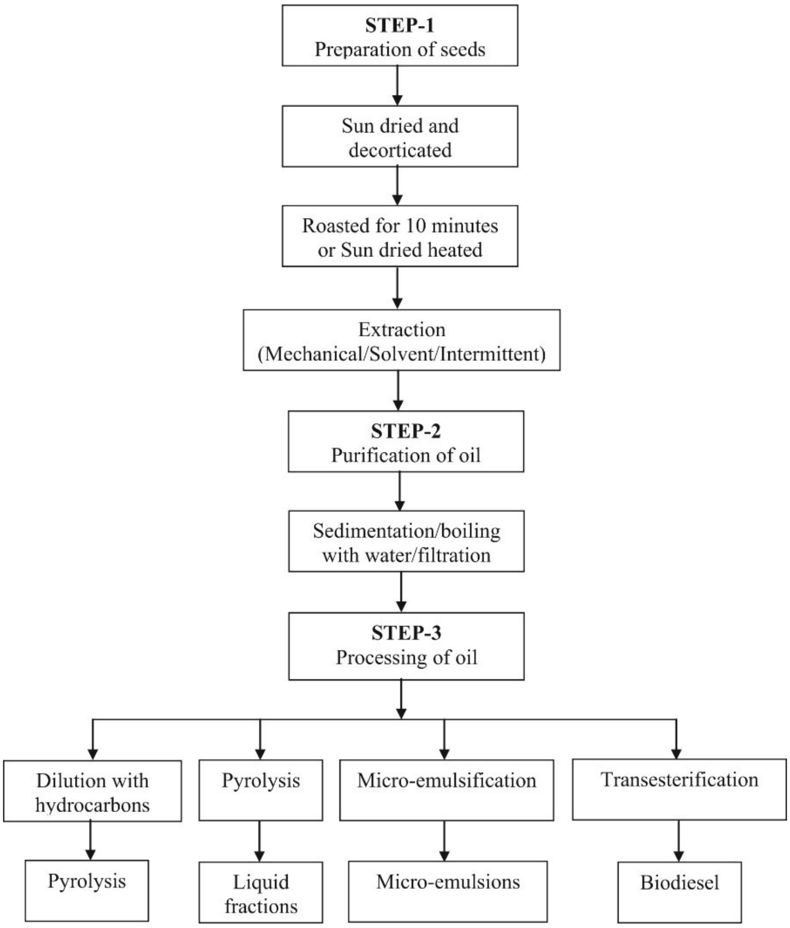


Figure 5. Process flow chart of non-edible oil seed (Bhuiya et al., 2016).

A crucial component of this process is oil extraction, which is critical for obtaining the raw material necessary for biodiesel synthesis. The extraction process begins with the preparation and drying of the feedstock to optimize oil yield. Oil can then be extracted by conventional mechanical, chemical, or solvent methods, accelerated solvent extraction (ASE) also referred to as pressurized solvent extraction (PSE), enzymatic extraction, or supercritical fluid extraction (SFE). Mechanical pressing and chemical extraction using n-hexane are the most widely employed commercial methods. Mechanical pressing, while more cost-effective, generally results in lower oil yields compared to chemical extraction, which can achieve extraction efficiencies of up to 99%. However, chemical extraction poses significant environmental and health risks due to the use of hazardous solvents (Bhuiya et al., 2016).

5. Bio-based fuels from thermochemical conversion processes

5.1 Direct combustion and gasification

Biomass combustion represents one of the most ancient and fundamental methods of energy generation, tracing back to the early human use of fire. The process involves directly burning organic materials, such as wood, agricultural residues, and other biodegradable waste, to produce heat, which can subsequently be converted into electricity. This thermochemical reaction between biomass and oxygen results in the production of carbon dioxide (CO_2), water vapor (H_2O), and heat - Eq. 1 (Quispe et al. 2017).

$$C_XO_YH_ZN_WS_V + aO_2 \rightarrow bH_2O + cCO_2 + dSO_r + eN_mO_p + \text{Energy (1)}$$

However, this simplified description does not capture the true complexity of the combustion process. For instance, the combustion of the simplest hydrocarbon, CH_4, involves 277 elementary steps and 49 species (Mandø, 2013). A comprehensive understanding of the intricate mechanisms involved in biomass combustion remains an ongoing challenge. Due to computational limitations, simulations of combustion processes generally only consider a limited number of reactions. A commonly used reaction framework simplifies the complexity by concentrating on six species -N_2, O_2, H_2O, CO_2, CO, and CH_xO_Y- and involves two primary reactions in the gas phase:

$$CH_XO_Y + aO_2 \rightarrow CO + bH_2O \text{ (2)}$$

$$CO + 0.5O_2 \rightarrow CO_2 \text{ (3)}$$

In this model, volatiles are represented by a single species, CH_xO_y, which combusts with oxygen to form carbon monoxide and water (Eq. 2). A further reaction consists in the conversion of carbon monoxide to carbon dioxide (Eq. 3).

One of the benefits of using biomass is its significantly higher volatile matter content compared to coal, with a fixed carbon-to-volatile matter ratio substantially lower than unity. Moreover, biomass also begins to release volatiles at a lower temperature than coal, which lowers its ignition temperature. As a result, careful design of the air supply is crucial to ensure adequate oxygen availability. This is important because the rapid release of volatiles could delay combustion if not properly managed. During the combustion process, the fuel releases volatiles as gases when heated, which then combusts upon mixing with oxygen (Mandø, 2013).

As mentioned above, the direct combustion of biomass offers a renewable energy source with the potential to reduce greenhouse gas emissions compared to fossil fuels. However, the process presents significant challenges related to pollutant emissions and waste management. The management of these aspects is crucial for environmental compliance and public acceptance, as the main pollutants, such as particulate matter (PM), carbon monoxide (CO), hydrocarbons (HC), nitrogen oxides (NOx) and sulfur oxides (SOx), are like those produced by the combustion of fossil fuels (Bhuiyan et al. 2018). Advanced combustion technologies and effective emission control measures are essential to mitigate these negative impacts. Furthermore, the by-products of biomass combustion, especially ash, can be valuable or problematic depending on their composition and potential uses. Biomass ashes can be used for fertilizer or cement production, contributing to the circular economy. However, it can also contain harmful trace elements such as lead, cadmium, and mercury, especially if it comes from municipal or industrial waste. If ashes contain high concentrations of toxic metals, they must be treated as hazardous waste with additional disposal costs.

Despite these challenges, biomass combustion remains a viable component of sustainable energy strategies, particularly in large-scale operations (30-100 MWe) using low-cost feedstocks such as agricultural residues and wood residues (Bauen, A. et al. 2009). These plants benefit from economies of scale that make them commercially viable, while smaller-scale plants (5-10 MWe) are also emerging, demonstrating the flexibility of biomass combustion for different scales of operation. Another important feedstock for biobased products from direct combustion is municipal solid waste (MSW), which can be converted to energy in Waste-to-Energy (WtE) plants. However, the heterogeneity and contamination of municipal solid waste require robust technologies and strict emission controls, resulting in higher operating costs. Biomass-based CHP plants further improve the overall efficiency of power plants by utilizing both the heat and electricity generated, with typical efficiencies of 80 to 90 %. In the lower capacity range, distributed cogeneration technologies such as the Stirling engine (10-100 kWe) and the Organic Rankine Cycle (ORC) (50-2000 kWe) are promising for biomass-fuelled applications, although these technologies are still in the demonstration phase and require improvements in terms of conversion efficiency, reliability, and cost. Depending on the fuel properties and combustion conditions, different furnace designs and firing parameters are selected to ensure optimum efficiency and uptime. Direct combustion is a well-established technology, and it is currently the principal method of generating electricity worldwide.

The valorization of biomass to produce value-added chemicals can be implemented through other thermochemical technologies which include pyrolysis, liquefaction, and gasification processes. Biomass gasification is a process resulting from sequential steps: drying, pyrolysis, oxidation, and reduction reactions. The conversion of biomass via gasification allows the production of H_2, CH_4, and C_2H_6 as high calorific-value gases, CO_2, and CO (Faizan et al. 2023).

The syngas from gasification technology is a mixture in which H_2 and CO are the main products, along with lower amounts of CH_4, CO_2, and trace compounds. Syngas (CO/H_2) could be used as a key industrial feedstock for the catalytic synthesis of chemicals, biofuel, power generation, and heating (Figure 6). Hydrogen from syngas finds applications as a building block for the design of fuel cells and NH_3 production. The catalytic conversion of syngas into liquid hydrocarbons via the Fischer-Tropsch (FT) process has a high potential for the utilization of renewable energy. FT synthesis includes the hydrogenation of carbon monoxide followed by polymerization steps leading to several products with a wide distribution in carbon number. Furthermore, syngas can be used as a starting precursor to produce dimethyl ether and methanol.

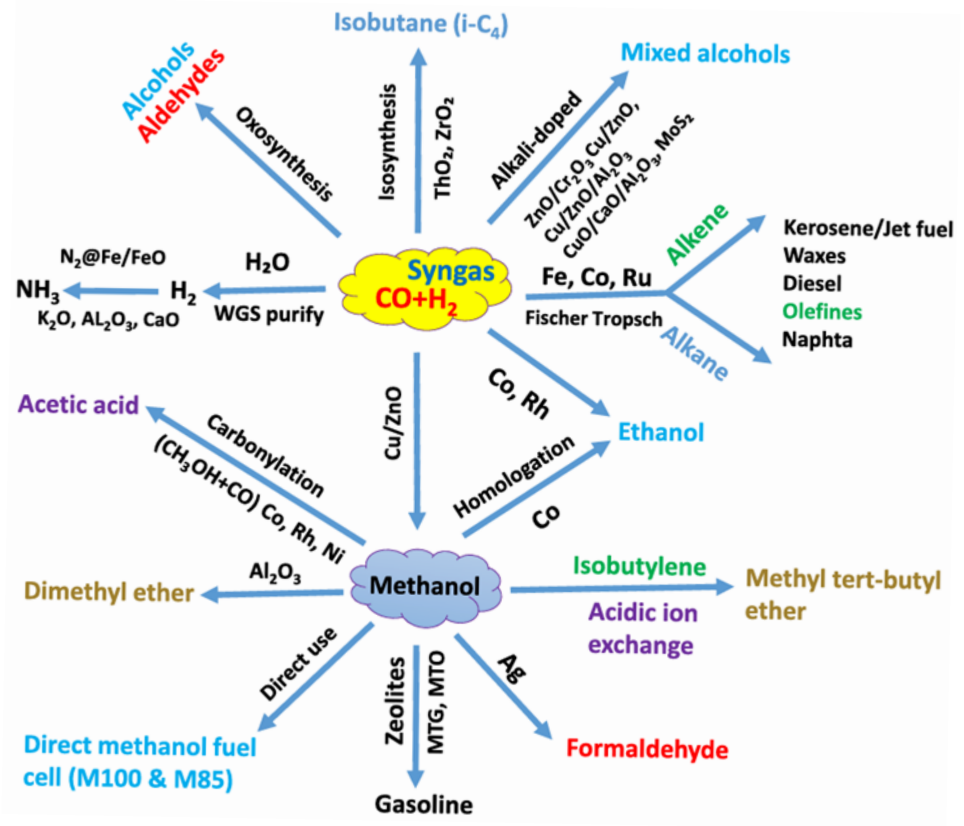


Figure 6. Biochemical/biofuel production routes from syngas (Faizan et al. 2023; Ciliberti et al. 2020).

The gasification process, by using biomass as a sustainable resource, is an alternative approach to generate syngas, conventionally produced through fossil fuel including natural gas steam reforming and coal gasification. During the gasification process heavy aromatics, termed tars, are generated. Tar represents an undesirable complex condensable product whose presence restricts the implementation of gasification in industry. Tar, indeed, condenses in particulate filters affecting the pipeline (gasifier) and thus the output gas quality and the overall equipment.

Before using syngas in chemical synthesis and biofuels, the contaminants resulting from gasification (tar, nitrogen compounds, sulphur compounds, halides, alkali compounds, particulates, etc.) should be removed. For instance, the separation of carbon dioxide, as an undesired contaminant, provides greater calorific value to the as-produced syngas.

The overall performance of the gasification process is strictly related to the gasification conditions, type of feedstock, and reactor setup. The quality of the process and product yields can be enhanced by tailoring process parameters such as particle density and size, operating condition (temperature, pressure), feedstock quality and moisture content, steam ratio, or other gas ratio to catalysts and biomass.

