Waste biorefinery technologies
for accelerating sustainable
energy processes

LESSONS LEARNED FROM 1ST GENERATION BIOREFINERIES

CA 20127

Waste biorefinery technologies for accelerating
sustainable energy processes (WIRE)

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List of acronyms

IEA: International Energy Agency

EU: European Union

FAME: Fatty Acid Methyl Ester

MSW: Municipal Solid Waste

1G: 1st Generation

FFA: Free Fatty Acid

PFR: Plug Flow Reactor

CSTR: Continuous Stirred Tank Reactor

FBR: Fixed Bed Reactor

AD: Anaerobic Digestion

ASTM: American Society for Testing and Materials

EN: European Norm

VFA: Volatile Fatty Acid

CN: Cetane Number

HDRD: Hydrogen-derived Renewable Diesel

CHP: Combined Heat and Power Unit

RED: Renewable Energy Directive

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Executive summary

This report underscores the significance of leveraging biomass as a viable alternative to conventional fossil fuels, aligning with stringent environmental regulations aimed at curbing greenhouse gas emissions. Biomass-based fuels emerge as a crucial element in the global energy matrix, serving as an additional and sustainable energy resource. The discussion within this report centers on first-generation biorefineries, initial generation feedstock-derived biofuels, leading biofuel-producing nations, and the key sustainability challenges associated with first-generation biofuels.

First-generation biofuels encompass bioethanol, biodiesel, and biogas, primarily sourced from feedstocks such as corn, sugar cane, soybeans, vegetable oil, palm oil, and animal fats. Despite their potential, these biofuels face significant sustainability challenges. Competition for land use between food and fuel production, alterations in land use patterns, and potential increases in greenhouse gas emissions from fossil fuel use in upstream processes are primary concerns. The economic viability of first-generation biofuels heavily relies on the type of feedstock and the geographical region of its production. The cultivation of energy crops for biofuel production may affect food prices and compete with food crop cultivation for available land. However, the large-scale production and conversion of biomass into biofuels present opportunities by creating jobs and boosting revenue within the agricultural sector.

In conclusion, promoting the use of first-generation biofuels requires a delicate balance between addressing sustainability challenges and capitalizing on their potential benefits. Strategic planning, policy interventions, and advancements in technology are essential to mitigate negative impacts and drive the adoption of biomass-based fuels towards a more sustainable and efficient energy future.

1. Introduction

Biomass is one of the most important renewable resources used as an alternative for the production of various value-added products and energy sources. The increasing trend towards the use of biomass is attributed to the environmental issues caused by the excessive use of fossil fuels. Biorefineries have emerged as promising alternatives for upgrading all biomass components for various production sectors [1]. The biorefinery definition formulated by IEA Bioenergy Task 42 is quite broad: "Biorefinery is the sustainable processing of biomass into a range of marketable products and energy" (Figure 1) [2].

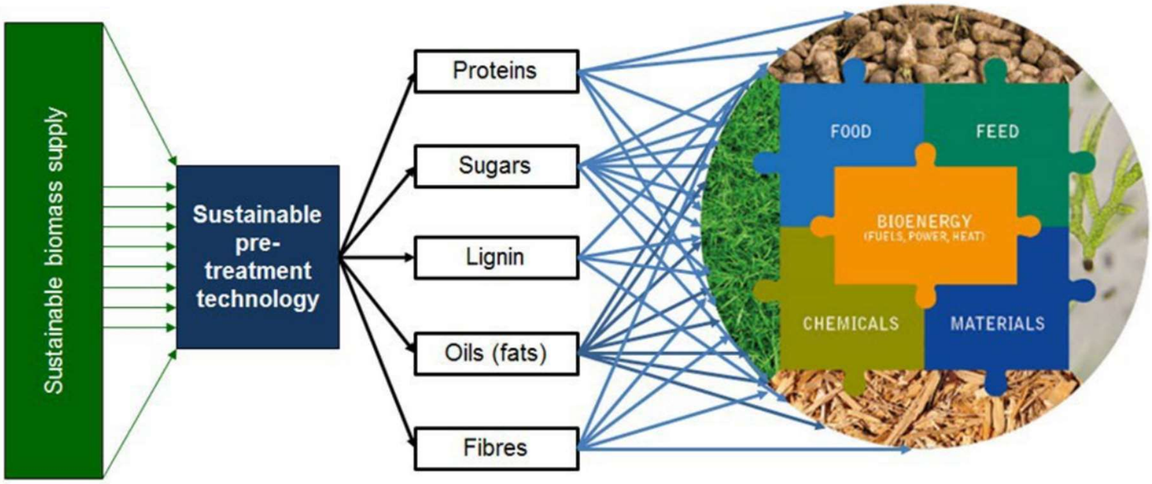


Figure 1 Schematic representation of a biorefinery [2]

Biorefineries are key to promoting sustainable development and implementing the bioeconomy in different regions, as biomass is a renewable resource available worldwide [1, 3]. Biorefineries have been researched and designed for many years. The product portfolio of existing plants can be expanded, as most biomass processing plants are focused on the production of energy feedstocks (i.e., biogas, biodiesel, bioethanol), some value-added products (e.g., levulinic acid, bioplastics), and bioenergy (heat and electricity) [1, 4].

Various types of biorefineries have been described in the literature. Most of them are defined mainly on the basis of the individual feedstocks, e.g., corn-based biorefinery, wood-based biorefinery, forest-based biorefinery, palm-based biorefinery, algae-based biorefinery, etc. [5]. On the other hand, some researchers have defined biorefineries according to the generation of feedstock [5]:

1. First-generation biorefinery (energy crops, edible oilseeds, food crops, animal fats, etc.),
2. Second-generation biorefinery (lignocellulosic biomass) and
3. Third or fourth-generation biorefinery (algae and other microbes).

First-generation biorefineries use feedstocks such as corn, sugar cane, soybeans, vegetable oil, animal fats, etc. that are renewable but face numerous challenges, including competition between food and fuel, changes in land use, and potentially increased greenhouse gas emissions due to the use of fossil fuels in upstream processes [5].

Based on different technologies, the three main types of first-generation commercial biofuels are biodiesel, bioethanol, and biogas [6, 7]. Biodiesel is produced by the transesterification of vegetable oils. Residual oils and fats can be used as a substitute for diesel in diesel engines with minor modifications. During transesterification, triglycerides react chemically with alcohol (e.g., biomethanol) in the presence of a catalyst or enzyme to produce biodiesel and glycerol [6, 8]. Bioethanol is produced by the fermentation of sugar or starch. It is used as a substitute for gasoline or as a starting material for ethyl tertiary butyl ether, which is easier to mix with gasoline. Biogas, a mixture of CH_4 and CO_2, is produced by anaerobic digestion of organic material [6, 9]. Biogas can be used as a vehicle fuel (if biogas is compressed) and as a replacement for natural gas (if biogas is cleaned up and upgraded to natural gas standards).

This report analyzes key characteristics of first-generation biorefineries, starting with the characteristics of the feedstock, the most commonly applied conversion technologies for first-generation biofuels, and brief discriptions of the advantages and disadvantages of first-generation biofuels.

2. Brief descriptions of key feedstock used/foreseen, as biofuel feedstocks

The production of biofuels (bioethanol, biodiesel, and biogas) has increased significantly in recent decades worldwide because they represent alternatives to fossil fuels due to the increasing demand for energy resources and elevated concerns about greenhouse gas emissions.

The most common first-generation biofuels (1G) include bioethanol, biodiesel, and biogas derived mainly from corn, sugar cane, soybean, vegetable oil, palm oil, animal wastes etc.

1G biofuels, except for biogas, are derived from edible biomass such as starchy feedstocks (corn, wheat, barley, ray, triticale, sorghum grain, and potato), sugary raw materials (sugar cane, sugar beet, fruit, and sugar-containing juices from processing of these crops, and whey), and oilseed crops (rapeseed, soybean, corn, sunflower, and palm) [10]. Approximately 90% of total biofuels are produced from edible biomass, e.g., grain and vegetable oil [6]. 1G biofuel production competes with the use of sugar and starch crops as food or feed, thus influencing their supply [11–14]. 1G biofuels showed a promising capability for minimizing fossil fuel combustion and lowering atmospheric levels of CO_2 which are consumed by crops as they grow.

Sugar and starch crops are conventional feedstocks for first-generation biofuels, primarily bioethanol. Bioethanol is worldwide manufactured by the alcoholic fermentation of carbohydrates from different types of starchy or sugary raw materials, usually by yeast (*Saccharomyces cerevisiae*, *Saccharomyces pastorianus, Schizosaccaharomyces pombe, and Kluyveromyces sp.*) [11]. The exploitation of sugar-containing feedstocks for industrial bioethanol production started at the beginning of the 20th century [15]. Nearly 60% of the global bioethanol production is produced from starch feedstocks, while approximately 40% is produced from sugar beet and sugar cane [16].

It is stated that 95% of worldwide biodiesel production is achieved by utilizing edible vegetable oils consisting of rapeseed, soybean, corn, sunflower, and palm mostly [17]. Besides, 80% of the total biodiesel demand is met by Indonesia, Brazil, the United States of America (USA), Malaysia, Argentina, Spain, Belgium, and Germany [18]. Presently, there are several technologies such as pyrolysis, supercritical fluid extraction, emulsification, and transesterification which are applied for biodiesel production. Among all these technologies, transesterification is the most common applied technology to obtain biodiesel [19].

Biogas, which is produced at most biological treatment plants, has been considered one of the most important renewable energy sources. Biogas is a mixture of methane (CH_4), carbon dioxide (CO_2), and several traces of gas. Methane is the most valued content of biogas because it is a hydrocarbon fuel. The range of biogas production from several organic waste materials is reported as 0.20-1.11 m^3/kg of dry solids [20]. Biogas can be utilized as a fuel in several ways, either as raw biogas or upgraded biomethane. Biogas, like other biofuels, has also been used for the displacement of conventional transport fuels (e.g., gasoline, diesel) in some countries like Sweden, Brazil, China, etc., in addition to bioethanol and biodiesel [21].

2.1 Feedstok for bioethanol production (sugar and starch crops)

Starch-based feedstocks include grains, such as corn or wheat, and tubers such as (sweet) potatoes and cassava (Figure 2).

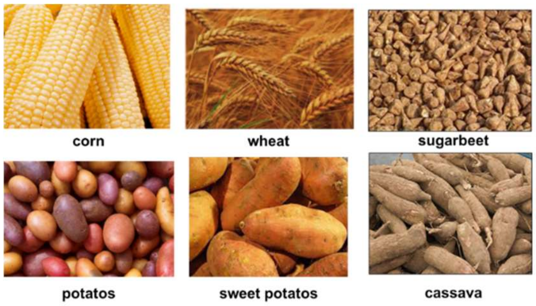
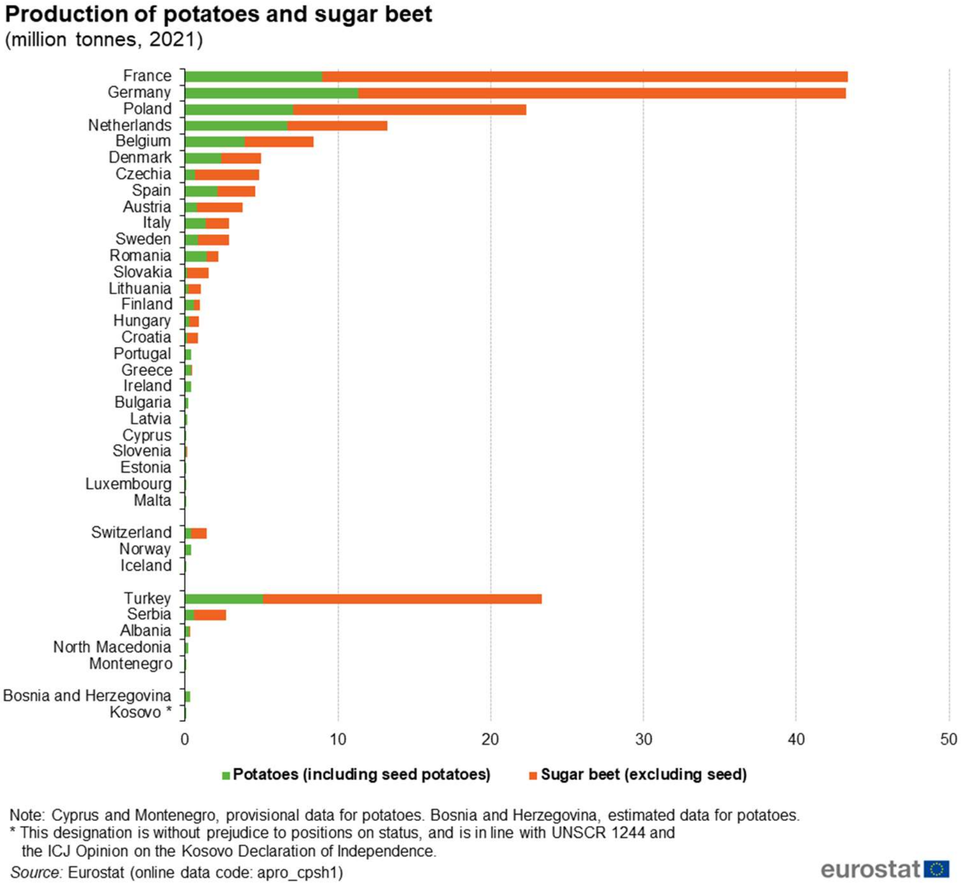