The choice of the gasifier agent impacts the producer gas composition from a typical biomass gasification which includes multiple chemical processes such as pyrolysis, drying, tar reforming or tar cracking, and char gasification (**Erro! A origem da referência não foi encontrada.**) (Faizan et al. 2023; Peng et al. 2017).

Air, oxygen, and steam have been explored as gasification agents. Air is straightforward and cost-effective, but the high nitrogen content, in the producer gas, is detrimental to the calorific value and the energy efficiency of the process as well. The use of oxygen solves this issue; however, the high cost of oxygen separation should be considered (Claude et al. 2016). Moreover, the use of oxygen as a gasification agent leads to the formation of CO_2 and H_2O which, in turn, promote oxidation reactions during the gasification process.

Lastly, steam as a gasification agent is cheaper than oxygen and, unlike conventional gasification agents, yields hydrogen from both the steam-methane reforming process and the steam-char reaction (Leijenhorst et al. 2015). However, gasification processes using steam as a gasification agent are endothermic and require heat (Meng et al. 2011).

Table 1. The composition of the producer gas of typical biomass based on different types of gasification agents and gasifiers. Reproduced from *Journal of Cleaner Production* 408 (2023) 137224.

Gasifier type	**Gasification agent**	**Gas composition (mol/mol, %)**					**Ref.**
		CO	H_2	CH_4	CO_2	N_2	
Downdraft fixed bed	Air	15-21	15-18	1-2	13-15	44-56	Galindo et al. 2014
Updraft fixed bed	Air	23	19	5	12	41	BTG Biomass Technology Group BV, The Netherlands (2005), pp. 115-161
	Steam	15-30	35-55	8-12	15-25	0	Saw et al. 2012
	Air	16-19	10-12	6-8	14-18	48-52	BTG Biomass Technology Group BV, The Netherlands (2005), pp. 115-161
	Oxygen	20-22	24-28	-	40-44	-	Meng et al. 2011
Entrained flow gasifier	Oxygen	20-25	28-33	2	46	-	Leijenhorst et al. 2015

Conventional spouted bed reactor	Steam	33	36	10	18	3 (C_2-C_4)	Cortazar et al. 2018
Fountain confined spouted bed reactor	Steam	31	43	7	16	4 (C_2-C_4)	Cortazar et al. 2018

Biomass gasification has been improved as a catalytic process. The development of heterogeneous catalysts is a promising way to reach high carbon gasification efficiency, huge recoverability, and excellent hydrogen selectivity. When the gasification process is carried out by using catalysts, a higher yield of syngas could be obtained together with a lower amount of tar.

Based on the specific goals of the process, biomass catalytic gasification can be performed through primary or secondary catalysts. Primary catalysts are added directly to the biomass feedstock, they support biomass conversion into syngas at lower temperatures and with less tar production (Devi et al. 2003). At the same time, primary catalysts can be expensive and additional steps to remove them from the final product could be required. In addition, secondary catalysts are used in the gasifier chamber to reduce tar generation and enhance syngas conversion into value-added products (de Lasa et al. 2011). The gasification of the biomass feedstock, however, is not as effective when secondary catalysts are solely used.

5.2 Pyrolysis

Thermochemical technologies for converting biomass into energy or chemicals primarily include torrefaction, pyrolysis, gasification, and high-pressure liquefaction. Among these, biomass pyrolysis, historically utilized for charcoal production, has evolved into a cutting-edge research area. Biomass pyrolysis is generally defined as the thermal decomposition in an inert environment of the biomass organic matrix resulting in three different products: volatile fraction (condensable phase recognized as liquid bio-oil, and not condensable fraction as permanent gas) and solid residue, namely char or biochar. The main pyrolysis conditions as the final temperature, heating rate, and residence time, as well as the reactor configurations, affect the yield and the properties of the products. Moderate temperature (450-650°C) and high heating are the conditions for bio-oil production, whereas when biochar production is the primary product of interest, slow or intermediate pyrolysis is the conditions of choice. Pyrolysis and its products such as bio-oil and biochar are increasingly playing a role in the biorefinery.

The need arises not only to integrate different processes to produce low-cost biofuels from waste biomass as bio-oil, but also to obtain materials with added value as biochar.

- **Bio-oil:**

Bio-oils have been widely evaluated as potential fuels for combustion-based electricity and heat generation in boilers, furnaces, and combustors (Freel et al.1996; Gust et al., 1997), as well as for use in diesel engines (Solantausta et al., 1993; Chiaramomnti et al.,2003) and gas turbines (Balat et al., 2011). Although bio-oils were successfully tested in a diesel engine under limited operational conditions, their long-term use is restricted by inherent shortcomings such as low volatility, high viscosity, corrosiveness, and a tendency to form coke deposits (Bridgwater et al., 1999).

It is generally recognized that further refinement of bio-oils is essential to enable their practical application in engines (Balat et al., 2011; Zhang et al., 2013). Upgraded bio-oils have been successfully converted into transportation fuels using catalytic cracking (Tang et al.., 2009; Wang et al., 2014; Bi et al., 2015) and high-pressure hydroprocessing (French et al., 2011; Rennard et al., 2010; Hu et al., 2010). Additionally, syngas and hydrogen can be produced from bio-oils via steam reforming and gasification Guo et al., 2014; detailed overviews provided by Butler et al. 2011 and Xiu et al. 2011.

The calorific value of bio-oil, typically ranging from 17 to 20 GJ/ton, is significantly lower than that of fuel oil, which is around 40 GJ/ton. This difference results in higher costs for transportation and storage. Additionally, the viscosity of bio-oil tends to increase over time, so it should not be stored for more than a few months. The competitiveness of bio-oil compared to petroleum fuel oil largely depends on the cost of the raw materials used to produce it and the local prices of fossil fuel oil.

As valued alternatives, bio-oils serve as valuable raw materials for chemical production, including phenols for resins, additives for fertilizers and pharmaceuticals, flavoring agents such as glycolaldehyde for the food industry, and various specialty chemicals. The pyrolysis oil market is categorized based on feedstock, production process, and applications.

Understanding the growth trends within these segments allows for identifying areas with limited expansion potential in the industry. This segmentation offers users a comprehensive market overview and valuable insights, enabling them to make informed strategic decisions and pinpoint key applications within the market.

However, regardless of the end use of the bio-oil, whether it is for heat and power or as a source of chemicals, there are economic and management considerations.

The cost of producing bio-oil depends on several factors, including the expense of feedstock (and its pre-treatment in case of wet biomass), plant size, and the specific technology used.

The global pyrolysis oil market was valued at USD 315.69 million in 2021 and is projected to grow to USD 448.95 million by 2029, with a compound annual growth rate (CAGR) of 4.50% during the forecast period from 2022 to 2029.

Research suggests that pyrolysis oils can be produced at costs ranging from 75 to 300 EUR per ton (equivalent to 4 to 18 EUR/GJ), depending on feedstock costs, which vary from 0 to 100 EUR per ton (0 to 1.9 EUR/GJ).

Fast pyrolysis technologies for producing liquid fuel have been successfully demonstrated on a small scale, with several large pilot plants and demonstration projects either operational or nearing completion. However, these technologies remain relatively costly compared to fossil-based energy, making it difficult for them to compete in energy markets due to economic and non-technical challenges. Fast pyrolysis can only succeed in energy markets like biomass gasification if fully integrated into a broader biomass system. Research and development efforts for flash pyrolysis continue to focus on improving the reliability of the processes, enhancing the quality and usability of the bio-oil, and achieving cost-effectiveness throughout the production process. Additionally, bio-oil production can serve as a method for pre-treating biomass, facilitating its transportation over long distances to large biorefineries or facilities dedicated to producing synthetic biofuels.

In Europe, some of the major players operating in the pyrolysis oil market for bio-oil production and for the development of the pyrolysis process integrated with other facilities. BTG Biomass Technology Group (Netherlands); OMV Aktiengesellschaft (Austria); ETIA Group (France); Ecomation Oy (Finland).

The common issue is the innovation and implementation of the existing technologies with a blend of biomasses and alternative sources, such as plastics in line with the environmental aspects and regulations.

Table 2 reports the list of the main European industries in the market for pyrolysis products.

Table 2. Pyrolysis company

Feedstock	Products	TRL	Company	Country
Lignocellulosic biomass	*Bio-oil*	*8-9*	BTG Biomass Technology Group	*Netherland*
Used cooking oil, nut shells, mixed woody biomass	Bio-oil, renewable diesel	*8-9*	Aktiengesellschaft	*Austria*
Agro-food products, woody biomass, industry residues	Syngas, biochar	*8-9*	ETIA Group	*France*

mixed plastic, rubber, bio-waste	Bio-oil	*8-9*	Ecomation Oy	*Finland*
Agricultural waste	Bio-oil,syngas, biochar	*6-7*	*Springkildeprojektet*	*Denmark*
Sewage sludge	Syngas, bio-oil, biochar	*6-7*	*Project AquaGreen PCE*	*Denmark*
Lignocellulosic biomass	Bio-aromatics	*4-5*	*Biorizon-TNO*	*Netherlands*
Biomass and plastic	Bio-oil	*4-5*	*VTT Technical research center of Finland*	*Finland*

- **Biochar:**

Biochar has been widely studied as a versatile material for applications in energy production, soil amendment, and environmental remediation (Lu et al., 2009; Vamuvka et al., 2011; Weber et al., 2018). In energy systems, biochar has been utilized as a co-firing fuel in coal power plants a precursor for activated carbon production (Lange et al., 2007). When applied to soils, biochar improves nutrient retention, water-holding capacity, and soil structure, although its efficacy depends on feedstock origin and production conditions (Giudicianni et al., 2017; Pinna et al., 2024). Challenges such as inconsistent quality, limited scalability, and high production costs hinder widespread adoption. Further advancements in biochar modification techniques are deemed essential to enhance its functionality and economic viability (Strezov et al., 2007; Strezo et al., 2009).

Advanced thermal or chemical treatments have demonstrated the potential to tailor biochar properties for specific uses, such as heavy metal adsorption and carbon sequestration (Pinna et al., 2024). Pyrolysis optimization and its integration into biorefineries have been proposed to reduce costs and improve overall efficiency (Var de Velden et al., 2010; Bridgwater et al., 2010; Stefanidis et al., 2014). Furthermore, biochar has been explored as a feedstock for synthesizing nanomaterials, bio-based composites, and specialty chemicals, broadening its utility across industrial sectors (Bartoli et al., 2022; Kiani et al.2024). Part of the studies and results were conducted under small-scale conditions, the challenge is to consider large-scale conditions.

In recent years, different organizations have been defined and formed at national, international, and continental levels to provide a platform to promote stakeholder collaboration, encourage best industry practices, and build environmental and ethical standards, ensuring that biochar systems are both safe and economically sustainable.

Some associations deal with the standardization of biochar starting from the agronomic sector.

USBI, based in the USA, is a not-for-profit organization promoting the sustainable production and use of biochar through research, policy, technology, and implementation. Also, U.S. Biochar

Coalition industry has a main mission to apply biochar to agronomic and food fields in North America. The U.S. Biochar Coalition industry trade association unifies the voice of biochar systems, agriculture, and forestry. Africa and Asia, there is the Biochar Life team possesses years of experience working with thousands of farmers in order to avoid open-field burning of biochar, but to make biochar from agricultural waste and use it to improve yields and mitigate climate change risk. In Australia and New Zealand, there is an industry group, The ANZ Biochar Industry Group (ANZBIG) that assists companies, governments, and institutions in the effective use and production of Biochar providing also contacts and collaboration between researchers and stakeholders.

In Europe, the International Biochar Initiative (IBI) provides a platform for fostering stakeholder collaboration, good industry practices, and environmental and ethical standards to support biochar systems that are safe and economically viable.

In addition, IBI is committed to promoting collaboration among biochar stakeholders and highlighting the activities of European level, national, and regional groups, and also outside of Europe, within the dynamic biochar community. These regional groups organize conferences and meetings, share updates on local biochar projects, conduct initiatives like field trials and biochar production, advocate for policies at local and regional levels, publish reports, and create networks for individuals engaged in biochar efforts within their areas.

The current European Biochar associations are for different countries:

- Biochar Lithuania (Lithuania),
- CharNet.ch (Swizterland),
- Finnish Biochar Association (Finland),
- ICHAR Italian Biochar Association (Italy),
- Montenegro Biochar Association (Montenegro),
- Nordic Biochar Network (North Europe),
- The UK Biochar Research Centre (UKBRC) (United Kingdom),
- V4 Biochar Platform (Czech Republic, Hungary, Poland, Slovakia).

On the other hand, the Biochar market is defined by a relatively consolidated structure, with a few key players holding significant influence. These companies include specialized producers dedicated to biochar as well as larger conglomerates that integrate biochar into a diverse range of products and services. Their strong networks with suppliers and customers reinforce their market positions. Competition and innovation are moderate, driven by growing sustainability initiatives and rising demand for soil improvement solutions. This dynamic positions the market for expansion, drawing interest from both regional and global stakeholders.

The Biochar Market features several prominent players known for focusing on quality and sustainable practices. These companies operate across various sectors, including agriculture, carbon sequestration, and waste management. Their competitive strategies often prioritize investments in research and development to enhance biochar production methods. A strong commitment to environmental standards and regulatory compliance further distinguishes these leading firms, aligning them with global sustainability objectives.

Table 3. Some of the main players with significant influence on the biochar market.

Country	*Company*	*General Overview*	*Market Segment*	*Strategies & Outlook*
Switzerland	*Swiss Biochar*	*Develops innovative pyrolysis technologies for efficient biochar production.*	*biochar*	*Aligning with industry regulations to drive bioenergy initiatives incorporating biochar.*
UK	*Carbon Gold Ltd*	*Develops carbon-rich biochar products aimed at enhancing soil health.* *.*	*Biochar integration*	*Leveraging digital platforms for outreach in organic farming communities.*
Germany	*Pyreg GmbH*	*Utilizes proprietary technology for efficient biochar production from biomass.*	*Biochar*	*Targeting niche segments in sustainable waste management to enhance revenue.*
Finalnd	*Carbofex*	*Plant system for production of 700 tons of biochar and 600 tons of high-quality pyrolysis oil per hour from spruce wood chips.*	*Biochar, Bio-oil*	*Captured 9,800,000 kilograms of CO2 since 2017, producing up to produce 700 tons of biochar and 600 tons of high-quality pyrolysis oil per hour from spruce wood chips.*
Finalnd	*Carboculture*	*Carbocultiure patented Carbolysis ™ reactors take waste biomass and convert it into stable biochar, locking carbon safely away for centuries and generating renewable energy in the process.*	*Biochar*	*The goal is to remove 1 billion tons of CO2 from the atmosphere each year. Its patented "carbolysis" process, a riff on the common pyrolysis process that uses pressure along with heat to*

				turn the organic material back into biochar.
Germany	*Carbon Cycle*	*Biochar farm inputs sector and the new carbon credits-based market*	*Biochar*	*high-quality biochar from woodchips which it sells to farming sectors across Europe.*
Sweden	*Ecoera*	*Sweden's first large-scale biochar producer. The company also creates synthetic gas for heating*	*Biochar, syngas*	*The company uses agricultural residues to create a carbon-rich pellet that is then heated to create the biochar.*

As for the biochar role in carbon sequestration into the soil and combating climate-changing emissions, it has a growing market (Chiaramonti et al.,2024).

An analysis by the Irish research company *Global Industry Analysts* predicts that its worldwide market will be worth USD 2 billion by 2027. This is an increase of 164% when compared to the values measured in 2022. It would mean an average growth rate over the period under analysis of 12.6 percent. However, the report also analyses in detail the different segments that make up the broader biochar sector: the woody biomass sector, for example, is expected to grow by 11.7% annually, to reach a value of USD 1.1 billion by 2027 alone. The IPCC itself, the Intergovernmental Panel on Climate Change, has pointed to it as an effective tool for controlling greenhouse gases and sequestering them in the soil. However, several factors will influence the growth of the biochar market. In particular, much will depend on how policies and regulations evolve, both at country and international level. Undoubtedly, all certification bodies are moving to offer the market reliable certification systems. In fact, biochar can generate carbon credits that can be used to offset emissions by obliged parties, such as the petrochemical, steel, cement, and aviation sectors. These credits currently have a value of around 20 €/tCO2 today and are likely to go towards 50 €/tCO2. A value that is starting to be interesting for biochar.

For the actual speed of growth, much will depend on the rules established at national and global level.

While these are the primary scenarios, the adaptability of the biochar opens opportunities in other fields, with new applications likely to emerge as research and technology advance. Its ultimate impact and broader adoption will depend on technological innovation, regulatory frameworks, and market acceptance.

5.2.1 Biochar in Ammonia Capture

Among the products resulting from the pyrolysis of biomass, biochar is a carbon-rich solid with the capacity to reduce emissions of greenhouse gases when applied to manure composting. It also serves to recover nutrients from wastewater due to its sorption capacity. Lately, it has been applied in livestock manure management context as a manure additive (Kalus et al., 2019) or a floating cover for manure storage tanks (Dougherty et al., 2017; Scotto di Perta et al., 2020b). Kalus et al. (2019) provided a comprehensive overview of the beneficial effects of biochar supplementation on diverse livestock manures, including dairy cattle slurry and poultry litter, in terms of GHG emissions abatement and nutrient retention. Likewise, biochar applied as a floating storage tank cover has demonstrated its efficacy in numerous studies. Holly and Larson (2017) observed a 96% reduction in NH_3 emissions when covering 16 L of dairy digestate for a seven-week storage period. Maurer et al. (2017) observed a reduction in emissions ranging from 13 to 23% following the application of biochar to a surface area of swine manure ranging from 2.28 to 4.56 kg/m². Scotto di Perta et al. (2020a) demonstrated that the application of a 2 cm layer of biochar can result in a reduction of NH_3 emissions from manure storage tanks by up to 80% in laboratory conditions. In a separate study, Covali et al. (2021) observed a 48% reduction in NH_3 emissions following the application of biochar to digestate surfaces.

The interaction of biochar with ammonia nitrogen occurs dynamically through a variety of mechanisms: (i) the adsorption of NH_4^+ in the liquid phase onto the biochar layer, which is partially immersed in the liquid at the top layer of the storage tank; (ii) the adsorption of gaseous NH_3, which volatilizes from the storage tank. (iii) the alteration of the NH_4^+/NH_3 equilibrium in the top layer of the liquid manure/digestate, due to its typically basic pH; and (iv) the formation of a physical barrier at the liquid–surface interface. All these mechanisms are present simultaneously and their relative importance is contingent upon the characteristics of the biochar in question. It is therefore essential to comprehend the interrelationship between biochar characteristics and NH_4^+ and NH_3 sorption, to direct biochar production towards enhanced ammonia sorption, or to select existing biochar types with specific properties for this objective (Viaene et al., 2023a). However, the biochar application method also proved to be a significant factor, with the use of biochar as a bio-mix (Viaene et al., 2023b) or bio-cover (Baral et al., 2023) being particularly noteworthy. Scotto di Perta et al. (2024) demonstrated that the primary adsorption mechanism involved NH_3 protonation on the biochar, whereby H+ abstraction from the acid group's surface resulted in the formation of NH_4^+. This was observed in biochar produced at 550°C and buffalo manure digestate. The adsorption of NH_4^+ through cation exchange is a relatively minor phenomenon, while the physisorption of gaseous NH_3 does not occur. Furthermore, when the biochar layer is in a floating and compact state, it introduces an additional resistance to the transfer of gases. This aspect is of greater significance than the adsorption phenomenon on the reduction of NH_3 emissions. Indeed, these findings indicate that the use of biochar as a floating cover of 2 cm, as opposed to its use as an additive, can result in a 43% reduction in NH_3 emissions.

5.3 Hydrothermal Liquefaction

Hydrothermal Liquefaction (HTL) technology is widely known for the transformation of organic biomass into biofuels through a series of process steps (Wikberg et al., 2015; Yin et al., 2010). The biofuel produced is the highest-valued product of HTL as it could replace conventional liquid fuels, without transfer or storage systems alterations. Besides the biocrude oil, a brown viscous liquid product that can be further treated to attain fuel-like properties, HTL leads to the following bio-based byproducts:

- **Biocrude oil**, a brown viscous liquid product which can utilized as a potential transportation biofuel
- **Aqueous phase**, a liquid phase mostly consisting of water, rich in inorganics
- **Gaseous products**, a mixture containing methane, CO_2 and other gases (H_2, N_2, C_3H_6 etc.)
- **Biochar**, a solid ash is being produced when processing specific feedstock types such as woody biomass

5.3.1 Current and promising applications

Due to the increasing demand for reliable biofuels for fossil fuel replacement, and the ongoing climate alterations, HTL technology has gained significant attention and researcher’s sight has turned to investigating cost-wise efficient ways of exploiting the bio-based products coming from it. In this context, the total of the products and byproducts are being characterized and tested to be applied in several sectors. Some of the current applications are explained below.

Biocrude oil production: The biocrude produced by HTL has properties lower than the conventional fuels due to the significant presence of O_2. However, the application of a post-process treatment such as hydrotreatment, converts the biocrude into valuable transportation biofuel (Mishra et al., 2022; Saengsuriwong et al., 2021). The hydrotreatment is totally like the ones applied to most conventional and bio-based fuels and can be performed in a typical refinery. The utilization of such types of biofuels in the marine and aviation sectors is a rising issue as the carbon footprint reduction in these two sectors has been targeted as a major issue for the next few years.

Fertilizers from by-products: The aqueous phase produced when conducting HTL is a mixture rich in nutrients like nitrogen, phosphorus, and potassium. The aqueous phase can be processed into fertilizers or soil amendments and become a sustainable byproduct, offering additional value in the total HTL process (Matayeva et al., 2022). Additionally, recent studies have been made to investigate the utilization of the aqueous phase as the process water for various applications (Cordova et al., 2020). The produced biochar is also a potential enhancement element for the soil fertility as it can improve soil water retention providing a nutritious habitat for various microorganisms (Ponnusamy et al., 2020).

Sustainable Aviation Fuels (SAF): The current need for decarbonization in the aviation sector, occurring from recent EU regulations and the general geopolitical situation has further highlighted the energy potential of HTL. The greenhouse gas emissions produced by the aviation industry has already forced the investigation of alternative fuels and sustainable solutions for the reduction of carbon footprint. Large-scale production of HTL biofuels exclusively for their use as aviation biofuels is gaining attraction and is being studied for immediate optimization and utilization considering its cost-related advantages in comparison to the alternative biofuels (Ramasamy et al., 2021; Farooq et al., 2020). Some of the remaining challenges that slow down the fast development can be found in the high-pressure needs of the process, as well as the product’s extensive refining process.

Marine fuels: Marine fuels, contrary to SAF require minimum after-process treatment for their exploitation. The basic construction of marine engines allows wider degrees of freedom regarding the fuels used. At the same time, electrification solutions seem to be far from realistic efficiency targets, while the alternative of hydrogen fuels is still in the preliminary stages of development. These facts underline the urgency for rapid progress on the growth of liquid renewable fuels, with similar properties to the existing ones, to avoid the cost of equipment and infrastructure of a transition (Lozano et al., 2022).

5.3.2 Geographical distribution

The potential and scalability of HTL is highly dependent on the availability and geographical distribution of the biomass feedstock as well as the industrial initiatives investing on the optimization and integration of the HTL technology based on both economic incentives and policy frameworks.

Residual biomass can be found from various sources through a regional ecosystem; however, a centralized system of biomass collection can contribute to the logistical aspects regarding the process viability by combining biomass sources and post-processing infrastructure availability (e.g. refineries). The distribution of biobased products is driven by technological maturity, investment in biorefineries, and demand for sustainable alternatives to fossil-based products.

Europe: Europe has been a global leader in the development and commercialization of HTL products, mainly due to the European Union's climate goals and policy frameworks on circular economy. In Denmark, pioneering steps have been made on HTL, where various biomass types have been converted into biofuels. The Danish company Steeper Energy is focusing on large-scale HTL biofuel production hosting a demo semi-continuous pilot-scale reactor. France, Germany, Greece and the Netherlands are also expanding their knowledge on HTL technology the last decade targeting on optimized, continuous systems and investigating scalability potentials (Moser et al., 2023; Matricon et al., 2023; Tsongidis et al., 2020; Biller & Ross, 2011).