Figure 2 Images of a selection of sugar and starch crops

Wheat (*Triticum* species) has a starch content of about 70% and it is the most produced crop worldwide after corn and rice. Corn contains about 70% starch and in 2020, in Europe Union (EU), 49.5% of the ethanol produced was from corn, followed by wheat (18.5%) and sugar (17.8%) [22]. Potatoes (*Solanum tuberosum*) contain up to 19% starch. The EU produced 54.0 million tons of potatoes in 2020 and the main potato producers were Germany, France, Poland, and Netherlands (Figure 3). Sweet potatoes are characterized by a starch content of around 70% and offer relatively high ethanol yields [23]. Sweet potatoes can be cultivated in tropical or warm regions and China is the biggest producer of sweet potatoes, and is active in their conversion to bioethanol [24]. Cassava is an important food and feed crop in many tropical countries since it can also be cultivated on drier or poorer soils. Cassava contains circa 40% of starch and China is a big promoter of cassava as biofuel feedstock [23].

Other starch-based feedstocks are: i) Barley, a winter crop that is planted in rotation with crops such as corn and soybean with a starch content ranging between 50 and 75%; ii) Rye, a rather robust grain with a starch content of around 60% able to grow on poorer soils; and iii) Millet/Sorghum species, able to grow on marginal soils with a starch content about 75%. Sugar beet is a root crop very rich in sucrose (up to 18%) [25]. The European Union is the world’s leading producer of sugar beet, with around 50% of the total amount [26]. However, sugar beet represents only 20% of the world’s sugar production, with the other 80% produced from sugar cane [26]. Most of the EU's sugar beet is grown in the northern half of EU (mainly in France, Germany, the Netherlands, Belgium and Poland). In 2020, the EU produced around 110 million tons of sugar beet, three quarters of which came from the four leading producers, Germany, France, Poland and the Netherlands [27] (Figure 3).



Note: Cyprus and Montenegro, provisional data for potatoes. Bosnia and Herzegovina, estimated data for potatoes.
* This designation is without prejudice to positions on status, and is in line with UNSCR 1244 and the ICJ Opinion on the Kosovo Declaration of Independence.
Source: Eurostat (online data code: apro_cpsh1)

Figure 3 Potatoes and sugar beet European production in 2021

Sugar cane is a perennial grass of the family Poaceae, primarily cultivated for its juice highly rich in sugar. Most of the world's sugar cane is grown in subtropical and tropical areas. Raw cane sugar (or brown sugar) normally contains 94–98.5% sucrose and 1.5–6% non-sucrose components (reducing sugars, organic acids, amino acids, proteins, starch, gums, coloring matter, and other suspended matters) [28].

Sugary feedstocks (e.g., sugars from sugar cane, molasses, sugar beet, and fruits) contain simple sugars, monosaccharides (glucose or fructose), or disaccharides (sucrose or saccharose), which can be extracted with water by simple technology and can be directly fermented using yeast to produce ethanol. On the other hand, starch and lignocellulose-containing feedstocks must be additionally pretreated and hydrolyzed into fermentable sugars by processes like milling, thermo-chemical pretreatment, enzyme hydrolysis, and/or detoxification prior to fermentation. Therefore, bioethanol production from sugary feedstocks is more feasible than from feedstocks containing starch or cellulose. In EU, sugar is mainly produced by sugar beet processing. Molasses is the main by-product of the beet sugar industry which is conventionally used in bioethanol and yeast production processes. The total residual sugar content in molasses is 50–60% (m/V), of which about 60% is sucrose, which makes this substrate suitable for large-scale bioethanol production. Also, intermediate products such as raw, thin, and thick juice, as well as high-purity crystal sugar are excellent raw materials for bioethanol production [11, 15, 29].

Starch-containing feedstocks (cereals or potatoes) must be mechanically prepared by milling or grinding and suspended in water to release starch granules from plant materials. Starch is a polyglucan consisted of amylose (long chains of more than 1000 glucose units linked by α-1,4 glycosidic linkages) and amylopectin (branched polyglucan of 1000–6000 units linked by α-1,4 and α-1,6 glycosidic linkages). For bioethanol production, it is necessary to perform the starch hydrolysis, usually by treatment with technical α-amylase and glucoamylase, into glucose, which can be converted into ethanol by s yeast. The potential of different sugary and starch feedstocks for bioethanol production is summarized in Table 1 [30].

Table 1 The potential of different sugary and starch feedstocks for bioethanol production (adapted from [30]).

Biomass	Major influential features
Sugar cane *(Saccharum officinarum)*	High biomass yield
	High sucrose content
	High efficiency to accumulate solar energy
	Global production is 360 million ton/year, crop yield is 60–79.5 t/ha
	Residues are good source for generating electricity and 2nd generation bioethanol
Sweet sorghum *(Sorghum bicolor)*	More drought tolerant crop than sugar cane
	Can grow in the arid land
	Stalk juice is a promising feedstock for bioethanol, while grains are used for food and starch-based ethanol production
	Stalks contain significant amounts of sucrose, glucose and fructose
	Average syrup yield from stalk is 1900 L/ha
Sugar beet *(Beta vulgaris)*	Major source of sugars in Europe and North America
	Crop yield is 79.1 t/ha
	Average syrup yield is 60–120 t/ha, average ethanol yield is 95 l/ton of stalk
Watermelon *(Citrullus lanatus)*	Around 20% of waste watermelons during or after harvesting of crops can be used as bioethanol feedstock
	Juice can be used as a diluent for molasses that increases overall sugar content in the feedstock and reduce water consumption
Dates *(Phoenix dactylifera)*	A good amount of dates is wasted each year in the date producing countries, which can be used as ethanol feedstock
	Contains high amounts of individual sugars (sucrose, glucose and fructose) as estimated for roughly 70% of total sugars
	Long time storage

Table 1 (continued) The potential of different sugary and starch feedstocks for bioethanol production (adapted from [30]).

Molasses	A renowned ethanol feedstock enriched with sucrose, glucose, and fructose
	An industrial waste and thus no debate of food versus fuel.
	Valorization of the waste material
	Molasses yield is approximately 3–7 t/100 t of sugar cane

Crops	Major influential features
Corn *(Zea mays)*	Corn ethanol is a mature technology
	Not only the main feed stream but also the wasted corn contributes to the overall supply of raw materials.
	Around 5% of the corn is wasted each year that can produce about 9.3×109l of ethanol with a replacement capability of about 6.7×109l of gasoline.
	Protein rich co-product of corn ethanol plant is used as animal feed
	High fermentable hybrids can easily be developed for improved ethanol yield
Wheat *(Triticum aestivum)*	Conversion efficiency of wheat starch into ethanol is around 95%
	The annual gross energy production for wheat derived bioethanol is 66 GJ/ha
	Kernel yield is 5.1 t/ha
Cassava *(Manihot esculenta)*	A tropical root crop produced by many countries
	Can be easily hydrolyzed by various techniques
	Cassava starch does not have much application in food industries compared to corn starch, thereby available with a lower price
	Available throughout the year due to its flexibility in terms of planting and harvesting
	Crop yield is 13.6 t/ha
Barley *(Hordeum vulgare)*	About two billion gallons of ethanol can be produced per year from barley in North America
	Yield may vary between 0.82 t/ha and 3.08 t/ha with a global average of 2.5 t/ha
	Can be grown in areas that normally not used for corn, and hence, a barley-based ethanol industry will benefit farmers and rural economy outside the ‘‘corn belt’
	Winter barley can be double-cropped with corn and soybean to give farmers three crops in each two-year cycle
	Winter barley as a cover crop can prevent loss of nitrates, phosphates, and sediments into watersheds and hence provide protection for the environment
Canna *(Canna edulis)*	A non-food biomass source, yearly output is approximately 4.5 kg/m2
	Can be cultivated in marginal lands and in subtropical highlands with low nutrient demand
Sorghum (grain) *(Sorghum bicolor)*	Enrich with starch like corn
	Ability to grow in a wide range of soil types and climates
	Efficient in water usage
	Drought tolerant
Sweet potato *(Ipomoea batatas)*	An important staple crop in terms of total biomass
	Produced globally
	Drought resistant crop requiring low chemical and fertilizer inputs
	Can be grown in marginal soils

Table 1 (continued) The potential of different sugary and starch feedstocks for bioethanol production (adapted from [30]).

Potato *(Solanum tuberosum)*	Cheap substrate and rich in starch
	Processing is easier than that of other grains
	Around 5–20% of the crops are wasted that can be used for bioethanol production
	Global production is more than 140 million ton/year
Yam *(Dioscorea rotundata)*	Large starchy tuber and produced both annually and perennially in Africa, America, Caribbean, South Africa and Asia
	Several principal species are widely grown throughout the tropics, which are white yam (*D. rotundata*), yellow yam (*D. cayenensis*), bitter yam (*D. dumetorum*) and water yam (*D. alata*)
Jerusalem artichoke *(Helianthus tuberosus)*	A tuberous-rooted perennial crop
	Tuber is rich in synanthrin and other fructose polymers
	Inulin content in fresh tuber is about 10–20% with an average of 15%
	Sugars are stored in the roots and tubers
	High alcohol potential
	No requirement of fertile soil for its growth
	Next season's crop is produced from small tubers left in the field, so no ploughing or seeding is necessary
Iles-iles *(Amorphophalus campanulatus)*	Can be used as basic material for bioethanol production
	Non-food ethanol feedstock
	High carbohydrate content
	Low price
Oat *(Avena sativa)*	Global oat production is 2.67×107 t/year
	Yield can vary from 1.54 to 2.31 t/ha with an average yield of 1.98 t/ha
	Utilization of only wasted oat grain could produce about 225 million liter of ethanol that can replace 161 million liters of gasoline
	Dry milling can produce 1.5 kg distiller's dried grains with soluble (DDGS) per kg of ethanol that can replace usage of oat as animal feed
Banana *(Musa sp.)*	Fruit, pulp, and skin are enriched with starch
	Valorization of waste if banana peel is used for ethanol production
	Ethanol production from banana has shown a positive energy balance

In EU, sugar beets are expected to be the primary ethanol feedstock in 2022 at 8.092 million metric tons, followed by corn at 6.64 million metric tons, wheat at 2.95 million metric tons, barley at 521,000 metric tons, rye at 487,000 metric tons and cellulosic biomass at 260,000 metric tons [31]. The cost-effectiveness of bioethanol production is highly dependent on the type and price of feedstocks which can contribute 40-75% of the total cost, and also, the cost of energy and chemicals used in the pretreatment of raw materials for the preparation of fermentation media [11].