Asia-Pacific: In the Asia-Pacific region, China, Japan, and Australia are taking the lead on HTL research and development. China is investing heavily in HTL technologies in an investigation of efficient solutions considering the massive waste management challenges, while in parallel addressing the need for alternative biofuels (Xu et al., 2019; Zhang et al., 2020). Agricultural residues and organic waste are being extensively studied as feedstocks for transportation biofuel production. Additionally, the large-scale algae cultivation in China has contributed to the wide utilization of algae as a feedstock to produce bioplastics and biochemicals. Australia, having similar organic content as China (agricultural residues, algae-based cultivations) has shown robust interest in HTL research to produce biocrude oil (Castello et al., 2018). In Japan, the focus of research initiatives related to HTL is concentrated on biochemical production for cosmetics.

North America: North America is a leading region, holding some strong investments in biofuel technologies, policy frameworks, and pilot projects. The U.S. part has the significant support of the Department of Energy which funds the research and development of biofuels production methods, including HTL (Chen et al., 2019). Companies such as Shell and Chevron are collaborating with research institutes to incorporate HTL and other alternative ways of biofuel production in their processes. Canada is also an innovative country regarding bio-based products from renewable energy resources and especially exploiting its large agricultural and forestry residues.

Latin America: Brazil and Argentina are in the early stages of HTL development positioning it among several renewable energy processes. While Brazil has extensive potential in bio-based products, mainly in ethanol and biodiesel, and is attempting to integrate HTL in biorefinery processes, Argentina is still in the preliminary steps of the specific research areas (Patel et al., 2016; Ocampo et al., 2023).

Africa: Although Africa presents a fertile ground for biomass management technologies and is currently in need of energy security solutions, HTL is yet to develop further than a lab-scale level. Spent coffee grounds, municipal soil waste and sugar cane bagasse are among the feedstocks that have been tested in South Africa, exploring the properties of HTL products (Marx et al., 2023; Marx et al., 22).

6. Advanced biofuels applications

6.1 Liquid biofuels

Biorefining is a valuable technique for producing biofuels due to their efficient and integrated approach to biomass conversion. This overview will explore the benefits of biorefineries, and the biofuels produced and used in Europe. Biorefineries offer several advantages in biofuel production. Firstly, they exhibit high resource efficiency by processing various feedstocks, including crops, agricultural residues, and waste streams, thus maximizing the use of available biomass resources (Skočibušić et al., 2010). Secondly, biorefineries can produce not only biofuels but also other valuable co-products such as chemicals, materials, heat, and power, which improves overall economic viability (Travis, 2012). Furthermore, they contribute to sustainability by utilizing non-food feedstocks and waste materials, enabling the production of advanced biofuels with lower environmental impacts and reduced competition with food production (www.fueloilnews.co.uk). The main biofuels produced in Europe include biodiesel, bioethanol, advanced biofuels, and renewable diesel (HVO). Biodiesel, specifically known as FAME (Fatty Acid Methyl Esters), is the most common biofuel in Europe, accounting for about 75% of total biofuel production (www.etipbioenergy.eu). FAME is produced by the transesterification of vegetable oils or animal fats, mainly from rapeseed oil, palm oil, soybean oil, used cooking oil, and animal fats. Germany is the largest FAME producer in the EU, with an estimated production capacity of 3.3 billion liters in 2020, followed by France, Spain, and the Netherlands (www.statista.com). The EU promotes FAME production under its Renewable Energy Directive. The physical properties of FAME are like those of fossil diesel, though they depend on the oil source used, see Table 4. FAME is biodegradable, non-toxic, and has similar combustion properties to conventional diesel (Szeto et al., 2022). The possible production processes were reviewed by Vyas et al. (2010).

Table 4.Properties of different fuels possible from biorefinery. (Roque et al., 2023; Szeto et al., 2022; www.sae.org).

Fuel	Bioethanol	Petrol	FAME	HVO	Diesel
Density in kg/L	0.79	0.74	0.88	0.78	0.83
Calorific value in MJ/kg	26.70	43.90	37.10	44.40	43.10
Calorific value in MJ/L	21.09	32.49	32.76	34.63	35.77

Bioethanol makes up about 25% of European biofuel production. Nevertheless, the raw products can be different. In Spain non-lignocellulosic mostly from corn and lignocellulosic mostly from winemaking by-products are important. Wheat is predominantly used in Germany and France; corn is used particularly in Hungary, Poland, the Netherlands, Spain, and recently Belgium. In France, Germany, the Czech Republic, Belgium, and Austria, sugar beets and their derivatives are also used to produce bioethanol (USDA 2024). Further in Denmark rapeseed oil, grain, sugar, butchery waste and other waste products from agriculture are used. Rapeseed oil is the most important raw material and makes up more than 40%. This is followed by cereals (mainly maize and wheat) and sugar, which together also make up more than 40% of the total raw materials (ENS, DrivKraft, IEA 2021). In Turkey the most production of biofuels is from fermentation of maize, sugar beet, molasses and wheat and in the recent years, studies on biodiesel production from algae have also been carried out (PWC, Figen). While Cyprus (CY-ES) mostly relies on cooking oil as waste product. Germany is increasingly utilizing a variety of waste and residue materials for the production of biofuel, demonstrating a commitment to sustainability and resource efficiency (www.etipbioenergy.eu). The country employs agricultural residues from various crops, including barley, maize, rye, triticale, wheat, sugar cane, and sugar beet. In addition to crop residues, Germany also uses waste materials from oilseed crops such as Ethiopian mustard, palm oil, rapeseed, soy, and sunflower (www.interreg-danube.eu). Furthermore, palm oil waste is specifically highlighted as a significant feedstock in Germany's biofuel production efforts.

Further reviews on this topic have been done by Callegari et al. (2020), Medipally et al. (2015) and Neuling and Kaltschmitt (2017).

Advanced biofuels include cellulosic ethanol, biomethane, and other biofuels derived from non-food feedstocks such as agricultural and forestry residues, algae, and municipal solid waste. European biofuels have various applications. In road transport, FAME (biodiesel) and bioethanol are blended with conventional fuels for use in passenger vehicles and heavy-duty trucks, with B7 (7% biodiesel blend) being the maximum blend currently permitted across the EU. FAME can also be used in pure form (B100) in adapted diesel engines (Panoutsou et al., 2021). In aviation, sustainable aviation fuels (SAFs) are being developed and implemented to reduce emissions in the aviation sector (Braun et al., 2024; Watson et al., 2024). In maritime transport, biofuels are explored as an option for decarbonizing shipping, especially for heavy-duty vessels where electrification is challenging. Biodiesel can also be used efficiently as a heating oil alternative, and some biofuels and their co-products find use in various industrial processes and as feedstocks for bio-based materials.

In Table 5 a comparison for Europe and UK have been done for 2020 to 2022 (www.ble.de). Emission savings refer to the comparison with fossil fuel emissions. The emissions in tons of CO2 equivalent (t CO2eq) per terajoule (TJ) of individual biofuels change from year to year because the mix of raw materials varies annually, and different raw materials cause different emissions. According to a study by the Institute for Energy and Environmental Research (www.ifeu.de), 5.27 million hectares across Europe and the UK are used exclusively for cultivating raw materials for biofuels that are consumed in Europe and the UK. This land could be reforested, potentially sequestering approximately 66 million tons of CO_2 annually.

If electric mobility powered by photovoltaic (PV) systems were used instead of fossil fuels, about 100 million tons of CO_2 could be saved or sequestered annually. In contrast, the use of biofuels only avoids 25 to 32 million tons of CO_2. It is important to note a limitation: while biofuels can be used universally, the study only considered and compared driven car kilometres.

Table 5. Comparison of bioethanol, FAME and HVO for Europe (IFEU).

	Bioethanol			FAME			HVO		
	2020	2021	2022	2020	2021	2022	2020	2021	2022
Production [TJ]	29 528	30 656	30 954	89 429	84 776	82 652	43 893	19 725	20 991
Emission [t CO_2eq/TJ]	7.44	9.18	9.39	17.97	16.86	14.93	19.82	16.02	12.24
Emission [t CO_2eq]	219 688	281 422	290658	1 607 039	1 429 323	1 233 994	869 959	315 995	256 930
Fossil comparison emissions [t CO_2eq/TJ]	93.30	93.30	93.30	95.10	95.10	95.10	95.10	95.10	95.10
Fossil comparison emissions [t CO2eq]	2 754 962	2 860 205	2 88 8008	8 504 698	8 062 198	7 860 205	4 174 224	1 87 5848	1 996 244
Savings [t CO_2eq]	2 535 274	2 578 783	2 597 350	6 897 659	6 632 874	6 626 211	3 304 265	1 559 853	1 739 314
Savings [%]	92.03	90.16	89.94	81.10	82.27	84.30	79.16	83.15	87.13

The sustainability of FAME production. particularly the use of food crops. is a topic of discussion. In 2021, most biofuels consumed in the EU were crop-based (ECA, based on SHARES). Advanced production methods for the second and third generation biofuels and the use of waste materials and non-food plants as raw materials are being researched to improve sustainability.

The European Union is actively promoting the development and use of biofuels to meet its renewable energy and greenhouse gas reduction targets. In 2020, 56.3% of the total transport fuel consumption in the EU was through the supply of biofuels (IEA 2023). The Renewable Energy Directive (RED II) sets a target of at least 14% renewable energy in the transport sector by 2030. including a minimum of 35% advanced biofuels (wwwjoint-research-centreeceuropa.eu). Renewable ethanol production and use by ePURE members and other EU producers reduced greenhouse gas emissions by an average of 79.1% compared to fossil fuels in 2023 (ePURE 2024). This policy framework. along with technological advancements in biorefining. is expected to drive further growth and innovation in the European biofuels sector FAME plays a crucial role in the EU's efforts to increase the share of renewable energy in the transport sector and reduce greenhouse gas emissions.

6.2 Gaseous biofuels

Gaseous biofuels unquestionably play a relevant role as CO_2-neutral energy sources in the heat and power sectors. In this respect, different types of biomasses, such as lignocellulosic biomass, animal or Municipal Solid Wastes (MSW) can be processed through bio-chemical (anaerobic digestion, etc.) or thermo-chemical technologies (pyrolysis, gasification, etc.), to obtain a wide palette of biofuels suitable for energy production (Achinas et al., 2017; Zhang et al., 2016).

Although these technologies can be considered mature, the obtained biogas composition strongly depends on the feedstock type and specific thermo-chemical process (Calby-Muzyka et al., 2022; Martínez-Gutiérrez et al., 2018), also suffering fluctuations over time due to changes in biomass characteristics (i.e. humidity), composition, or process breakdown/failure. Generally, carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), and hydrogen (H_2) are the main constituents, with traces of higher hydrocarbons (C1-C5) (Sabia et al., 2021; Chin et al., 2020), nitrogen (N_2) (Awe et al., 2017; Yang et al., 2016) and other undesired components such as ammonia (NH_3) and hydrogen sulphide (H_2S).

As a result, gaseous biofuels are usually characterized by very low Lower Heating Values (LHV) compared with conventional hydrocarbon fuels and possible undesired by-products in the exhausted gases from combustion systems, that strongly hinder their utilization in traditional combustion systems. In this respect, biogas upgrading processes are often needed, such as purification processes (pressurized water scrubbing, amine swing absorption, membrane technologies, etc.) and/or biogas combustion properties enhancement through the addition of more reactive fuels (H_2, etc.) (Starr et al., 2012). On the other hand, advanced combustion technologies such as MILD combustion (Sabia et al., 2021), have already proven to enable the efficient and direct utilization of biogases for energy production, overcoming the need for biogas upgrading processes (Ariemma et al., 2024).

Worldwide, many different plants and facilities couple biogas/syngas production from highly diversified input materials with their direct use for both heat and electrical energy and/or synthetic fuels production. These distinguish in terms of installed capacity, raw materials and feedstock type (agricultural feedstocks, animal manure, etc.), biomass treatment processes (anaerobic digestion, gasification, pyrolysis, etc.), and final use of the produced biogas/syngas (energy or valuable products production).

In respect of plants using biomass treatment to produce biogas then used for the direct production of electricity and heat, they usually involve biomass anaerobic digestion processes, biogas upgraded treatments and combustion units. Noteworthy are:

- **Bioenergy Park Güstrow**: largest integrated bio-LNG plant with bio-CO_2 liquefaction plant in Germany and Europe (https://www.envitec-biogas.com/references/guestrow).

Capacity: 150.000 tonnes of agricultural material processed with 9.600 metric tonnes of bio-LNG (liquefied natural gas) and 15.000 metric tonnes of bio-LCO2 produced, per year. ~22 MW of electrical power produced.

Biogas supply: the plant processes a significant amount of input materials of agricultural feedstocks, such as maize silage, straw, and animal manure, to produce biogas. It also uses corn silage and other organic materials, converting them through anaerobic digestion into biomethane.