2.2 Feedstok for biodiesel production (oilseed crops)

Raw materials have crucial role on the cost of biodiesel production which is estimated to be in the range from 60% to 80%. However, usage of high-cost first generation biodiesel feedstock is not an attractive alternative which is currently at 30% higher cost than that of petroleum-based feedstock [32]. Among the feedstock for biodiesel production, oilseeds account for 20% of the world grain production. The major use of oilseed crops is the oil, which, in many cases accounts for up to 80% of the crop value. The major oilseed crops of the world include soybean, cottonseed, rapeseed, sunflower, groundnut (or peanut), sesame seed, linseed, safflower, and mustard seed (Figure 4). Many other crops can be used for oilseed production including castor beans, grape seed, tobacco seed, flax, corn oil, tung beans, and okra.

Figure 4 The major oilseed crops of the world [33]

Oil palm, soybean, rapeseed, sunflower, peanut and cotton are the most abundant oils, produced and traded around the world. They account for over 90% of the total oil production worldwide. Soybean, rapeseed, and sunflower oils are the most produced oils (Figure 5, panel A). The largest producer of soybean oil is China (29%), followed by the USA (19%) and Brazil (16%). Canada (17%), China (15%) and Germany (13%) are the main producers of rapeseed. Sunflower oil production is dominated by Ukraine and the Russian Federation, accounting for over 50% of the world's production. Regarding flaxseed, China is the main producer (30%), followed by Belgium (16%). More details regarding the worldwide production of oilseed crops are reported in panel B, Figure 5 [34].

The oil content, quality, and composition factors vary considerably on the crop species or cultivar and upon the environmental conditions in which the crop is grown. Vegetable oils contain 95-98% triacylglycerols (or triglycerides). The remaining fraction consists of phospholipids, mono and diacylglycerols, and unsaponifiable components including sterols and tocopherols. The oil and protein contents of the major oilseed crops are shown in Table 2 along details about the contents in fatty acids [35].

Table 2 Composition of the major oilseed crops (adapted from [35])

Oilseed	Classi_ fication	Main use	Oil (%)	Proteins (%)	% Palmitic (C16:0)	% Palmitoleic (C16:1)	% Stearic (C18:0)	% Oleic (C18:1)	% Linoleic (C18:2)	% Linolenic (C18:3)	% Arachidic (C20:0)	% Gadoleic (C20:1)	% Behenic (C22:0)	% Erucic (C22:1)
Soybean	normal	food	20	46	8-14	<0.2	2-6	17-30	48-59	4-11	<0.6	<0.5	<0.7	<0.3
	high oleic				6		3	84	2	4				
Cotton	normal	fiber	16	37	21-26	<1.2	2-3	15-22	47-58	<0.5	0.2-0.5	<0.1	<0.6	<0.3
Peanut	normal	food	41	46	8.3		3.1	56	26		2			
Rapeseed	low erucic	oil	41	34	2-7	<0.6	1-3	51-70	15-30	5-14	0.2-1.5	0.1-5	<0.6	<2
	high erucic				1.5-6	<3	0.5-3	8-60	11-23	5-13	<3	3-15	<2	2-60
	high oleic				3-4		2-3	63-76	13-25	2-3		1-2	<0.6	<0.2
Sunflower	linoleic	oil	40	28	5-8	<0.3	2-7	14-40	48-74	<0.3	0.1-0.5	<0.3	0.3-1.5	<0.3
	mid-oleic				4-5		3-4	50-75	20-30	<1				
	oleic				2-5	<0.1	3-7	75-91	2-17	<0.3	0.2-0.5	0.1-0.5	0.5-1.5	<0.3
Sesame	normal	food	40-60	42	8-12	<0.2	5-6	36-42	42-48	0.3-0.4	0.3-0.6	<0.3	<0.3	
Flaxeseed	normal	oil	40	32-34	5-7	<0.3	3-4	19-20	14-17	52-61	<0.5	<0.6		
	low linoleic				6		3-4	15	73	2-3				
Safflower	linoleic	oil	34	23	5-8	<0.2	2-3	8-22	68-33	<0.1	0.2-0.4	<0.3	<1	<1.8
	oleic				3-6	<0.2	1-3	70-84	9-20	<1	0.3-0.6	<0.5	<0.4	<0.3
Mustard	*B. carinata*	Condi-ment	20-50	35	4-10		<2	8-23	15-22	18-27		<2		20-50
	B. nigra				2-7		<2	10-27	15-22	11-27				33-45
	B. juncea				3-10		1-3	15-64	14-28	9-24		1-3		<40

Figure 5 Worldwide production of the main oilseed crops (adapted from [34]).

Details regarding the characteristics and the properties of the oilseed crops mainly produced worldwide and used in biorefinery processes [34–36].

Sunflower is an ancient oilseed crop, indigenous to North America. Currently, oil-sunflower is one of the major oil-producing crops grown throughout the world. Sunflower is grown for the seed oil, which is 80% of the seed value. Sunflower oil is a low-cholesterol edible oil, rich in monounsaturated and polyunsaturated fatty acids (ca. 90%, Table.2), lecithin, sterols, tocopherols, phenolic compounds, peptides, vitamins and minerals. Sunflower can be used as food, for livestock feed, or in industry (paint, cosmetics, biodiesel, lubricants).

Rapeseed or canola is one of the world's most abundant oil crops. It is grown in more than 120 countries around the world. China is among the large producers of canola (27.5% of the world production). The oil is the main value of the crop yielding 42% oil, while the meal contains 35% protein. Triacylglycerol of canola oils constitute from 94.4 to 99.1% of the total lipid. It is rich in erucic acid (∼ 50%), monounsaturated and polyunsaturated fatty acids, but also contains low amounts of saturated fatty acids (Table 2). It also lacks in cholesterol and contains fat-soluble vitamins, phenolic compounds, sterols and tocopherols. Because of health concerns, traditional rapeseed oil is currently used in industrial applications and for the production of biofuels rather than in edible purposes.

Soybean is an ancient crop. USA, Brazil, Argentina, and China cover almost 90% of the world's soybean production. Soybean oil contains relatively low amounts of saturated and monounsaturated fatty acids, with linoleic acid as the major component followed by oleic acid (Table 2). Soybean oil contains also sterols, tocopherols, and hydrocarbons. The seeds are rich in protein, mainly globulins, which make up 90% of the total proteins and 36% of the seed weight. In addition to its food application, soybean oil or its FAME (methyl soyate) are exploited in industry, mainly for the production of inks, coatings, composites, lubricants, soap, plastics, papers, paints, varnishes, cosmetics, and pesticides.

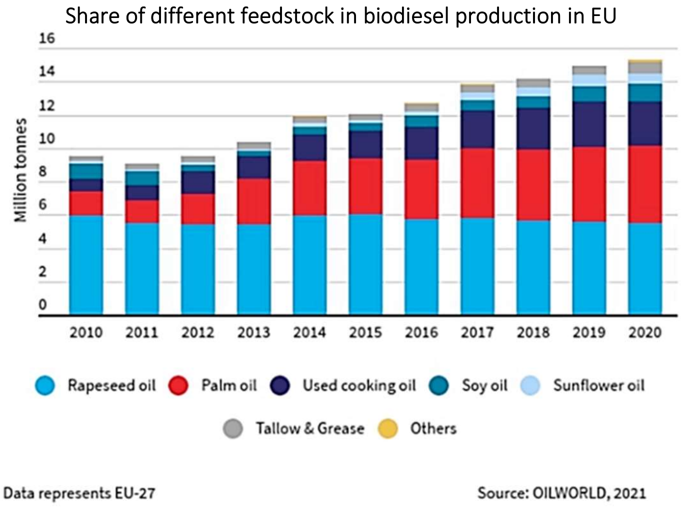
Cottonseed is a by-product of cotton ginning, and 16–17% of its weight is cottonseed oil. More than a quarter of the world cotton is cultivated in India, followed by the USA (16%), China (14%), and Pakistan (8%). The remaining production comes from Turkey, Australia, Greece, Brazil, and Egypt. Linoleic acid is the major fatty acid, followed by palmitic and oleic acids and other small quantities of other fatty acids (Table 2). The minor components are phospholipids, tocopherols, sterols, resins, carbohydrates, pesticides, gossypol, and other pigments. Cottonseed oil is used as liquid oil and in the manufacturing of shortening and margarine. It can be also used in the manufacture of soap, lubricant sulfonated oil, pharmaceuticals, rubber, as a carrier for nickel catalysts, and, to a lesser degree, in the manufacture of leather, textiles, printing ink, polishes, synthetic plastics, and resins.

Sesame is one of the oldest traditional oilseed crops. Asia covers more than 50%, while Africa is covering 43% of world production. Sesame seeds consist of oil at 44–57%, protein at 18–25%, and carbohydrates at 13–14%. Linoleic acid and α-linolenic acid are the most abundant fatty acids in sesame oil constituting more than 80% of fatty acids in the oil (Table 2). Sesame seeds are used intact or as oil and meal. Sesame seeds are rich in fat, protein, carbohydrates, fiber, and essential minerals, and for that, its seed is highly valuable in nutritional and medicinal purposes.

Groundnut/peanut seed is an herbaceous annual legume cultivated in tropical and subtropical regions. Groundnut is the major oilseed crop in Asian and African countries, and together, they contribute 80% of the total production area of groundnut. It is a good source of edible oil and protein. Kernel of groundnut contains 40–54% oil, 22–36% protein, and 10–20% carbohydrate. Peanut oil is rich in mono unsaturated oleic acid followed by diunsaturated linoleic acid followed by saturated palmitic fatty acid. Sterols are the minor constituents in groundnut oil, and they range from 0.09 to 0.3%. The main product is the oil that has 80% unsaturated fatty acids making it a nutritionally favorable oil.

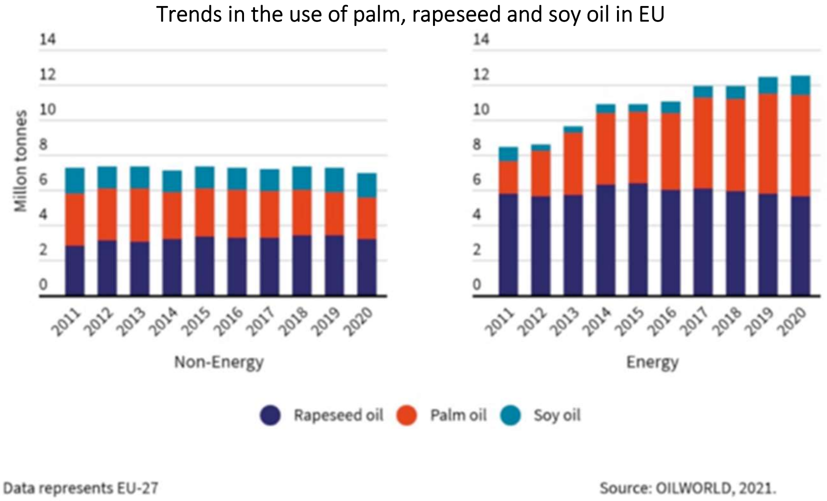
Flaxseed is an ancient oilseed crop cultivated around the world. Its oil content ranges between 28 and 30%. Major fatty acid of flaxseed oil is linolenic acid followed by oleic acid, linoleic acid, and palmitic and stearic acids (Table 2). Flaxseed is an important source of bioactive molecules, indeed, its oil can be used as a supplemental nutritional component because of the presence of omega-3-α-linolenic acid. Due to its content of highly unsaturated fatty acids, flaxseed oil is unsuitable for cooking purposes, anyway it has been industrially used for the production of paints, plastics, soap, coatings, inks, varnishes, linoleum and herbicide adjuvants.

Nonfood uses of vegetable oils in developed countries is high due to developments in the oleochemical industries with a shift away from petroleum-based products to environmentally friendly oleochemicals. In addition, there is an increase in technological developments, particularly with the genetic modification of oilseeds to create a new range of products. The graphics reported in the following Figure 6 highlight the use of oilseed oil in the production of biodiesel in 2020 in EU [37].


Share of different feedstock in biodiesel production in EU

Data represents EU-27

Source: OILWORLD, 2021


Trends in the use of palm, rapeseed and soy oil in EU

Data represents EU-27

Source: OILWORLD, 2021.

Figure 6 Use of oilseed oil in the production of biodiesel in 2020 in EU (adapted from [37])

3.1 Feedstock for biogas production

As it is mentioned, biogas is produced by implementing anaerobic digestion. The anaerobic digestion technological process has the capacity to accommodate a wide variety of feedstocks and produce biogas/biomethane. These feedstocks include biomass of agricultural origin such as primary energy crops, crop residues, and animal manure; the organic fraction of Municipal Solid Waste, biomass from agro-industrial byproducts, and wastewater sludge, better explained hereunder.

- *Primary energy crops* have largely been used as biomass for biogas production such as sugar beet, corn/maize and other energy rich crops usually cultivated as monocrops with no crop rotation. Recently, sequential crops or *double crops*, are being cultivated between two harvested crops as a soil management tool to help preserve soil fertility, safeguarding soil organic carbon content and to mitigate against erosion.
- *Crop residues* come from the harvest of wheat, maize, rice, sugar beet, sugar cane, soybean and other oilseeds; they also include sequential/double crops.
- *Animal manure* includes all farm animals such as cattle, pigs, poultry, horses and sheep. Depending on the housing system, livestock manure can be in the dry form or as a liquid slurry.
- *Organic fraction of MSW* includes urban wet waste, wood and green waste (e.g. leaves and grass), paper and cardboard; includes also industrial waste from the agro-food processing sector (e.g., molasses, straw, maize stalks, olive pomace, tomato peels, vegetable and fruits manufacturing residues, etc..).
- *Wastewater sludge* comprises a semi-solid organic matter recovered in the form of sewage gas from municipal wastewater treatment plants.

The utilization of biomass from biowaste and residues as feedstock as opposed to primary energy crops avoids the potential land-use conflict and the food vs. fuel market competition. Energy crops also require fertilizer input (generally manufactured from fossil fuels), which needs to be considered when assessing the life-cycle emissions from different biogas production pathways. To this effect, every EU country has specific legislation on the permissible feedstocks, usually trending away from the use of energy crops and promoting the utilization of residues and biowaste.

Agricultural feedstocks constitute the highest feedstock in EU for their extensive use in Germany, Italy and the United Kingdom, three of the biggest biogas producers in EU. As illustrated in Figure 7, agriculture-based biogas and biomethane plants make up the lion's share of production, with 64% of the biogas and of the biomethane produced in EU originated from agricultural biogas plants. The second biggest source of biomethane production is organic municipal solid waste (11%); the second biggest source of biogas production is landfill (14%) [38].

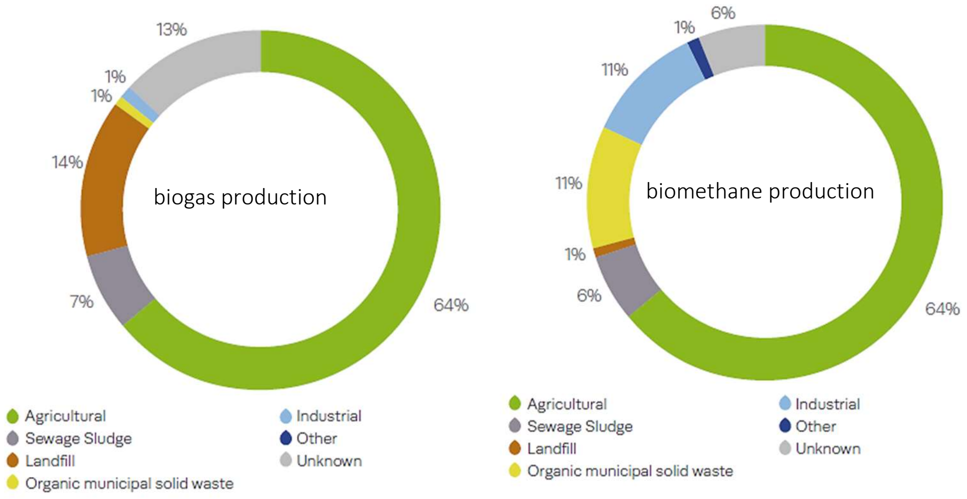


Figure 7 Percentage of EU`s biogas and biomethane production per feedstock type in 2021 [38]

3. Conversion technologies

First generation biofuels are produced by well known technologies and processes such as fermentation, transesterification and anaerobic digestion.

3.1 Fermentation

For the production of 1G bioethanol, edible plants with a high sugar and starch content are used. This process is well known and most often used for the commercial production of bioethanol. Figure 8 shows the process of 1G bioethanol production from sugar (a) and starch (b) raw materials [39].

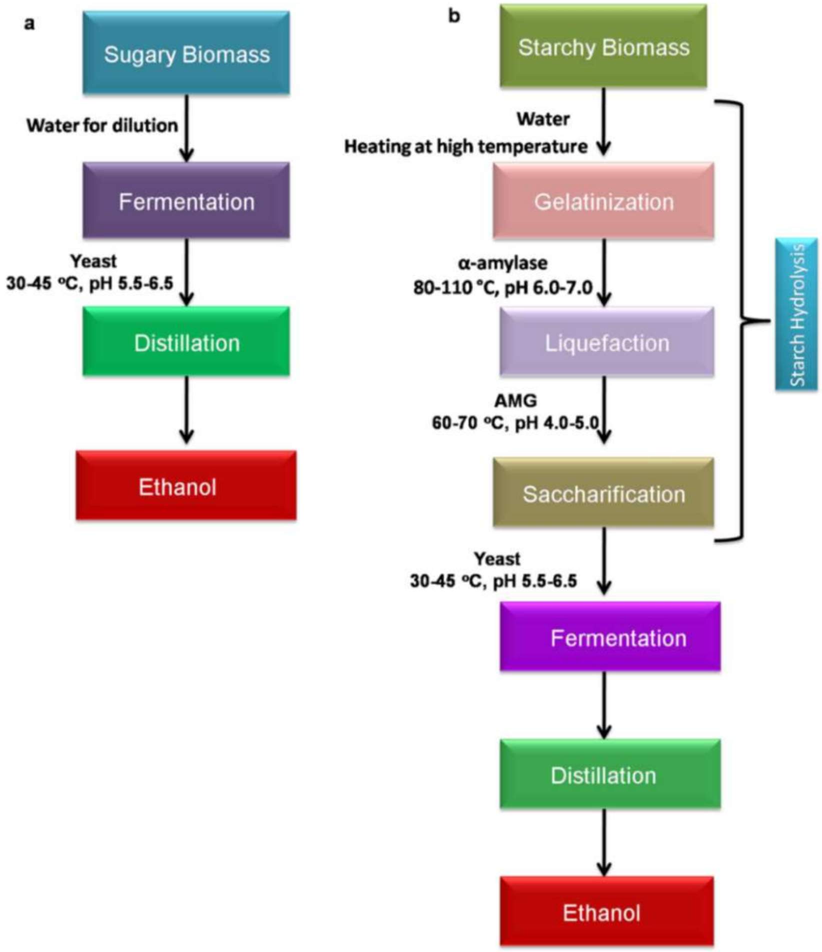


Figure 8 Process of 1G ethanol production from sugary feedstocks (a) and from starchy feedstocks (b) AMG: Amyloglucosidase [39]

The process for producing bioethanol from sugar feedstocks involves the extraction of sugars by milling and subsequent fermentation to bioethanol with suitable production microorganisms. The enzyme invertase, present in yeast cells, is required to convert disaccharides, such as sucrose, into monosaccharides. On the other hand, the use of starch raw materials in bioethanol production also involves their processing. Starch must be hydrolysed in order to be used as raw material for ethanol production [40].

Hydrolysis of starch can be carried out by acids or enzymes, and acid hydrolysis was widely used in the last century. Due to the need to avoid the use of corrosion-resistant equipment, reduce energy consumption and increase environmental awareness, enzymatic hydrolysis has replaced acid hydrolysis.The hydrolysis of starch into glucose includes three steps: gelatinization, liquefaction, and saccharification, and it represents a crucial factor for overall bioprocess efficiency because the efficiency of the hydrolysis will determine the amount of glucose available for ethanol fermentation [41]. Gelatinization is a process in which the raw material is heated in water to expand the starch granules and thus extract the starch. The resulting starch suspension is further liquefied by the enzyme amylase, which catalyses the cleavage of the long amylose starch polymers into short oligosaccharides. Subsequent treatment with glucoamylase and amyloglucosidase converts the oligomers into monomeric sugars during saccharification. Afterwards, the sugars are fermented into bioethanol using the appropriate production microorganism [15, 40].Metin girmek için buraya tıklayın veya dokunun.

Table 3 The Ability of Saccharomyces and Kluyveromyces Species to Ferment Sugars [15]

Carbon number of basic subunits	Type of basic subunit	Sugar	Basic unit	Yeast		
				S. cerevisiae	*S. uvarum (carlsbergensis)*	*Kluyveromyces fragilis*
6	aldoses	glucose	glucose	+	+	+
		maltose	glucose	+	+	-
		maltotriose	glucose	+	+	-
		cellobiose	glucose	-	-	-
		trehalose	glucose	+/-	+/-	-
		galactose	galactose	+	+	+
		mannose	mannose	+	+	+
		lactose	glucose, galactose	-	-	+
		melibiose	glucose, galactose	-	+	
	ketoses	fructose	fructose	+	+	+
		sorbose	sorbose	-	-	-
	aldoses	sucrose	glucose, fructose	+	+	+
	and					
	ketoses	raffinose	glucose, fructose, galactose	+/-	+	+/-
	deoxy-sugars	rhamnose	6-deoxymannose	-	-	-
		deoxyribose	2-deoxyribose	+/-	+/-	+/-
5	aldoses	arabinose	arabinose	-	-	-
		xylose	xylose	-	-	-

The fermentation of sugar to ethanol by yeast represents an important industrial process, and *Saccharomyces cerevisiae, Saccharomyces uvarum (carlsbergensis), Schizosaccharomyces pombe*, and *Kluyveromyces species* are of primary interest to industrial operations. Yeasts can utilise various substrates (Table 3) and can grow and efficiently produce ethanol at pH values of 3.5-6.0 and temperatures of 28-35 °C [15].

Yeasts are facultative anaerobes and can ferment sugars under both anaerobic and aerobic conditions. Under anaerobic conditions yeasts metabolize glucose to ethanol primarily by the Embden–Meyerhof–Parnas or EMP pathway (Figure 9 [42]).

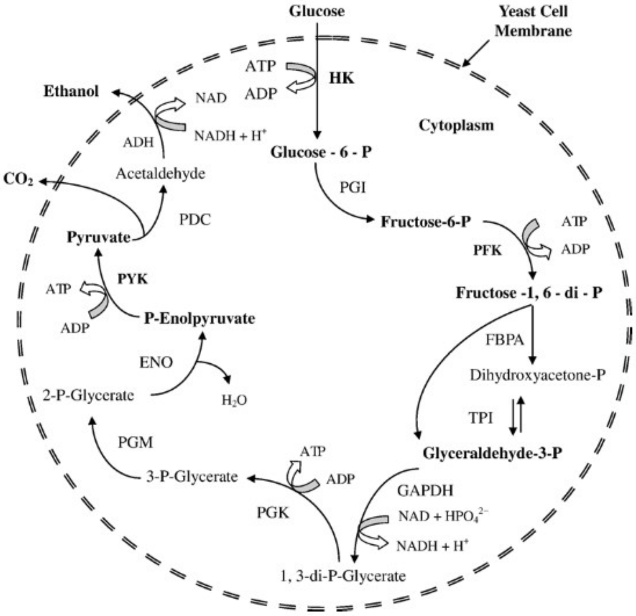


Figure 9 Metabolic pathway of ethanol fermentation in *S. Cerevisiae* [42]

Abbreviations: HK: hexokinase, PGI: phosphoglucoisomerase, PFK: phosphofructokinase, FBPA: fructose bisphosphate aldolase, TPI: triose phosphate isomerase, GAPDH: glyceraldehydes-3-phosphate dehydrogenase, PGK: phosphoglycerate kinase, PGM: phosphoglyceromutase, ENO: enolase, PYK: pyruvate kinase, PDC: pyruvate decarboxylase, ADH: alcohol dehydrogenase.