Operation: the produced biogas is purified and upgraded into biomethane (a form of methane) to natural gas quality and injected into the national natural gas grid for heating and energy production. This integration into the gas grid makes it unique, as most biogas plants produce electricity and heat directly onsite. In this respect, the obtained biomethane is converted to electricity and heat through a combined heat and power (CHP) system. Instead, the CO2-enriched mixtures coming from the upgraded process, and containing very small amount of methane is transferred to a CO_2 liquefaction plant to produce liquid carbon dioxide usable in the food production sector.

- **Foulum Biogas Plant**: located at Aarhus University's Foulum campus in Denmark, it is a significant research facility dedicated to biogas production and development (https://bce.au.dk/en/research/facilities/biogas-plant).

Capacity: 85.000 tonnes of organic waste processed with 5 million cubic meters of biogas produced per year; ~8 MW of power and heat produced.

Biogas supply: the plant processes a mix of animal manure from local farms and other organic wastes, like industrial food waste. Farmers in the surrounding area contribute manure, silage, straw, and other organic materials, which are transported to the plant for anaerobic digestion to produce biogas.

Operation: the obtained biogas is primarily used for energy production, both electricity and heat for the campus, and provides biogas-derived electricity for external projects. Furthermore, this is also used for research purposes, such as investigating advanced biogas production and ammonia reduction techniques.

- **Changi Water Reclamation Plant**: one of Singapore's largest and most advanced wastewater treatment facilities (https://www.pub.gov.sg/Resources/News-Room/PressReleases/2024/06/Changi-WRP-to-undergo-third-phase-of-expansion).

Capacity: 800.000 cubic meters of wastewater daily processed from both domestic and industrial sources. It is designed to treat used water from Singapore's eastern half and is part of the city's Deep Tunnel Sewerage System (DTSS), which conveys wastewater to centralized facilities.

Biogas supply: The plant produces biogas from anaerobic digestion of sewage sludge, which is a by-product of wastewater treatment generated during the treatment process to produce methane.

Operation: The produced biogas is captured and used to produce electricity and heat to power the plant's operations. Besides biogas, the plant also focuses on maximizing resource recovery by extracting valuable by-products like biosolids, which are treated and reused in several applications such as fertilizers.

- **Rio de Janeiro Biogas Power Plant**: one of the largest landfill gas-to-energy plants in Latin America, focused on capturing and utilizing methane gas from landfill waste to generate electricity (https://firmgreen.com/novo-gramacho-opens-green-energy-center/).

Capacity: ~70 million cubic meters of biogas produced, and 3.2 MW of electricity fed into the local grid.

Biogas supply: The power plant captures methane emitted from the decomposition of organic waste and municipal solid waste.

Operation: The biogas, primarily composed of methane, is extracted through a series of wells and pipes installed in the landfill, preventing the release of harmful greenhouse gases into the atmosphere.

- **Yorii Biomass Power Plant**: significant renewable energy facility that primarily utilizes biomass for electricity generation in Japan (https://firmgreen.com/novo-gramacho-opens-green-energy-center/).

Capacity: 100 tons of waste processed per day, with a generation capacity of 1,600 kW and a power generation capacity of approximately 9.8 million kWh per year. The produced electricity is fed to the local energy grid.

Biogas supply: This power plant is part of a circular economy project, where food waste from local businesses and industries is converted into biogas through anaerobic digestion. Additionally, waste from agricultural and livestock operations is supplied to ensure consistent biogas production.

Operation: the produced biogas is utilized in combined heat and power (CHP) systems for electricity and thermal energy simultaneous production.

- **Biogas Plant Avedøre**: combined heat and power (CHP) facility using biomass in Copenhagen, Denmark (https://orsted.com/en/what-we-do/renewable-energy-solutions/bioenergy/our-bioenergy-plants).

Capacity: the plant has a total power-generating capacity of 793 MW and a heat-generating capacity of 918 MW.

Biogas supply: Agricultural waste, organic waste from food industries, and manure are used to generate biogas.

Operation: The plant is integrated into the city's district heating system, providing both electricity and heat, with the capability to utilize natural gas and oil as secondary fuels. Furthermore, the plant is designed to maximize the efficiency of energy conversion.

- **Didcot Biogas Plant**: located in Oxfordshire, UK, this facility is notable for being one of the first in the UK to inject biomethane directly into the gas grid (https://www.theengineer.co.uk/content/news/project-feeds-biomethane-to-gas-grid/).

Capacity: ~1.4 MW of electric power.

Biogas supply: the facility primarily utilizes organic waste, such as sewage sludge and agricultural byproducts, to produce biogas through anaerobic digestion.

Operation: the produced biogas, primarily composed of methane and carbon dioxide, undergoes a cleaning process to remove impurities. Afterwards, the biogas is upgraded to meet the required standards before being injected into the national gas grid.

- **Amersfoort Waste-to-Energy Plant**: located in the Netherlands, this plant processes wastewater from approximately 300,000 residents in the surrounding areas (https://www.ostara.com/case-study-ammersfoort-wastewater-treatment-plant/).

Capacity: ~9.500 MWh of energy in the form of electricity and heat, along with 900 tonnes of fertilizer annually, which is directly usable in agriculture. This accounts for about 1.86 million kilograms of fertilizer per year.
Biogas supply: the plant utilizes anaerobic digestion processes to produce biogas from organic waste and innovative technologies to extract phosphorus from wastewater.
Operation: the produced biogas is converted in the form of electricity and heat, supporting the plant's goal of becoming fully energy-neutral. Furthermore, the plant also realizes the nutrient recovery from wastewater, particularly phosphorus, to produce fertilizers directly usable in the agriculture.

- **Ulsan Biogas Plant**: located in Ulsan, South Korea, allows to process of food waste and sludge from city's residents and the local wastewater treatment process (https://www.biokraft.com/korea).

Capacity: 183 tonnes of food waste are daily processed, with an annual production capacity of about 60 GWh of biogas.
Biogas supply: the plant primarily manages food waste generated by over one million residents, as well as primary sludge from an adjacent wastewater treatment plant. This integration allows biogas production through effective anaerobic digestion.
Operation: the plant employs innovative technologies to optimize biogas production and conversion, becoming one of the most efficient biogas facilities in the country.

With respect to solutions using raw material treatments to produce syngas then used for both synthetic fuels and energy production, these usually couple pyrolysis processes and combustion stages. Noteworthy are:

- **ENCORE Advanced Pyrolysis Technology**: waste management solution developed to convert various types of organic waste into renewable energy and valuable products (https://wteinternational.com/solutions/pyrolysis/encore-advanced-pyrolysis-technology/).

Capacity: depending on the specific installed capacity, plants operating with this technology can manage biomass amounts between 8,000 up to 53 000 tons per year:

- Hudson, Colorado, USA: facility managing 52,500 tons per year of used tires, producing approximately 27.6 million L of synthetic fuel per year.
- Seoul, South Korea: this facility processes 1000 tons per year of used tires, annually producing 600 000 L of synthetic fuel.
- Chino, California, USA: ~0.8 MW of electricity deriving from the conversion of 12.000 tons per year of cow manure.
- Bistrita, Romania: plant annually managing ~8 400 tons of MSW and producing ~1 MW of electricity.

Raw material supply: various waste types, including biomass and plastic materials.

Operation: the pyrolysis process converts organic material into syngas, which is primarily composed of hydrogen, carbon monoxide, and small amounts of methane. These syngas can be used for generating electricity or further processed into synthetic fuels. In addition to syngas, the process also produces biochar, which can be used as a soil amendment or carbon sequestration agent.

- **Kansai Electric Power Company (KEPCO)**: actively involved in the implementation of advanced technologies like pyrolysis and gasification (https://www.kepco.co.jp/english/). Their facilities employ a pyrolysis-gasification process combined with combustion. The treated waste is converted into syngas, which is then used to generate electricity. However, detailed specifics on their pyrolysis facilities are less publicly available.

- **BioEnergy Technologies (BETO):** BETO facilitates numerous pilot and demonstration projects that convert biomass into biofuels and bioproducts (https://www.energy.gov/eere/bioenergy/bioenergy-technologies-office). However, information about specific "BioEnergy Technologies" plants is not available.

The listed facilities and plants are only some among the many initiatives and technologies based on the waste materials valorisation through energy and valuable products production, set a wider trend towards integrated waste materials management systems that prioritize sustainability and energy efficiency.

6.3 Sustainable Aviation Fuels (SAFs) for carbon-neutral aviation

Commercial aviation accounts for approximately 13% of transportation-related greenhouse gas (GHG) emissions and 2% of global CO_2 emissions, totaling around 914 million tons of CO_2 released into the upper atmosphere each year. Airlines have guaranteed to achieve carbon-neutral growth for international commercial aviation starting in 2021, with a goal to reduce carbon dioxide emissions by 50% by 2050 compared to 2005 levels. Despite several achievements in emission reduction, such as enhanced aircraft fuel efficiency and improved air traffic control aimed at ensuring safe, efficient, and sustainable air travel, these advancements have only resulted in a carbon emission reduction of less than 15% (Undavalli et al., 2023).

To achieve a net reduction in CO_2 emissions soon, the only promising approach is the development of SAFs produced from renewable raw materials (biomass) or by employing Power-to-Liquid (PtL) technology based on hydrogen, utilizing (excess) renewable electricity, e.g., from wind power or photovoltaics, and a carbon source such as carbon dioxide. The use of alternative (non-fossil-sourced) SAFs can result in a further 50-80% reduction in carbon emissions and is therefore considered the most efficient way to achieve carbon-neutral aviation operations (Undavalli et al., 2023; Borrill et al., 2024).

To fastener the transition to SAF-driven aircraft, efforts are focused on developing drop-in jet fuels, namely fuels that possess essentially the same properties and composition as the petroleum-derived jet fuels currently used in commercial and military aircraft. Because these SAFs are nearly identical to traditional jet fuels, they are compatible with the existing fleet of aircraft and the current jet fuel distribution infrastructure. This compatibility is a significant advantage of SAF compared to electric or hydrogen-powered aircraft (Borrill et al., 2024).

The approval of new aviation fuels is a long-lasting process. In 2009, ASTM International Committee on Petroleum Products and Lubricants issued ASTM Standard Specification D7566, to certify drop-in jet fuel from alternative feedstock. SAFs are approved for usage via a Tiered Test or Fast Track Programs under ASTM D4054 (ASTM International, 2019), defining the bio-jet fuel specifications blended with conventional jet fuel certified by D1655 ASTM standard (ASTM International, 2020). It currently allows approved blend ratios up to 50% with conventional fuel.

As of July 2023, there are 11 approved pathways for SAF production, encompassing variations of four key technologies: Gasification and Fischer-Tropsch (G-FT), Hydroprocessed Esters and Fatty Acids (HEFA), Hydroprocessed Fermented Sugars (HFS), Alcohol-to-Jet (ATJ). Some of the approved biofuel technologies are listed below (Undavalli et al., 2023; Borrill et al., 2024).:

- **Fischer-Tropsch Synthetic Paraffinic Kerosene** (FT-SPK, up to 50% blend – produced by Red Rock Biofuels, USA Oregon): the process is based on the gasification of biomass (usually lignocellulosic biomass) followed by a water-gas shift to produce syngas with the optimal H_2/CO ratio for Fischer-Tropsch synthesis. The process can also entail the addition of aromatics from non-fossil fuels (FT-SKA).

- **Hydro-processed Esters and Fatty Acids Synthetic Paraffinic Kerosene** (HEFA-SPK, up to 50% blend – produced by AltAir, USA California or Neste, Island): the process utilizes feedstocks such as vegetable oils, animal fats, waste cooking oil, pyrolysis oil, and algae oil, which undergo hydro-processing. It involves extracting fatty acids from the biomass, followed by isomerization to rearrange the molecular structure, and hydrocracking to shorten the carbon chain lengths, ensuring the fuel meets the required specifications.

- **Alcohol to Jet Synthetic Paraffinic Kerosene** (AtJ-SPK, up to 30% blend – produced by Gevo USA, Texas): the production pathways convert alcohol into SAF. The alcohol can be produced through biochemical conversion processes such as fermentation of sugar or starch-rich crops, or via thermochemical methods like gasification or pyrolysis of lignocellulosic feedstocks. Various alcohols, such as ethanol, methanol, and iso-butanol, can be used to undergo the following processes: dehydration to olefinic gas, oligomerization, hydrogenation, and fractionation. The final fuel consists mainly of two highly branched iso-alkanes namely 83% of i-$C_{12}H_{26}$ (iso-dodecane) and 17% of i-$C_{16}H_{34}$ (iso-cetane).