Under anaerobic conditions, while fermenting sugars yeasts produce ethanol and carbon dioxide while releasing a certain amount of energy in the form of heat according to the Gay-Lissac equation:

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH+2CO_2+117\ \text{kJ}$$

From this equation, the theoretical yield of ethanol per kilogram of fermented glucose is 0.511 kg [43, 44]. However, the actual yield of ethanol that can be achieved during the fermentation process depends on several factors, such as the type of sugar that is fermented, the type of producing microorganisms and the applied process conditions (temperature, agitation, pH value, sugar concentration in the fermentation medium, the concentration of other nutrients in the fermentation medium, the possible presence of inhibitors in the fermentation medium, etc.). The yield obtained in fermentation does not usually exceed 90-95% of the theoretical value. This is due to the requirement for some nutrients to be utilised in synthesising new biomass and other cell maintenance-related reactions. Alcoholic fermentation is a naturally protected process because the alcohol produced is an inhibitor for most bacterial species, so they gradually disappear from the fermentation medium as the alcoholic fermentation progresses. Also, anaerobic conditions gradually arise due to the production of CO_2 and its accumulation on the surface of the substrate. This prevents the reproduction of obligate aerobes. However, in order to achieve the highest possible yield, spontaneous fermentation of the nutrient substrate is not allowed, so the substrates for ethanol production are sterilised. Along with ethanol and carbon dioxide, the primary products of alcoholic fermentation, many by-products, such as glycerol, acetaldehyde, esters, higher alcohols, acetic acid, etc., are produced. Additionally, part of the carbohydrates is utilised to increase the biomass concentration of the fermenting yeast [15, 42]. A significant number of bacteria are capable of ethanol production however, they usually generate multiple additional products. Although some mesophilic *Clostridium* strains can yield higher concentrations, only *Zymomonas mobilis* can be a strict ethanol producer [15]. *Zymomonas mobilis* can achieve a higher ethanol yield and productivity, compared to *Saccharomyces cerevisiae*, since less biomass is produced and a higher metabolic rate of glucose is maintained through its special Entner–Doudoroff pathway. However, *Z. mobilis* cannot readily replace *S. cerevisiae* in ethanol production because it has a specific substrate spectrum (D-glucose, D-fructose, and sucrose), and the obtained biomass is inadequate for use as animal feed [42].

The process of bioethanol production is influenced by several factors: temperature, sugar concentration, pH, fermentation time, agitation rate and size of the inoculum [45]. Temperature directly affects the growth rate of the microorganisms; high temperatures represent a stress factor for microorganisms. The most favourable temperature range for fermentation is between 20 and 35 °C [45]. Increasing the sugar concentration to a certain amount will cause an increase in the fermentation rate. In contrast, the excessive use of sugar will cause a steady fermentation rate because the concentration of sugar is beyond the cells' uptake capacity. Generally, the maximum ethanol fermentation rate is achieved using a sugar concentration of 150 g/L [45]. The pH value of the fermentation medium affects bacterial contamination, yeast growth, fermentation rate and by-product formation, and the permeability of some essential nutrients into the cells.

The pH influences the yeast cells in the range of 2.75–4.25; in ethanol production, the optimum pH range of *S. cerevisiae* is 4.0–5.0 [45–47]. The growth of microorganisms is influenced by the timing of fermentation. Shorter times result in inefficient fermentation due to insufficient growth, while longer fermentation times have a toxic effect on microbial growth, especially in batch mode due to the high ethanol concentration. The agitation rate increases the amount of sugar consumption and reduces the inhibition of ethanol on cells. The typical agitation rate for fermentation by yeast cells is 150–200 rpm [45]. Excess agitation rate is not suitable as it causes limitations to metabolic activities. Inoculum concentration affects the consumption rate of sugar and ethanol productivity. The production of ethanol was seen to be increased with the increase in cell numbers from 1×104 to 1×107 cells per ml [45].

Starch-based raw materials can be fermented after saccharification (Separate Hydrolysis and Fermentation, SHF) or simultaneously (Simultaneous Saccharification and Fermentation, SSF). In the SSF process, the substrate concentration is relatively low, because the sugars produced by the hydrolysis of starch are immediately consumed for the growth of yeast cells. Due to the low concentration of sugars, there is no inhibition of amylase and yeast cells, and the productivity of the bioprocess increases. Furthermore, the advantages of the SSF process are the reduced possibility of contamination, reduction of the osmotic pressure of the substrate and better energy efficiency [48].

Ayodele et al. [49] have comprehensively reviewed the production of 1G bioethanol from sugar-based raw material. The review of these authors has shown that 1G bioethanol has been produced using juice extracted from sugar-based feedstocks such as sugar cane, sweet sorghum, watermelon, sugar beet, and the cashew apple. For lab-scale production, the most commonly used batch mode bioreactors, *S. cerevisiae* as a production microorganism, and pH value, temperature and agitation range were 3.7-5.5, 30-40°C, and 150-300 rpm, respectively [49]. Figure 10 represents a comparison of bioethanol yield from different 1G sugar-based feedstock and shows that the ethanol yields vary with the type of sugar-based raw material and the mode of the bioreactor used. Additionally, the use of the unengineered *S. cerevisiae* for converting the sugar obtained from the various juice resulted in a lower ethanol yield compared to higher ethanol yields obtained with an engineered strain of the *S. cerevisiae*.

The cereal grains (Table 4), as significant components, contain starch and protein, while the minor components include vitamins, phytic acid, lipids, non-starch carbohydrates and minerals. The efficiency of the production process depends upon the substrate starch content, process parameters and process implemented for ethanol production [50]. In commercial bioethanol production, there are three main strategies for fermentation: submerged (liquid state) fermentation, the solid-state fermentation, and very high gravity fermentation, and their comparison is shown in Table 5.

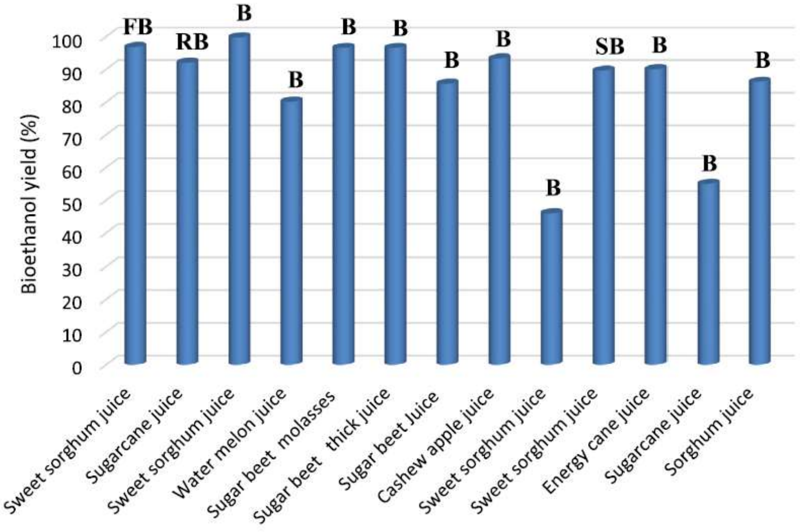


Figure 10 Comparison of bioethanol yield from different 1G sugar-based feedstocks[49]

FB: fed-batch, RB: repeated batch, SB: Sequential batch, B: Batch

Table 4 Starch content, gelatinization temperature and ethanol yield of starch-based raw materials [50]

Raw material	Starch content (%)	Gelatinization temperature (°C)	Ethanol yield (l/100 kg)
Wheat	58-62	58-65	36-39
Rice	55-70	62-80	48-57
Barley	54-65	53-63	34-41
Maize	60-63	68-74	38-40
Sorghum	55-65	70-78	36-42
Rye	56-70	57-70	35-42
Oats	54-64	75-80	36-42

Table 5 Comparison of submerged, solid-state and very high gravity fermentation [51]

Submerged/Liquid-State Fermentation	Solid-State Fermentation	Very High Gravity Fermentation
-Uses liquid medium to grow microorganisms -Requires larger operational footprint -Increased usage of water and energy -Better monitoring and ease of handling -Shorter fermentation time -High waste generation -High ethanol yield	-Uses solid substrate to grow microorganisms -Smaller vessels -Less water and energy requirements -Not easy to monitor or change parameters -Longer fermentation time -Reduced waste generation	-Uses increased concentrations of sugar substrate to increase final ethanol concentration in the medium -Less water and energy requirements

The selection of an optimal batch type (batch, fed-batch, and continuous) is a significant factor influencing fermentation efficiency, and Table 6 compares different fermentation types. Kinetics of the used microorganisms and the characteristics of raw material influence the optimal batch type [51].

Table 6 Comparison between batch, fed-batch, and continuous fermentation [51]

Batch	Fed-Batch	Continuous
Microorganisms are provided with a fixed volume of medium (nutrients and other ingredients). Culture environment is consistently changing as nutrients are consumed.	Media is inoculated with microorganisms which then grow under a batch regime for a certain amount of time, then nutrients are added incrementally throughout the fermentation.	Fresh media is continuously added to the fermenter, replacing the consumed nutrients. Ethanol, used media, and toxic metabolites are continuously removed.
Advantages:	Advantages:	Advantages:
-Low cost -Low risk of contamination -Less control required -Easier sterilization	-Maintenance of maximum viable cell concentration -Extended lifespan of cells -Higher ethanol accumulation -By-product accumulation is limited -Control of factors (e.g., pH, temperature, dissolved oxygen)	-Less downtime for vessel cleaning -Increased productivity -Lower cost -Higher degree of control -Ability to automate, more cost-efficient and less sensitive to human error.
Disadvantages:	Disadvantages:	Disadvantages:
-Lower cell densities, ethanol production -Longer downtime between batches due to cleaning, vessel setup, and sterilization	-Increased costs for process control -Longer downtime between batches due to cleaning, vessel setup, and sterilization	-Less control for non-growth-related products -Cell aggregation can prevent optimum steady-state growth -Long growth periods can increase risk of contamination -Can be difficult to maintain filamentous organisms due to viscosity and heterogeneity of the medium

3.2 Transesterification

Biodiesel is becoming increasingly important as an attractive fuel due to dwindling fossil fuel resources. Chemically, biodiesel is a monoalkyl ester of long-chain fatty acids derived from renewable feedstocks such as vegetable oils and animal fats [52]. Presently, biodiesel is produced on industrial scale by the catalytic transesterification method, in which oil or fat is reacted with a monohydric alcohol in the presence of an acid, base, or enzyme catalyst [18].

In the transesterification process, fatty acid alkyl ester and glycerin are produced in the chemical reaction of triglycerides and alcohol in the presence of catalysts. Transesterification is the most applied method for biodiesel production from oils due to its effective viscosity reduction which is significantly desired for biodiesel production [53]. It is a stoichiometric reaction of 3 molecules of alcohol with 1 molecule of triglycerides and it is also titled as alcoholysis. The alcohols used in the reaction are methanol, ethanol, propanol, butanol, and amyl alcohol [53, 54]. The reaction is carried out in the presence of a catalyst, which results in the formation of alkyl esters (biodiesel) and glycerin as a byproduct [54]. Transesterification is an environmental friendly process in the overall since it converts a wide range of oil feedstocks into biodiesel at the temperature range of 60 to 100°C, mostly [54–56]. The major factors that affects the reaction are temperature, time, pressure, the ratio of alcohol to oil, concentration, type of catalyst, mixing intensity, and feedstock oil [18, 53]. Transesterification occur in three steps: 1-triglycerides are converted to diglycerides, 2-diglycerides are subsequently converted to monoglycerides, 3- monoglycerides are converted into glycerol [53, 57]. During the reaction, three molecules of alkyl esters are produced for each glycerol molecule. Figure 11 shows the biodiesel production reactions by the transesterification of triglycerides with alcohol.

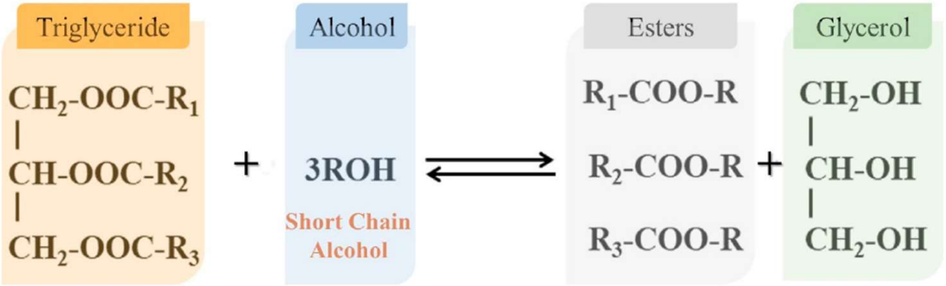


Figure 11 Biodiesel production reaction[53]

Transesterification process can be examined in two groups according to catalyst utilization: catalytic biodiesel transesterification and non-catalytic transesterification [53]

Catalyst is the input element of a reaction which increase the reaction rate, decreasing the time required for biodiesel production by improving surface interaction. A catalyst can enhance the efficiency and product formation in a reaction. As a result it decreases the biodiesel production costs. In transesterification process, catalysts can be grouped into three general categories: homogeneous, heterogeneous, and enzymatic catalysts [53, 54].

Homogeneous catalytic transesterification

If the physical phase of the reactants stay the same during and at the end of the reaction, the process is called homogeneous. This is one of the traditional and most used commercial method for biodiesel production. In this method, alkali and acid catalysts are applied to increase the reaction rate. The catalysts that are used the most in the reaction are NaOH, KOH, HCl, H_2SO_4, and HNO_3 [53, 54]. The benefits of homogeneous catalysts are they impose high activity which lowers the reaction time, efficient reaction at low temperature and pressure compared to heterogeneous catalysts. The drawbacks of the homogeneous catalysts can be sorted as: soap formation (saponification) in case of high free fatty acid content in feedstock, difficult recovery of the by product, acidic and alkaline wastewater need to be trated at the end of the process (downstream purification and recovery of catalyst), slow reaction in the case of acid catalysts which then result in need of high oil to alcohol ratio and high amount of catalyst, disturbance of the reaction with the increase in water content in the feedstock, high energy consumption and capital equipment costs, increment in viscosity, toxicity, corrosiveness, highly flammable nature, and etc [54, 56]. It is essential to choose the catalysts according to the feedstock type, water content and free fatty acid content of the feedstock. The efficiency of homogeneous catalytic transesterification can be as high as 90 % and more [56].

Heterogeneous catalytic transesterification

The catalyst that remain in a different phase respect to the reactant during the reaction is called as heterogenous catalyst. Most used heterogeneous catalysts are ion exchange resins, sulfated oxides, and heterogeneous base catalysts like transition metal oxides, , alkaline earth metal oxides, mixed metal oxides, alkali metal oxides, and also waste material based heterogeneous catalysts [54, 58]. They exist in solid form and they are efficient and suitable catalysts for biodiesel synthesis due to their higher catalytic performance, environmental acceptability, and recyclability. The down-stream process is simple and cheaper compared to homogeneous catalysts separation. They pose less risk of hazardous material leakage; and less production of toxic wastewater [58]. Heterogeneous catalysts are very suitable for industrial level because they can easily be separated and reused which decreases the production cost of the product [53, 59]. Therefore researchs are focused on obtaining different and more appropriate heterogeneous catalysts for they have the potential of lowering biodiesel production costs and overcome the obstacles that homogeneous catalysts cause. On the other hand these catalysts have low stability and are highly expensive. They have a big attraction to moisture during storage. High free fatty acid content causes washing problems in the presence of solid catalysts [60].

Biomass-derived catalytic transesterification and biocatalysts

Recently, investigations carried out for cheaper and stable catalyst production have given a potential result, biomass-derived heterogeneous catalysts. Biomass-derived heterogeneous catalysts can be easily accessible and prepared from renewable resources. They are non-toxic, have high activity and stability in acidic and basic conditions. They can tolerate to a high water content. The use of various wastes such as biomass, waste shell, and animal bones has been reported for the preparation of heterogeneous catalysts. The use of biomass-derived heterogeneous catalysts appears to be an ecofriendly and economic approach for biodiesel production due to its high efficiency more than 90% same as heterogeneous catalysts [18, 61].

Table 7 Comparison of different biodiesel production methods [58]

Variable	Alkali catalysis	Acid catalysis	Enzyme catalysis	Supercritical alcohol
Reaction temperature (°C)	60-70	55-80	30-40	240-400
Free fatty acid in raw materiasal	Saponifed products	Esters	Methyl esters	Esters
Effect of water	Interference with reaction	Interference with reaction	No influence	-
Yield of methyl esters	Normal	Normal	Higher	Good
Recovery of glycerol	Difficult	Difficult	Easy	-
Purification of methyl esters	Repeated washing	Repeated washing	None	-
Production cost of catalysty	Cheap	Cheap	Relatively expensive	Medium

Chemical catalysts used in biodiesel production cause to an energy intensive pathway since they lead to impurities and soap formation [18, 61]. These undesired by-products impose difficulties in seperation of biodiesel product [61]. Therefore biocatalysts were developped to prevent the problems that chemical catalysts cause. Biocatalysts do not change chemically during the reactions. Enzymes such as lipase and/or microbial cells that include/synthesize lipase are used as biocatalysts. Recovery or reuse of the microbial biocatalysts is not crucial because they can be produced more cheaper compared to the cost of the recovery processes [54]. Biocatalysts also hold a plus point upon chemical catalysts as they can be applied to an extensive variety of oil sources that contain high free fatty acid content. Table 7 presents comparison of different biodiesel production methods.

Enzymatic transesterification

Nowadays, intensive research is exerted to provide novel biodiesel production methods. Enzymatical transesterification is one of the promosing techniques that have the potential to increase the biodiesel yields. They are renewable biocatalysts and can decrease the costs of the production. Enzymes are not affectted by the water content of the feedstock and concentration of the free fatty acids therefore they are highly suitable for transesterification of waste cooking oils (WCO) and other oil sources [53, 58]. No by-product, easy product removal, reusability without any separation step and lower operating temperature are the key advantages [60]. Lipase is the main enzyme involved in the transesterification process [53] . Lipase can be obtained from different sources such as animals, plants, fungi, yeasts, or bacteria . Most used lipase source is the microbial lipase. Enzymes hydrolyze triglycerides to convert into glycerol and fatty acids [53].

The advantages of enzyme catalysts in transesterification are immobilized or soluble lipases are environmentally friendly, they are not affected from the presence of large amounts of free fatty acid (FFA) and water. The enzymes can be regenerated to be used more than once. The process energy consumption is lower compared to other catalysts [53, 58, 62]. However since lipase is soluble in aqueous solution, it loses its activity upon exposure to unfavorable medium conditions such as pH and temperature [58]. To overcome the obstacles and generate reusability and instability, various immobilization techniques can be applied such as adding support materials which increase the surface area and hydrophilicity . One of the main disadvantages of the enzymes is that they are expensive for the large scale biodiesel production [58]. Table 8 presents the advantages and disadvantages of different types of catalysts used in transeseterification of waste cooking oil.

Non-catalytic transesterification

Non catalytic transesterification occurs at the absence of a catalyst. Reaction that is free of a catalyst simplifies the industrial process, inhibits the formation of by-products. Due to the cost of the catalyst, non-catalytic process is more economical compared to catalytic processes [53]. There are two types of non-catalytic transesterification processes. One of them is known as supercritical alcohol transterification. In this type of process, purification of the process and drying of the feedstock are not required. Any kind of oil source is suitable for this method. The process of supercritical transesterification is very fast such as in minutes. On the other hand high pressure and temperature are needed for supercritical transesterification, which in turn cause the breakdown of unsaturated fatty acid, which ultimately affects the fuel's fluidity at lower temperatures. In other words, it is stated that supercritical transesterification is not feasible and it consumes high energy [53, 58]. To overcome the disadvantages mentioned above, some scientists added a small quantity of co-solvent or solid catalysts such as calcium oxide with supercritical methanol to produce biodiesel [58]. In Table 8 are presented advantages and disadvantages of different types of catalysts used in transesterification of waste cooking oil.

3.2.2. Transesterification Reactors

There are various reactor types applied for biodiesel production from oils and alcohols. Batch, semi-continuous and continuous reactors which are used for mixing the reactants and reagents with temperature and agitation control in a tank [18]. The reactor types used for biodiesel production vary due to the required conditions in the reactor. Those conditions are determined based on the chemical properties and physical operating parameters of the reactants, reagents, and products .

Conventional Reactors

Batch mode reactors and continuously stirred tank reactors (CSTR) are the most commonly used reactors at industrial-scale production optimizing the feed rate, reaction temperature, and agitation (mixing) system and period [54, 56]. Batch stirred reactors have a shaft in the center to achieve the mixing with impellers however the common disadvantage of this reactor is the inefficient mixing of the solution.

Table 8 Advantages and disadvantages of different types of catalysts used in transesterification of waste cooking oil [60]

Type of catalyst	Advantages	Disadvantages
Homogeneouse base catalyst	- Very fast reaction rate, 4000 times faster than acid-catalyzed transesterification - Reaction can occur at mild reaction condition and less energy intensive - Catalysts such as NaOH and KOH are relatively cheap and widely available - For low quality feedstock - Simultaneous transesterification	- Sensitive to FFA in the oil - Soap will be formed if the FFA content in the oil is more than 2 wt.% - Too much soap formation will decrease the biodiesel yield and can cause problem during product purification - Generate huge amount wastewater - Acid catalysts are corrosive - Waste separation and disposal is problematic - Confined to batch reactors
Heterogeneous base catalyst	- Relatively faster reaction rate than acid-catalysed transesterification - Reaction can occur at mild reaction condition and less energy intensive - Easy separation of catalyst from product - High possibility to reuse and regenerate the catalyst - Simultaneous transesterification - High selectivity, easy separation - Useful in continuous fixed bed reactors	- Poisoning of the catalyst when exposed to ambient air - Sensitive to FFA content in the oil due to its basicity property - Soap will be formed if the FFA content in the oil is more than 2 wt.% - Too much soap formation will decrease the biodiesel yield and can cause problem during product purification - Leaching of catalyst active sites may result to product contamination
Homogeneouse acid catalyst	- Insensitive to FFA and water content in the oil - Preferred method if low-grade oil is used - Esterification and transesterification occur simultaneously - Reaction can occur at mild reaction condition and less energy intensive	- Very slow reaction rate - Corrosive catalyst such as H_2SO_4 can lead to corrosion on reactor and pipelines - Separation of catalyst from product is problematic
Heterogeneous acid catalyst	- Insensitive to FFA and water content in the oil - Preferred method if low-grade oil is used - Esterification and transesterification occur simultaneously - Easy separation of catalyst from product - High possibility to reuse and regenerate the catalyst	- Complicated catalyst synthesis procedures lead to higher cost - Normally, high reaction temperatures, high alcohol to oil molar ratio and long reaction time are required - Energy intensive - Leaching of catalyst active sites may result to product contamination - Required high temperature and pressure
Enzyme catalyst	- Insensitive to FFA and water content in the oil - Preferred method if low-grade oil is used - Transesterification can be carried out at low reaction temperatures compared to other methods - Only simple step purification is required	- Very slow reaction rate, slower than acid catalysed transesterification - High cost - Sensitive to alcohol, typically methanol that can deactivate the enzyme
Biocatalysts	- Easy separation of product and by-product - FFA are converted to biodiesel - Very selective - Low reaction temperature - Reusability	- Expensive - Methanol inhibition can occur

The common stirrer types applied in the batch and continuous reactors are the turbine and impeller stirrers. Optimization of stirring speed and improvement of the impeller is necessary for high productivity. However in transesterification process, inefficient mixing of the reactants lead to limited mass-transfer ratio and prolonged reaction time [18]. Also batch reactors need high temperature and pressure. In Table 9, comparison of batch, semi-batch and continuous process modes are presented

Table 9 Comparison of batch, semi-batch and continuous process modes [56]

Parameter	Batch	Semi-Batch (Semi Continuous)	Continuous
Space requirement (volume)	High	Medium	Low
Capital cost	High	Medium	Low
Operational cost	High	Medium	Low
Product quality	Varies	Uniform	Uniform
Running time	Until chemical equilibrium	Until chemical equilibrium	Until catalyst inactivation or process maintainance
Production rate	Low	High	Highest
Reactor application	-Low selectivity -Higher versatility -Good flexibility -Simple scale-up -Inferior heat transfer -Suitable for slow reaction	-High selectivity -Lover versatility -Good flexibility -Complex scale-up -Superior heat transfer -Suitable for faster reaction	-High selectivity -Lover versatility -Good flexibility -Complex scale-up -Superior heat transfer -Suitable for quick reaction

Batch processes still contribute to a major portion of the biodiesel production plants worldwide. Small and medium scale batch processes are easy to construct and operate [54]. However, biodiesel industry is shifting towards continuous operation as it offers lower operating costs and produce higher quality end products [56]. In Table 9 comparison of batch, semi-batch and continuous process modes are presented.