- **Synthesized iso-paraffins** (SIP, up to 10% blend – produced by Total & Amyris, Brazil): The production process for HFS synthetic iso-paraffins (HFS-SIP) is a biological conversion method, which involves the pretreatment of the biomass feedstock to separate sugars from lignin. Then, the sugars are then converted into farnesene ($C_{15}H_{24}$) through enzymatic hydrolysis and fermentation, where genetically modified yeasts consume the sugars to produce long-chain liquid alkenes.

Producing SAFs from a variety of feedstocks, including renewable and non-petroleum sources, enhances energy security and resilience by diversifying and creating a more sustainable fuel supply chain. However, key challenges include sourcing sufficient feedstocks that do not compete with food production and ensuring that the supply chain remains both diverse and sustainable.

Bio-based SAFs can be categorized based on the types of feedstocks used for fuel production. The CORSIA program (https://www.icao.int/environmental-protection/CORSIA/Pages/default.aspx), established by the International Civil Aviation Organization (ICAO), identifies five categories of feedstocks for fuel production: primary products, co-products, by-products, residues, and wastes, which are classified into different generations.

The availability of feedstocks for SAF production varies by region due to a combination of geographical, climatic, agricultural, and economic factors. Moreover, many feedstocks serve multiple industries, such as biodiesel production or animal feed, complicating the assessment of how much is specifically available for SAF production. A recent study by O'malley et al. 2021, estimated that with a total feedstock availability of 124.4 million tons, approximately 3.4 million tons of SAF could be produced, meeting about 5.5% of the projected jet fuel demand for 2030. Therefore, further research is essential to explore methods for expanding the sustainable feedstock supply for SAF production and improving conversion efficiency, ultimately increasing total SAF output.

7. A summary on added-value end products from biorefineries

7.1 Xylitol

Xylitol is a naturally occurring five-carbon sugar alcohol ($C_5H_{12}O_5$) found in most materials derived from plants, including many fruits and vegetables. Xylitol can be industrially produced by the fermentation of xylose extracted from hemicelluloses as an alternative to the expensive chemical process. All major xylitol producers (China in Asia Pacific and Finland in Europe) employ a chemical production process involving the hemicellulosic fraction of lignocellulosic biomass as feedstock. The production process consists of four steps, namely 1) the biomass pretreatment, 2) the purification of the obtained xylose, 3) the chemical conversion of xylose to xylitol, and 4) the purification of the produced xylitol. Both the purification steps and the operating conditions required for the conversion process induce high costs, which explains the high product price of xylitol compared to similar molecules. An alternative production route for xylitol is the fermentation with suitable organisms in a biotechnological process (Vollmer et al. 2022) with expected comparatively lower associated costs.

Xylitol as a product has gained attraction throughout research for several decades. Due to the high interest and potentially high product prices, the US Department of Energy declared xylitol one of the top 12 chemicals to be produced in a biorefinery already in 2004 (Werpy and Petersen, 2004).

Applications*:* Xylitol is used as a sweetening agent (e.g. chewing gum, candies) and it is perfectly suitable for diabetic nutrition as a sugar substitute. Moreover, unlike sugar, it doesn't cause tooth decay and cavities. It can be also an important chemical platform for the sustainable production of bioproducts.

Market: The global xylitol market size was valued at USD 447.88 million in 2020 and is expected to expand at a compound annual growth rate (CAGR) of 6.4% from 2020 to 2028. Asia Pacific led the global market in 2020 accounting for the largest revenue share of more than 39%. China is the leading producer of xylitol, whereas China, India, and Thailand are among the leading consumers of xylitol in the region. China is the key exporter across the globe. The U.S., Europe, India, and other South Asia countries are the key export destinations for China in the market. Europe is anticipated to witness the fastest CAGR of 7.0% over the forecast period. Finland is one of the top producers in the European regional market. The majority of the xylitol produced in Finland is exported to neighbouring European countries (https://www.icao.int/environmental-protection/CORSIA/Pages/default.aspx).

Producers worldwide*:* Cargill, Inc.; DuPont Danisco; Roquette Freres; ZuChem, Inc.; Thomson Biotech (Xiamen) Co., Ltd.; NovaGreen, Inc.; DFI Corp.; Zhejiang Huakang Pharmaceutical Co., Ltd.; Jining Hengda Green Engineering Co., Ltd.; Shandong Biobridge Technology Co., Ltd.; Shandong Futaste Co., Ltd.; Foodchem International Corp.; Mitsubishi Shoji Foodtech Co., Ltd.; A & Z Food Additives Co., Ltd.; Herboveda India; Shandong Lujian Biological Technology Co. Ltd.; Godavari Biorefineries Ltd.; Shandong Longlive Bio-Technology Co., Ltd (https://www.grandviewresearch.com/industry-analysis/levulinic-acid-market).

7.2 Levulinic acid

Levulinic acid (LA) or 4-oxopentanoic acid ($CH_3C(O)CH_2CH_2CO_2H$) is an organic compound classified as a keto acid. It is soluble in water and polar organic solvents. LA is also classified as a platform molecule, and it is one of the top twelve chemicals listed by the US Department of Energy that can be obtained from biomass. LA can be produced through cellulose hydrolysis together with formic acid (FA). Various biomass feedstock, such as agricultural wastes, marine macroalgae, and freshwater microalgae were successfully converted to LA in high yields (Victor et al., 2022). In 2019 the global LA market achieved $27.2 million, and it is expected to reach $60.2 million by 2030 (Sessa et al., 2024).

Applications*:* LA serves as a building block for producing a variety of chemicals, fuels and materials. Alkyl levulinates (e.g ethyl levulinate) are potential fuel blends and additives and can be obtained via esterification of LA. LA can be converted into γ-valerolactone via hydrogenation. γ-valerolactone is a biochemical and biofuel precursor. N-substituted pyrrolidones, useful for food security and for the pharmaceutical industry, can be obtained from LA via reductive amination (Victor et al., 2022)

Market: The global levulinic acid market size was valued at USD 80.7 million in 2022 and is projected to grow at a compound annual growth rate (CAGR) of 8.2% from 2023 to 2030. Europe region dominated the market with more than 50% of the total revenue share in 2022. This is attributed to favourable government regulations, substantial production capacities, easy availability of raw materials, and early adoption of bio-based chemicals. The Asia Pacific region has experienced growing demand for levulinic acid owing to various government policies regarding environmental protection coupled with shift of consumer preferences toward bio-based products. Being a leader in industrial biotechnology, the U.S. has a significant share of the market.

Producers worldwide: Segetis; Biofine Technology LLC; DuPont; Hebei Langfang Triple Well Chemicals Co. Ltd; Hebei Shijiazhuang Worldwide Furfural & Furfuryl Alcohol Furan Resin Co. Ltd.; Jiangsu Yancheng China Flavor Chemicals Co. Ltd; Shijiazhuang Pharmaceutical Group Ouyi Pharmaceutical Co. Ltd; Shanghai Apple Flavor & Fragrance Co. Ltd.

7.3 Bio-acetic acid

Acetic acid is an important platform chemical traditionally used as a food preservative. It is a clear, colorless, corrosive liquid with a sour taste and pungent odor. Acetic acid is produced both synthetically and by bacterial fermentation. Today, the biological route accounts for only about 10 percent of global production (Vidra and Németh, 2018). However, the fermentation process from renewable biomass remains challenging due to the difficulty of separating acetic acid from a mixture of several dilute components and other organic acids with similar properties. Current methodologies for acetic acid recovery have limitations and need to be improved to increase yield, purity, and energy consumption.

Applications: Bio-acetic acid is a renewable alternative to synthetic acetic acid produced from petroleum-based products. It is used in a wide range of applications, such as the manufacture of adhesives, films, textiles, paints, coatings, and other end-use products. Acetic acid is primarily used in the production of vinyl acetate, acetic anhydride, acetate esters, monochloroacetic acid and as a solvent in the production of dimethyl terephthalate and terephthalic acid. Vinyl acetate is used in the manufacture of latex emulsion resins for use in paints, adhesives, paper coatings, and textile treatments; it is a key ingredient in the manufacture of copolymers used in various types of coatings, such as automotive and industrial coatings, due to its excellent adhesion properties. Acetic anhydride is used in the manufacture of cellulose acetate textile fibers, cigarette filter tow, and cellulosic plastics. Acetic acid is also used to make polyvinyl alcohol

(PVOH), which is used in coatings and adhesives for its film-forming properties. In addition, bioacetic acid is an essential raw material consumed as a pH regulator and preservative in the production of personal care products such as shampoos, creams, and conditioners (Vidra and Németh, 2018).

Market: The global bio-acetic acid market size was valued at USD 209.6 million in 2022 and is expected to grow at a compounded annual growth rate (CAGR) of 5.3% from 2023 to 2030. The U.S. is the largest consumer of the product in North America with a revenue share of 73.2% in 2022. The bio-acetic acid market is characterized by high competition due to the presence of many large- and small-scale manufacturers and suppliers.

Producers worldwide: Airedale Chemicals, Bio-Corn Products EPZ Ltd., GODAVARI BIOREFINERIES LTD, Sucroal SA, Cargill, Inc., Novozymes A/S, LanzaTech, Afyren SAS, BTG Bioliquids.

7.4 Furfural

Furfural is a heterocyclic aldehyde, with molecular formula $C_5H_4O_2$. This chemical can be produced using lignocellulosic biomass through a two-step process based on the hydrolysis of pentose-rich polysaccharides, mainly xylans. The first step, hydrolysis, involves breaking down polysaccharides into monosaccharides, resulting in a xylose-rich hydrolysate. In the second step, the pentoses, mainly xylose, undergo dehydration to form furfural. This process can be carried out either in a single reactor (one stage) or in two separate stages. In the two-stage process, the hydrolysate can be separated from the insoluble solids after the first step and can be valorized in the subsequent conversion process, allowing for more efficient utilization of the lignocellulosic feedstock. It can also enable the optimization of each of the stages to increase yields (Padilla-Rascón et al., 2020). During pentose dehydration, three carbon atoms in the sugar ring are protonated, leading to the removal of three water molecules and the formation of furanic compounds. This reaction typically occurs in an aqueous medium due to its polarity, availability, sustainability, and low cost. However, undesirable side reactions also take place during the dehydration process (Padilla-Rascón et al., 2021). However, the use of diluted acid hydrolysis with sulphuric acid can prevent the degradation of xylose, obtaining high yields (Padilla-Rascón et al., 2021). Additionally, the presence of Lewis acid sites promotes carbohydrate isomerization, followed by dehydration through Brønsted sites. These catalysts can be homogeneous or heterogeneous. While the former generates a corrosive acid stream, the second type is costlier and more complex to synthesize, among other disadvantages to be challenged (Padilla-Rascón et al., 2020). Examples of Brønsted acids used as homogeneous catalysts are inorganic salts, especially chlorides ($FeCl_3$, NaCl, $AlCl_3$, etc.) (Padilla-Rascón et al., 2021). One-step conversion of corncob xylans has been proposed using an organo-catalyst in biphasic systems but with a lower yield than if the reaction was carried out directly from xylose (Dias Castro et al., 2023). For recovery, distillation, extraction, absorption, membrane separation, and CO_2-assisted phase separation methods are reported (Alphy et al., 2022). Currently, steam stripping followed by double distillation is used for furfural purification (Mariscal et al., 2016). In commercial production, furfural is typically obtained through the acid hydrolysis of biomass, commonly using sulfuric acid. However, producing furfural via fossil-based methods is not economically feasible (Komesu et al., 2022). Key furfural production methods are detailed in the review by Adhami et al. (2023).

Application: Furfural has numerous industrial applications and increasing market demand since it is utilized in a range of industries, such as pharmaceuticals, cosmetics, herbicides, and resin production. For example, it serves as an intermediate in the synthesis of chemicals like furfuryl alcohol and other furans like furan, methylfuran, furfurylamine, furoic acid, and tetrahydrofuran (THF) (Alphy et al., 2022; Mariscal et al., 2016; Silvateam, 2024). It can also be applied as a precursor of levulinic acid and γ-valerolactone, among other compounds (Mariscal et al., 2016; García et al., 2023). The latter can be used at the same time to produce chemicals and fuels, and as a green and low-toxicity solvent (García et al., 2023).

Market: The global furfural market was valued at USD 556.8 million in 2022 and is projected to grow in the coming years, largely driven by the increasing demand for furfuryl alcohol (Grand View Research, 2024).

Producer: China is the largest producer of furfural, accounting for approximately 70% of the global production capacity (Mariscal et al., 2016). An example of a Chinese industry is Hongye Holding Group Corporation Limited (Hongye Holding Group, 2024). A key producer is the Dominican Republic, with Central Romana Corporation, with a production of around 41 kt/year. It uses sugarcane bagasse and other agricultural waste such as corn husks and peanut shells (Central Romana Corporation, 2024). These two countries, along with South Africa (around 20 kt/year), contribute around 90% of the global furfural production capacity (Mariscal et al., 2016). In this country, for example, Illovo Sugar Africa produces furfural as a downstream product from sugar cane (ILLOVO SUGAR AFRICA, 2024). Other industries are Silvateam in Argentina (SILVATEAM, 2023a) and Pennakem in the US (Pennakem, 2024). Lenzing group with biorefineries placed on Lenzing (Austria), Paskov (Czech Republic) and Indianópolis (Brazil) produces several biobased chemicals from wood including furfural (Lenzing, 2024).

7.5 Furfuryl alcohol

Furfuryl alcohol or 2-(hydroxymethyl)furan ($C_5H_6O_2$), as furfural may occur naturally in foods (Scientific Committee on Food. 2003), but industrially, its production involves the utilization of about 65% of the furfural globally produced. It is produced using catalytic hydrogenation at high pressure in the gas or liquid phase, the former the most common route in the industry (Mariscal et al., 2016). It is possible to connect the conversion of xylose to furfural and furfural to furfuryl alcohol through Lewis acids sites and H-donor or metal sites, and H_2 (Sanches Jorqueira et al., 2023).

Applications: This important building block compound has applications in the chemical industry, primarily used to produce polyfurfuryl resins and molds for metal casting in the foundry industry, as an additive for phenolic resins and epoxy resins, in the manufacture of polyurethane foams and polyesters. It is a precursor for ethyl furfuryl ether, levulinic acid, and γ-valerolactone (Mariscal et al., 2016). In the pharmaceutical industry, it serves to produce drugs (e.g., ranitidine), tetrahydrofurfuryl alcohol (THFA), which is used as a solvent, and it also found applications in the manufacture of fragrances and flavors (Grosse et al., 2019).

Market: The industry size reached about USD 1,125 million in 2023, driven by the rapid expansion of the foundry sector, particularly in India and China. It is expected to nearly double this USD value by 2034 (FMI, 2024).

Producer: Its market and the market of other furans are highly linked to furfural production. For example, Hongye Holding Group Corporation Limited (Hongye Holding Group, 2024), Silvateam in Argentina, using wood residue resulting from the production of quebracho extract (SILVATEAM, 2023b), and Illovo Sugar Africa (ILLOVO SUGAR AFRICA, 2024) produce both furfural and furfuryl alcohol. However, TransFurans Chemicals, based in Belgium, produces furfural chemicals from sugar cane waste, leading the production of furfuryl alcohol from agricultural waste (TFC Biomass based chemicals, 2021).

7.6 Biobutanol

Biobutanol (C_4H_9OH) is a key platform compound with broad industrial applications in the pharmaceutical and chemical sectors and it is also a renewable fuel and solvent. Biobutanol can be obtained by the conversion route known as acetone–butanol–ethanol (ABE) fermentation using anaerobic bacteria like *Clostridium* spp., e.g., *C. acetobutylicum*, *C. beijerinckii*, *C. saccharoperbutylacetonicum*, and *C. saccharobutylicum* (Lin et al., 2023). Although the history of butanol started with Louis Pasteur in the 1860s, the industrial production of biobutanol has suffered ups and downs. The ABE fermentation process, initially developed before the First World War and associated with synthetic rubber production, expanded rapidly during both World Wars for solvent production, reaching its peak in the 1950s with plants in eleven countries. However, by the 1960s, advances in petrochemical technology led to its decline, with most plants closing by the 1980s, except for some plants in the USSR, China, and Egypt, which also eventually ceased (Jones et al., 2024). The technology around this process still presents challenges, including advanced metabolic engineering techniques to increase yield, limit product inhibition and enhance inhibitor tolerance, and cost-efficient solvent recovery and purification methods. It can make biobutanol production more profitable, e.g., it has been estimated that the price of biobutanol ($1.87/kg) is more than that of synthetic butanol ($1.52/kg of butanol) (Karthick & Nanthagopal, 2021). Alternatively, these authors have summarized other conversion routes to produce biobutanol based on thermochemical conversion routes or using other types of microorganisms like photosynthetic ones.

Applications: Butanol serves as an alternative or complementary fuel to bioethanol and gasoline or can be used as an additive for engine applications. Among butanol isomers, *n*-butanol and iso-butanol are preferred for blending (Karthick & Nanthagopal, 2021; Liu et al., 2022). These compounds have high calorific values, with lower heating values of 33.2 MJ/kg and 33.96 MJ/kg, respectively, octane numbers of 96 and 105.1, respectively, and auto ignition temperatures of 343 °C and 415.6 °C, respectively (Karthick & Nanthagopal, 2021). In the pharmaceutical and chemical industry, butanol is primarily used as a solvent or a raw material for chemical synthesis (Lin et al., 2023). For example, *n*-butanol is used to produce butyl acrylate, which presents industrial applications in paint and coating industries (Constantinos et al., 2019).

Market: It has been estimated that the global biobutanol market size reached USD 1.4 billion in 2023, and the demand for butanol is increasing (ImarcGroup, 2024), e.g., it can reach USD 1.8 billion by 2027 (Biswas, 2023).

Producers: There is growing interest in the production of butanol via fermentation as newsletters have been published by various producers in the last 15 years but with uncertain or no production today, e.g., Butamax Advanced Biofuels, LLC (BP, 2017), Cobalt Technologies (RenewableEnergyWord, 2010) or Green Biologics (C&En, 2019). However, if we focus on currently operating plants, in the USA, Gevo, Inc. is producing isobutanol together with bioethanol “in a side-by-side operation” using residual starches/sugars (Gevo, 2024). In India, Godavari Biorefineries, LTD, produces sugarcane-based biobutanol, among other specialty chemicals (Godavari Biorefineries LTD, 2016). Also, technologies have recently been launched, e.g., by GranBio from Brazil (GranBio, 2022).

7.7 Biosurfactants

Biosurfactants are metabolites of animal, vegetable, or microbial origin, with an amphipathic structure, with outstanding physical-chemical and biological properties, and can be used in various industrial sectors. In addition to the versatility of applications, biosurfactants are considered ecofriendly products and may act as possible substitutes for synthetic surfactants. Some examples (Franco Marcelino et al., 2023) are:

- Surfactin from hemicellulosic hydrolysate by a *Lactobacillus pentosus* strain,
- Glycolipid biosurfactants by yeast in hemicellulosic hydrolysate of sugarcane bagasse,
- Mannosylerythritol lipids (MELs) by a yeast of the genus Pseudozyma in semi-synthetic media using purified xylan as a carbon source,
- Rhamnolipids by bacteria such as *Pseudomonas aeruginosa*, *Acinetobacter calcoaceticus* and some of the genus Lactobacillus using the cellulosic hydrolysate of wheat straw and waste from fruit products;
- Glycolipids can be produced from oleaginous raw materials bacteria with microorganisms such as Pseudomonas, Bacillus and Serratia, and yeasts such as Candida, Starmerella and Pseudozyma.

Applications: Biosurfactants are currently used in remediation of pollutants in substitution of synthetic surfactants and show potential applications in many sectors of food, including food processing, in household detergents and personal care products (cleaning and hygiene products), medicines, and agriculture.

Market: The global biosurfactants market size was valued at USD 3.13 billion in 2023 and is projected to grow at a CAGR of 6.1% from 2024 to 2030. Europe dominated the global biosurfactants market with a share of 52.6% in 2023. The biosurfactants market in the U.S. is expected to grow rapidly in the coming years due to a growing demand for natural and organic products across all sectors.

Producers: Evonik Industries AG; Allied Carbon Solutions Co., Ltd.; Saraya Co., Ltd.; Jeneil Biotech, Inc. Solvay S.A.; Givaudan; Synthezyme LLC; Kaneka Corporation; GlycoSurf LLC; Stepan Company.

7.8 Biolubricants

A biolubricant is a biodegradable lubricant that is neither detrimental to health nor harmful to the environment. Their main advantages of most biolubricants, compared to the use of conventional lubricants, are biodegradability, sustainability and compliance with current legislation and customers' needs, focused on environmentally friendly products. Apart from that, other physical properties that are improved compared to mineral lubricants are: better lubricity, higher flash and combustion points, or higher viscosity index, and good resistance to shear among others. However, there are some disadvantages such as their lower oxidative stability and overall cold flow properties. Nevertheless, the use of additives-like antioxidants can improve the performance of this product. Biolubricants can be classified according to their chemical fluid composition in natural and synthetic oils. Natural oils are made using vegetable oils or animal fats, while synthetic oils use the natural oils as starting materials to form more advanced biolubricants. The main raw materials for biolubricant production are vegetable oils, such as rapeseed, sunflower, soybean, safflower, etc., which are mainly composed of triglycerides. There are several processes to obtain products (from vegetable oils) that can be used as biolubricants, such as selective hydrogenation, estolide formation process (a class of long-chain oligomeric structures containing fatty acid repeat units, with secondary ester linkages on the alkyl backbone), epoxidation or double transesterification. Biolubricants derived from vegetable oils are gaining importance for many applications, because they are biodegradable, have low ecotoxicity, strong oxidative stability, good emulsibility and do not contribute to volatile organic chemicals (Encinar et al., 2021; Cecilia et al., 2020).

Applications*:* Biolubricants can be used in substitution of synthetic or fossil-fuel derived lubricants in various industrial sectors, mainly transportation and manufacturing industries as emulsifiers, lubricants, plasticizers, surfactants, plastics, solvents, and resins (Cecilia et al., 2020).

Market: North America dominated the biolubricants market and accounted for the largest revenue share of 35.2% in 2022. European production of lubricants is approximately 4.5 million tonnes per year, and it is estimated that biolubricants represent about 3% of this production. The leading countries are Germany, France and the Netherlands."

Producers: ARIAL OIL (Germany), Bio-Circle Surface Technology GmbH (Germany), Thommen-Furler AG (Switzerland), TIPP-OIL.

7.9 Biopolymers

7.9.1 Polyhydroxyalkanoates (PHAs)

Polyhydroxyalkanoates (PHAs) are linear polymers of hydroxyalkanoates which are produced using microbial fermentation (>300 bacterial species and some archaea). (DA V. Kumar et al. International Journal of Biological Macromolecules 234 (2023) 123733). PHAs belong to polyesters superfamily and function as storage compounds under nutrient limiting conditions. PHAs have gained immense popularity over other bioplastics due to their versatile material properties and amenability for various applications. They have a high degree of biodegradability and biocompatibility. Further the possibility of easy blending with other biopolymers makes them a great material of choice in the biomaterial industry. The commercialization of PHAs is still hampered by technological limitations in the production process, low yields, and environmental concerns compared to their petroleum counterparts [16–18]. One major factor restricting the commercialization of PHAs production is the high cost associated with the production media components [19]. The use of renewable feedstock, especially agro-industrial wastes as cost effective fermentable substrate for PHA production, has gained importance in the last few decades. Examples of possible wastes are crop residues, post-harvest wastes, lignocellulosic wastes, sewage and municipal solid wastes.

Applications: Production of packaging materials (e.g. wrapping films), bottles, fibres, containers, bags, drug delivery carriers, bone screws, surgical pins, fuel additives and biofuels.

Market*:* The global polyhydroxyalkanoates market size was estimated at USD 650.66 million in 2023 and is projected to grow at a CAGR of 9.35% from 2024 to 2030. Europe dominated the polyhydroxyalkanoates market with the largest revenue share of 42.60% in 2023.

Producers worldwide: Bio-on SpA., PolyFerm Canada, Danimer Scientific, Tianjin GreenBio Materials Co., Ltd., Kaneka Corporation.