One of the simply constructed reactors is tubular, also known as pipe or plug flow reactor (PFR). Tubular or plug flow reactors (packed bed or trickle bed type) are kind of easily constructed reactors that use packing material surface and the flow pressure by adjustment for efficient mixing. Such reactors can save time and energy by static mixing [56]. They are commonly used reactors for continuous operations. Immobilized lipases, solid alkali, or acid materials are applied as the packed material. Due to the surface area of catalysts material per unit volume, they are more favorable to CSTRs in industrial processes . Reaction temperature, alcohol to oil ratio, flow rate and type of catalysts are considered optimization parameters for the biodiesel production [17]. Flow rate is the most crucial parameter due to its determination of retention time in the reactor which can increase the production yield in one hand and leads to glycerol generated to settle on the surface of the packed material which can decrease the efficiency on the other. The disadvantages of PBR are high-pressure drop with little carrier size and obstacles in mass transfer [17, 56].

Table 10 Characteristics of different types of reactors for the production of biodiesel [18]

Reactor design	Residen-ce time	Mass transfer	Current status	Advantages	Disadvantages
Batch	1 to several hours	Medium	Industrial	Simple to operate Suitable for slow reactions Easy to scale up	High operation cost Quality of product may vary batch to batch Running time is long until the reaction complete Heat transfer is low
CSTR	>60 min	Good	Industrial	Product quality is uniform Superior heat transfer Suitable for quick reactions The maintenance cost is low -asy to scale up	High agitation cause foaming problem More power is needed for mixing
Packed bed reactor	30 min to several hours	Good	Industrial	-More contact achieved between catalyst and reactant compared to other conventional reactors -Reduced energy and alcohol/oil consumption. Easy to scale up.	Temperature control is difficult A temperature gradient may occur
Microtubular	>40s	Excellent	Lab scale	Offer a small diffusion distance Provide a larga surface area to volume ratio Reactions are faster than batch reactor	Design is complex and biodiesel yield is affected by the channel design The mixing of the reactant is poor and requires an additional mixer Extra steps are required for the downstream processes
Membrane	1-3h	Low	Pilot scale	Purification of biodiesel is easy Separated glycerol can be used to produce other value-added products	Pressure is required to support the filtration Polimeric based membranes have low resistance to mech., chem. and thermal damage
Micro-channel	Several minutes	Excellent	Lab scale	Higher conversion than batch reactor but less then microtubular	A micromixer is required Design is complex and scale-up is not easy An extra purification step is needed
Microwave	Several minutes	Good	Lab scale	Microwave heating consumes less energy than conventional heating	Ethanol loss under extra power Heating uniformity is an issue
Reactive distillation	>5 minutes	Excellent	Pilot scale	Simultaneous product recovery at reduced cost. Require less alcohol as compare to other transesterification procedure. Low production cost	Higher energy consumption
Centrifugal contanctor	Several minutes	Excellent	Pilot scale	Easy recovery and separation of products -Provide intense mixing and increase mass transfer	Energy consumption is high

In PFR, reactants and reagents are entered in one end, spent specific time for passing through pipes at a constant velocity, this time determines the conversion yield as well, and mixed while flowing towards the outlet. Mixing of the reactants are performed by highly turbulent flow through the pipe. An appropriate amount of pressure application for the reaction in PFR, can decrease the mixing lenth and retention time as well as volume of the reactor [17]. However, if the viscosity of the fluid is high more laminar flow operating conditions occur. To avoid this, and also to further improve the reaction rate and production yield, in-line mechanical mixers and/or static mixer can be applied [56].

Limitations such as mass-transfer ratio, extended reaction time, high reaction temperature and pressure needed in conventional reactors (batch, CSTR, FBR, PFR) led the way for different and efficient reactor designing for shorter retention time and higher production yield [17, 56]. In Table 10, advantages and disadvantages of different types of biodiesel production reactors and their characteristics are presented. Besides, in Table 11, advantages and disadvantages of present studied transesterification processes are shown.

3.3 Anaerobic Digestion

The Anaerobic Digestion (AD) process is a robust technology for the conversion of biomass (animal manure, crop residues, organic fraction of municipal solid waste, biomass from agro-industrial byproducts, wastewater sludge) into renewable energy. The core component of this technology consists of a microbial mediated process by which organic biomass, in the absence of oxygen and within a strictly controlled temperature range, is gradually converted into biogas, a mixture of methane (35–75%), carbon dioxide (25–65%,) hydrogen (1-5%), nitrogen (0.3–3%) along with traces of water vapor, ammonia, hydrogen sulfide, and mercaptans (e.g., methanethiol), halides and siloxanes [63, 64]. However, the composition of the raw materials and operaring conditions during anaerobic digestion have considerable impact on the chemical composition of biogas [32].

Table 11 Advantages and disadvantages of studied transesterification process [53]

	Process	Advantages	Disadvantages
Traditional Technique	Homogeneous Base Catalyst	20-120 min at 25-70 ^{o}C and normal pressure. Higher yield than acidic (more than 97%). Inexpensive and widely available.	High energy consumption. Sensitive to the presence of water. Soap formation. Suitable only for pure vegetable oils.
	Homogeneous Acid Catalyst	Catalyze both transesterification and esterification. Not sensitive to feedstock FFA content. Economical compared to base process.	Sensitive to the presence of water. Prolonged reaction time and high temperature. The high molar ratio of oil/alcohol. Environmental impact and corrosion problem. Difficulty in separation and catalyst recycling
	Heterogeneous Base Catalyst	A small amount of waste production with less environmental impact. Recyclable catalyst. Cheap and fast process at a low temperature. Easy production and purification process.	High energy consumption. Expensive and challenging recovery of glycerol. Downstream process treatment is essential which increases the procedure cost
	Heterogeneous Acid Catalyst	Insensitive to feedstock. FFA content. A low amount of catalyst required. No washing step is required and environmentally friendly. Easy catalyst separation and purification step.	Long time (8-20 h) and high temperature (200 ^{o}C). Waste solvent reduces the activity of catalysts. The purification process is required due to the catalyst leaching which increases the procedure costs.
Recent Technique	Ionic liquids	High chemical and thermal stability. Structure and property tuning, High catalytic activity. Low or negligible vapour pressure and flammability. Lower toxicity versus organic solvents. Wide range of applications. Liquids at room temperature. Possible recyclability.	High synthesis costs. Limitations in large scale applications. Some of them are moisture sensitive. Non-biodegradability. Inconvenient separation procedure. High viscosity.
	Deep eutectic solvents	Easy preparation. High purity. Low cost. No reactivity with water. Non-toxicity and biodegradability.	Enzymatic heterogeneous transesterification involves a complicated liquid-liquid interface. Uncertainty regarding prolonged use stability. Lack of information on the whole life-cycle assesment.
	Enzyme	Highly selective and specific. Reusable enzymes and environmentally friendly. Insensitive to the high amount of FFA. Low-cost process. The produced biodiesel is pure.	The enzyme is sensitive to high temperature and denature. Low biodiesel yield and slow reaction rate. Require organic solvent and water. Inhibitory effect of glycerol.
	Magnetic-assisted	Not limited by the filtration drawbacks. Accelerate the production cycle. Using porous catalysts enhances their activity. Less drop in pressure. Efficient separation steps.	Agglomeration of the acidic magnetic catalyst. Require coating pre-step for organic catalysts.
	Microwave-assisted	Fast reaction time. The lower molar ratio of oil/methanol. Less by-product. Lower energy consumption. High yield and purer biodiesel.	Difficult to scale up the process to a commercial scale. Uncontrolled heating. Low depth penetration of microwave radiation.
	Ultrasound-assisted	Increase the reaction speed. High yield method. Low energy and low amount of catalyst (enzyme).	A large amount of catalyst is used which increases the soap formation, wastewater, environmental impact, and subsequently cost of the process. Remained catalysts increase the biodiesel pH.
	Plasma-assisted	Super short reaction time. Independent to catalyts. No soap formation and glycerol formation.	Difficult to control the reaction mechanism. Blind chemical bond excitation and ionization. Difficult to stop the reaction.
	Electrolysis-assisted	Does not require elevated temperature. Shorter reaction time. Lesser wastewater production. Inexpensive. Water presence enhances the yield. Insensitive to the high amount of FFA and water.	Sensitive to high pH. Electrolyte conductivity should be monitored constantly.
	Supercritical	Independent to catalyst. High reaction rate. Independent to the presence of water in feedstock. Independent to the excess amount of FFA. No pre-treatment step is required.	Costly. Very high temperature (250-400 ^{o}C) and pressure (40 Mpa). The high molar ratio of oil/alcohol. Not feasible to scale up to industrial size.
	BIOX co-solvent	One-phase solution system and fast reaction time Ambient temperature and pressure. Reusability of cosolvent A wide variety of feedstock can be used.	Toxicity of the tetrahydrofuran. Difficult separation of methanol and co-solvent. Environmental impact.

The biological route during the degradation of the feedstock is catalyzed by a wide range of microorganisms acting synergically under anaerobic conditions at mesophilic (39-44 °C) or thermophilic (50-55 °C) temperatures, in sealed reactors in the absence of oxygen commonly known as anaerobic digesters. The balance inside the trophic chain is maintained within optimal limits of operational parameters such as temperature, pH and reaction intermediates, and processing parameters like hydraulic retention time (HRT) of the biomass inside the digester, and organic loading rate (OLR), which is the amount of organic material loaded inside the digester over a specific period of time. The methane is the only non-reactive compound in the entire AD process, and also the fuel component; therefore, it is considered as the final product of the trophic chain [65].

The microbiological process of AD basically follows 4 subsequent steps: hydrolysis, acidogenesis, acetogenesis and methanogenesis.

- The **hydrolytic phase** consists in the degradation of complex organic substrates, i.e. carbohydrates, proteins and lipids, into simple soluble monomers, such as monosaccharides, amino acids and fatty acids, by *hydrolytic bacteria*;
- The **acidogenic phase** consist in the conversion of oligomers and monomers, i.e. sugars, fatty acids and amino acids, into volatile fatty acids (VFA), carbon dioxide and some alcohols (e.g. methanol, ethanol) by *fermentative bacteria*. VFA are short chain fatty acids provided of a tail with no more than 6 carbon atoms;
- In the **acetogenic phase**, starting from volatile fatty acids, *acetogenic bacteria* produce acetate, hydrogen and carbon dioxide;
- The **methanogenic phase**, the last and most delicate step, is mediated by *methane-producing archaea*, a group of strictly anaerobes microorganisms included in the oldest domain of *Archaebacteria*.