7.9.2 Alginates

Alginates are anionic hydrophilic edible heteropolysaccharides that exist both as components in brown seaweed (Phaeophyceae) and as capsular polysaccharides of some soil bacteria. Alginates consist of (1,4) linked b-D-mannuronic andL-guluronic acids, arranged in homogeneous (MM or GG) and heterogeneous (MG or GM) blocks, leading to a large diversity of structures, molecular

weights, and physicochemical properties. The physical and chemical properties of alginates depend on the percentage of each monomer, on how each monomer is placed in the chain, and on molecular weight. These factors affect the colour (ranging from white to yellowish-brown), the functional properties of alginate, solubility, reaction with metal ions, viscosity, and gel-forming properties. Commercial alginates are available in filamentous, granular, or powdered forms and are produced using Laminaria hyperborea, Laminaria digitata, Macrocystis pyrifera, Ascophyllum nodosum, Ecklonia maxima, Saccharina japonica (formerly Laminaria japonica), Lessonia nigrescens, Durvillea antarctica and Sargassum spp. It is estimated that 23,000 tons of alginate are produced from about 85,000 tons of algae annually (Abka-Khajouei, et al. 2022).
Applications: as an active ingredient in food texture, biofilms and pharmaceutics.

Market: The global alginate market size was valued at USD 728.4 million in 2020 and is expected to grow at a compound annual growth rate (CAGR) of 5.0% from 2021 to 2028. In terms of volume, Asia Pacific region dominated the market with a share of 37.05% in 2020 and is expected to maintain the leading position over the forecast period. The presence of numerous manufacturers and the easy availability of raw materials are responsible for the region’s growth. The presence of a large consumer base in countries like China and India also drives the regional alginate market. In terms of revenue, Europe is the leading regional market.

Producers*:* Íslandsþari, Algaia, Marine Biopolymers Limited, DuPont de Nemours, Inc., Ingredients Solutions, Inc., KIMICA, Ceamsa, Algae, Shandong Jiejing Group Corporation.

7.9.3 Xanthan gum

Xanthan gum is a natural, high-molecular-weight (approximately 2×10^6 Da) branched polysaccharide obtained by aerobic fermentation as an exopolysaccharide from the microorganism Xanthomonas campestris. The polymer backbone is identical to cellulose, consisting of β-D, 1,4 linked glucose units decorated with trisaccharide side chains attached to C-3 on alternating rings. The trisaccharide side chains consist of a D-glucuronic acid unit between two D-mannose units, and these align with the polymer backbone, thereby stiffening the chain. Xanthan gum is an anionic and nongelling polysaccharide; its viscosity is unaffected by pH or most salts. It behaves as if it were a neutral gum. Xanthan gum forms solutions exhibiting highly shear-thinning behavior, which is due to the stiffness of its molecules and/or the intermolecular associations of two or more molecules (Layek B., 2024). Xanthan gum is produced by fermentation based on renewable carbohydrate raw materials, such as glucose syrup, sucrose, or starch.

Applications*:* Xanthan gum is one of the important microbial bioplastics that find its applicability in main sectors such as food, cosmetics, pharmaceuticals and petrochemical industries as thickening and stabilizing agent.

Market: The global xanthan gum market size was valued at USD 622.4 million in 2023 and is projected to grow at a compound annual growth rate (CAGR) of 5.7% from 2024 to 2030. Asia Pacific xanthan gum market dominated the global xanthan gum market with a revenue share of 42.0% in 2023. Europe xanthan gum market was identified as a lucrative region in 2023. Germany, France, and the UK, leading chemical producers in the region, facilitate large-scale production.

Producers: ADM; Foodchem International Corporation; Deosen Biochemical (Ordos) Ltd.; Cargill, Incorporated; and Ingredion.

7.10 Proteins

The growing global population creates an urgent need for affordable, abundant, safe, and sustainable protein sources to meet rising nutritional demands and various diet types of requirements, e.g., vegans, vegetarians, or high-protein diets. Alternative proteins from agricultural sources, such as high-protein crops like pulses and oilseed cakes, agricultural (e.g., leaves) and food side streams, and fungi, algae, and insect sources (IEA Bioenergy, 2016; Ute Schweiggert-Weisz et al., 2020). Proteins derived from certain agri-food byproducts offer nutritional properties comparable to commonly consumed protein sources, as they contain essential amino acids or can be combined with other protein sources to help balance if there is any amino acid deficiency. Additionally, proteins can be extracted for use in their intact form or as hydrolysates or being produced by fermentation. Hydrolysis, which breaks peptide bonds, can be designed to enhance solubility, digestibility, and/or functional properties (Contreras et al., 2019). Overall, these scenarios are good for utilizing proteins, protein hydrolysates, or derived products within biorefinery processes. Moreover, biomass resources used for protein production in the food and feed sectors can also use the residual fraction as the feedstock of biorefineries (IEA Bioenergy, 2016). Another case is the valorisation of common foods' wasted stream to obtain multiple products, like the case of cheese whey, which contains proteins, lactose and other nutrients (Lappa et al., 2019). Some challenges include the variation in protein content among potential sources and finding appropriate technology for high-quality protein recovery and production. For example, besides traditional alkaline extraction, new technologies are being evaluated to intensify the process or even modify the protein features, like ultrasound, microwave, screw extrusion, and electro-based technologies, and the use of enzymes (Contreras et al., 2019).

Applications: Examples of applications include the use of protein isolates, concentrates, and hydrolysates for food and feed uses, e.g., flours, meat analogues, techno-functional ingredients (emulsifiers, foaming agents, among others), as surface active agents and for coatings, adhesives and film formulations (Contreras et al., 2020; IEA Bioenergy, 2016; Ute Schweiggert-Weisz et al., 2020).

Market: Regardless of the protein origin, the market sector of proteins is categorized in several ways, e.g., protein ingredients, alternative proteins, protein supplements, functional protein, protein hydrolysates, etc., although there could be some overlapping applications. As an example, the first one was valued at USD 77.7 billion in 2022 and is projected to grow driven by the rising demand for food products such as bakery items, yogurt, sausages, etc. Increased consumption of these products among health-conscious and elderly consumers is further fuelling the market's expansion, as well as the innovation in protein ingredients offering specific benefits like satiety, muscle repair, weight loss, etc. (Gran View Research, 2024). The alternative protein market size was about USD 15.4 billion in 2023, particularly dominated by the USA, followed by Europe (Procedence Research, 2024).

Producers: To focus on producers of biobased proteins or obtainment proteins in biorefinery approaches, some examples are Biofabrik in Germany, producing amino acids from pasture grass (Biofabrik, 2024), and, in the Netherlands, Enough that launched the mycoprotein-based protein ABUNDA (Enough, 2024) proposing a biorefinery scheme to also produce bioethanol from the waste stream within the Project PLENITUDE (Circular Bio-based Europe, 2023). In another approach to protein production, Arkeon produces several protein-based products by fermentation with archaea that use CO_2 (Arkeon, 2024).

Ongoing innovation: The ALEHOOP project is promoting pilot-scale biorefineries to produce proteins from algae- and plant-based biomass with feed and food uses (e.g., snacks, sports products, meat analogues, etc.) (CORDIS - EU research results, 2024), while the project Farmyng aims to produce marketable products using mealworms including protein in France (Circular Bio-based Europe, 2024). Another example is found in Africa, BIO4Africa, which aims to produce green protein concentrate powder from banana leaf protein and other residues (BIO4Africa, 2021).

8. Non-bio-based technologies relevant to biorefineries

8.1 Chemical Recycling of Plastics with Pyrolysis or Gasification

The production of plastic waste is a major global environmental challenge. In 2020, around 353 million tonnes of plastic waste were produced worldwide. In Europe, around 29.5 million tonnes of plastic waste are produced every year. Around 35% to 40% of this waste is recycled in Europe, whereas globally less than 20% of plastic waste is recycled . The rest ends up in landfill sites, incinerators or in the environment. With the tightening of policies in favour of the circular economy, Europe and other regions are redoubling their efforts to manage plastic waste, stimulating interest in advanced recycling technologies such as pyrolysis and gasification.
Broad comparison of technologies: batch vs. continuous plants, pyrolysis vs. gasification.

- **Batch Processing Plants**: These smaller, modular systems, like those used by Greenlina in Switzerland, offer flexibility in handling mixed or contaminated plastic waste. They require lower capital investment, are easier to maintain, and provide decentralized solutions for local waste management. These plants are suited for smaller-scale production, pilot projects, and niche markets where diverse feedstocks or specialized products are prioritized. However, they do not benefit from the major investments made by the major oil producers in the centralised chemical recycling of plastics. The interest in these smaller plants comes mainly from waste recyclers and local communities.
- **Continuous Processing Plants**: Larger, continuous systems used by companies like Brightmark Energy (USA) and Plastic Energy (EU) are designed for high efficiency and larger throughput. These plants typically have capacities ranging from 20,000 to 100,000 tons/year and are optimized for producing large quantities of pyrolysis oil or syngas. Continuous plants are preferred for commercial-scale operations due to their higher efficiency and ability to run non-stop. However, the centralised logistics raises questions on sustainability, including waste transport, energy consumption and dependence on continuous plastic production. These large-scale operations are less suited to decentralised waste management and may inadvertently contribute to maintaining the current reliance on fossil fuels for plastic production. A more balanced approach would be to integrate smaller decentralised plants closer to waste sources, promote plastics reduction and reuse, and accelerate the transition to sustainable materials and energy sources.

Pyrolysis is a more mature technology than gasification for processing plastic and mixed wastes. Pyrolysis thermally decomposes plastics in the absence of oxygen, producing pyrolysis oil, syngas, and char. Pyrolysis plants have larger capacities and are more commercially established, with pilot and demonstration plants at scales of 5 -100 ktons/year. The primary product, pyro-oil, can be refined into fuels or used as a chemical feedstock, making pyrolysis well-suited for integration into petrochemical processes. Syngas is burnt to produce energy, while char can also be burnt or transformed into carbon black, which is used as a reinforcing filler in rubber products (such as tyres) and in pigments, coatings and plastics.

There are also several laboratory scale experiments exploring the production of hydrogen from the pyrolysis oil.

On the other hand, plastic gasification is still in the developmental stage. Gasification involves partial oxidation of plastic waste, producing syngas (a mixture of hydrogen, carbon monoxide, and other gases) that can be converted into hydrogen, methanol, or other chemicals. Companies like Enerkem and PowerHouse Energy are pioneering this technology, but capacities are generally smaller (often below 25,000 tons/year) due to the complexity of syngas cleaning and processing. Gasification has high potential for hydrogen and methanol production but requires more advanced infrastructure compared to pyrolysis.

8.1.1 Existing companies with continuous pyrolysis processes

- Plastic Energy: Operating in Spain and the UK, with capacities ranging from 5,000 to 20,000 tons/year, producing TACOIL from plastic waste for use in fuel and chemical production.
- Brightmark Energy: A US-based company with a plant in Indiana that can process 100,000 tons/year of plastic waste, focusing on fuel production.
- Agilyx: Operating in the US and Norway, with a capacity of around 3,650 tons/year, specializing in turning polystyrene into feedstocks.
- Quantafuel: Based in Norway, running a plant with a capacity of 16,000 tons/year, converting plastics into liquid fuels and chemicals.

Existing companies with gasification processes:

- Enerkem: Focused on producing methanol and ethanol from mixed waste, including plastics, with a commercial-scale facility processing 100,000 tons/year in Canada.
- PowerHouse Energy: A UK company using modular gasification systems with capacities around 25 tons/day, focusing on hydrogen and electricity from plastic waste.

Both pyrolysis and gasification fit well with the biorefinery concept by converting plastic waste into valuable chemicals and fuels. These technologies enhance biorefinery operations by enabling the recycling of plastic waste back into valuable products, reducing the dependency on virgin fossil resources.

8.1.2 Outlook

The outlook for both pyrolysis and gasification is promising due to the growing focus on sustainability, waste reduction, and renewable energy. Pyrolysis is expected to continue scaling up, driven by demand for pyrolysis oil and chemical recycling, with an emphasis on integrating recycled materials into the petrochemical industry. Gasification, while currently at a smaller scale, holds significant potential, particularly in regions investing in hydrogen economies and clean fuel production.

The expansion of regulations around plastic waste management and the development of more efficient, economically viable technologies are expected to accelerate the adoption of both pyrolysis and gasification in the coming years. Increased investment and policy support, particularly in Europe and Asia, will likely drive the commercialization of these technologies.

Both technologies fit well within the biorefinery concept, supporting circular economy initiatives by converting plastic waste into feedstocks for new materials and fuels, reducing reliance on fossil resources. As technological advancements continue and market demand grows, both pyrolysis and gasification are likely to play key roles in the future of waste management and sustainable energy production.

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