There are several bioreactor configurations for anaerobic digestion. The first group consist of conventional anaerobic bioreactors (e.g., anaerobic sequencing batch reactor, continuous stirred tank reactor, and anaerobic plug-flow reactor) whereas the second group consists of sludge retention bioreactors (e.g., anaerobic contact reactor, internal circulation reactor, up-flow anaerobic sludge bed reactor, up-flow anaerobic solid-state reactor, anaerobic baffled reactor). There is also a third group anaerobic bioreactors which include membrane (e.g., anaerobic filter reactor) [32, 66]. By these anaerobic processes, different product streams are produced such as VFA, biohydrogen, and biogas that have high economic potential. On the other hand, methane can be also generated depending on the operating conditions and the content of the feedstock (i.e., carbohydrates, cellulose, proteins, fats, and hemicellulose) which have also crucial role on the quality of the biogas obtained, and the methane yield. In addition, biosludge (i.e., digestate) collection at the end of digestion period can be also used as fertilizer. However, availabilty of feedstock and its continuous supply strongly affect the proper development of these anaerobic digestion based products which exhibits the importance of the sustainable use of raw materials. In this context, the production of second generation biofuels is more sustainable than the first generation in terms of effective waste management, as well as contributing to the production of different energy sources and reducing dependence on fossil fuels [67, 68]

Biogas / Biomethane

In EU, biogas and biomethane are being produced in increasing quantities. The term “biogas” refers to the raw gas originating from anaerobic digestion, whilst biomethane is the purified form of biogas, consisting of almost 100% methane and approximately equals the quality found in natural gas. Hence, the application of more sophisticated purification techniques in production of pure biomethane from biogas allows its delivery to natural gas grid and its subsequent use [32]. Biogas is most often used in a CHP (cogeneration plant) to generate both electricity and heat, while biomethane is used for a variety of end-use applications, i.e. fuel for transport, as well as electricity and heat (Figure 12). The end-uses of biomethane are influenced by market mechanisms, regulations and support mechanisms, all of which vary between the EU countries [38].

Digestate

In addition to VFA, biohydrogen, and biogas/methane, biosludge or also known as digestate can be also collected at the end of anaerobic digestion and used as nutrient-rich fertilizer [67]. This residual substrate left by the digestion process (Figure 12), is composed of liquid and solid fractions that are often separated and handled independently. With appropriate treatment, both the solid and liquid fractions of digestate can be used in many other beneficial applications, such as animal bedding (solids), organic-rich compost and/or simply as soil amendment (solids).

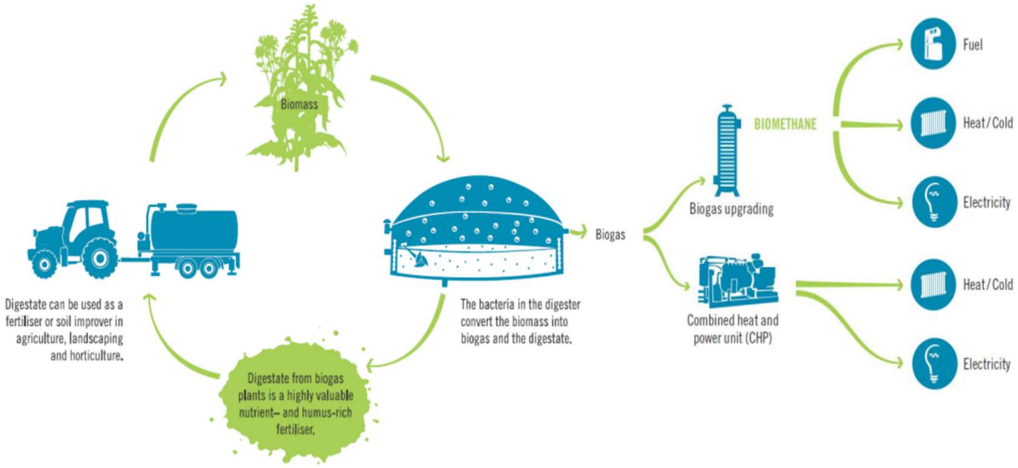


Figure 12 Anaerobic digestion process and products (adapted from [69])

4. Descriptions of first-generation products

First-generation biofuels are also called as 'conventional biofuels' which are provided from vegetable oil, sugar, corn, wheat, and starch like traditional crop-based feedstock. For example, vegetable oil is used for biodiesel through esterification and sugar crops for bioethanol through fermentation. In this context, the most common first-generation biofuels are biodiesel and bio-based alcohol as well as biogas. Since the resultant fuels are distinctive and of high quality; the production and usage of these biofuels has gained considerable attention in recent years. Moreover, when derived from plant-based biomass; biofuels are considered as renewable and environmentally acceptable energy source compared to fossil fuels [32].

4.1 Biodiesel

Biodiesel is a liquid biofuel that is produced through the transesterification process. It is stated that worldwide biodiesel production is achieved by utilizing edible vegetable oils consisting of rapeseed, soybean, corn, sunflower, and palm mostly [17].

Properties of biodiesel

The different sources of biodiesel are produced by different qualities and properties of biodiesel. The Austria became the first country to set standards for esters as diesel fuel obtained from rapeseed oil [70]. In Italy, France, the Czech Republic, Germany and the USA, standard qualities and properties of biodiesel were defined [70, 71]. The properties and characteristics of biodiesel must comply with the general biodiesel specifications. These specifications are compliant with the American Society for Testing and Materials (ASTM 6751) or the European Biodiesel Fuel Standards (EN 14214) [71, 72]. Some of these properties are cetane number, flash and fire point, calorific value, acid value, cloud and pour point, density, viscosity, ash content, copper corrosion, distillate ranges, sediment, the residue of carbon, sulfur concentration, presence of glycerine and phosphorus [72, 73]. The Biodiesel specifications in the European Union and the Unated States of America (USA) are presented in Table 12.

Viscosity plays a critical role in fuel injection and atomization, especially when an increase in viscosity affects fuel flowability at low temperatures [70, 74]. The viscosity of biodiesel is 10–15 times higher than fossil fuel diesel due to its high molecular mass and complex chemical composition [70, 75]. Biodiesel is highly viscous or even solidifies at low temperatures, which affects the mechanical stability of pump drive systems [76]. According to EU and USA standards, the maximum appropriate viscosity value is 1.9–6.0 mm^2/s and 3.5–5.0 mm^2/s, respectively (Table 12).

Table 12 Biodiesel specifications in the European Union and the USA [77]

Property	Biodiesel		Ultra-low sulfur diesel
	Europe EN 14214:2008	USA ASTM D6751	Europe EN 590
Density (kg/m^3 at 15°C)	860–900 (EN 12185)	–	820–845
Viscosity (mm^2/s at 40°C)	3.5–5.0 (EN 3104)	1.9–6.0 (D445)	2.0–4.5
Distillation (°C)	–	<360 at 90% (D1160)	350 at 85% ¸ 360 at 95%
Flash point (°C)	>101 (EN 3679)	>93 (D93)	>55
Cold filter plugging point (°C)	country specific (EN 116)	–	country specific
Cloud point (°C)	country specific	– (D2500)	–
Sulfur content (mg/kg)	<10 (EN 20884)	<15 (D5453)	<10
Carbon residue (% w/w)	<0.30 (10% dist. residue) (EN 10370)	<0.05 (100% dist. residue) (D4530)	<0.30 (10% dist. residue)
Sulfated ash (% w/w)	<0.02 (EN 3987)	<0.02 (D874)	<0.01
Water (mg/kg)	<500 (EN 12937)	<500 (D2709)	<200
Contamination (mg/kg)	<24 (EN 12662)	-	<24
Copper strip corrosion (3h at 50°C)	Class 1 (EN 2160)	Class 3 (D130)	Class 1
Oxidation stability (h at110°C)	>6h (EN 14112)	>3h (EN 14112)	(25 g/m^3)
Cetane number (-)	>51 (EN 5165)	>47 (D613)	>51
Acid value (mg KOH/g)	<0.5 (EN 14104)	<0.5 (D664)	–
Methanol (% w/w)	<0.20 (EN 14110)	-	–
Ester content (% w/w)	>96.5 (EN 14103)	-	–
Monoglyceride (% w/w)	<0.80 (EN 14105)	-	–
Diglyceride (% w/w)	<0.20 (EN 14105)	-	–
Triglyceride (% w/w)	<0.20 (EN 14105)	-	–
Free glycerol (% w/w)	<0.02 (EN 14105)	<0.02 (D6584)	–
Total glycerol (% w/w)	<0.25 (EN 14105)	<0.24 (D6584)	–
Iodine value (-)	<120 (EN 14111)	–	–
Linolenic acid ME (% w/w)	<12 (EN 14103)	-	–
Poly-unsaturated acid MEs (% w/w)	<1 (EN 14103)	-	-
Phosphorus (mg/kg)	<4 (EN 14107)	<10 (D4951)	–
Gp I metal (Na, K) (mg/kg)	<5 (EN 14538)	-	–
Gp II metals (Ca, Mg) (mg/kg)			–
PAHs (% w/w)	-	-	<11
Lubricity/wear (µm at 60°C)	–	-	<460

The flash point of a fuel sample is the lowest temperature at which a liquid fuel provides enough vapour to ignite when an ignition source is placed near the surface of the liquid fuel and causes a brief flash. If this flash lasts longer than 5 s, the fuel is said to have a flash point [70]. Biodiesel must have a flash point above the prescribed limit for diesel fuel that is safe for transportation, handling, and storage [70, 78]. The flash point of biomass diesel is above 150 °C, while the flash point of conventional diesel is 55–66 °C [70]. The flash point values for fatty acid methyl esters are significantly lower than those of vegetable oils [70, 79]. The flash point limit is 93 °C in USA standards and 101 °C in EU standards (Table 12).

The cetane number (CN) of fuels indicates their ignition characteristics or ability to self-ignite after injection [70]. A higher CN value is also related to better ignition efficiency and lower ignition retardation. CN is one of the most important factors for biodiesel with ethyl or methyl esters [70, 80]. As the fatty acid chain length and saturation increases, the CN value increases. A higher CN value is an indicator of a shorter time between ignition and the start of fuel injection into the engine combustion chamber [70, 80]. Biodiesel has a higher CN value than conventional gasoline, indicating better combustion performance [70]. ASTM D613 and EN ISO 5165 have set the CN of diesel at 47 and 51 minutes, respectively (Table 12).

The amount of glycerol remaining in the finished biodiesel is free glycerol [58]. Glycerin is insoluble in biodiesel, and it is easy to settle or centrifuge out almost all of the glycerin. Free glycerol can lead to coking injections and fuel damage [70, 81]. The maximum allowable amount of free glycerol is 0.02% according to USA and EU standards (Table 12).

After combustion, the characteristic of the fuel to deposit carbon is the measure of carbon residue [58]. Carbon contamination is closely related to fatty acids, soap, glycerides, polymers, and inorganic impurities [70, 78]. The limits of USA and EU standards for carbon residue are 0.05% and 0.30%, respectively (Table 12).

Ash material characterizes inorganic impurities such as coarse solids, catalyst residues and soluble metal soap in the fuel [70]. The USA and EU standard allows a maximum percentage of 0.02% of sulfated ash extracted from the samples (Table 12).

From the perspective of biodiesel

The current energy scenario shows that biodiesel is one of the key components to reduce energy dependence on fossil fuels. The production and consumption of biodiesel have increased significantly over the years, and this trend will increase in view of sustainable development and energy standards [70].

The main obstacle to the production of biodiesel is the feedstock, which contributes most to the cost. The ideal feedstock should not only be readily available in sufficient quantities, but also should not create a debate between food and fuel [70]. This can be achieved through low-grade feedstocks, which should be readily available and require less land to grow [70]. Distributed feedstock sources make it difficult to control biodiesel quality [70]. Unlike developed countries where cooking oil is abundant, in developing countries waste cooking oil can become one of the most important feedstocks for biodiesel production.

The choice of catalyst is also a key parameter for defining the biodiesel cost. The catalyst still needs to be decided based on pilot plant performance. The catalyst cost can be minimized by using a catalyst that is easy to synthesize and requires minimum to no purification step. The deep eutectic solvents (DESs) emerged as one of the potential alternatives for biodiesel production [70]. However, the raw material cost along with the separation of catalyst from the product formed as well as purification of biodiesel is a major challenge that needs to be investigated and should require a minimum cost.

EU demand for biodiesel

Both biodiesel and bioethanol represented over 3.5% of the total global transport energy demand in 2022 and the share of these sources increases each year [82]. 90% of the total renewable transport fuels was obtained from ethanol and biodiesel production [2]. In 2022, over 9000 million of liters of biofuel was produced worldwide [82].

Table 13 EU27 biodiesel (FAME/HDRD) main producers (Million Liters) [84]

Year	2014^{r}	2015^{r}	2016^{r}	2017^{r}	2018^{r}	2019^{r}	2020^{r}	2021^{e}	2022^{f}
FAME production									
Germany	3,808	3,505	3,543	3,644	3,799	4,070	3,875	3,919	3,860
France	2,386	2,866	3,152	3,135	2,806	2,556	2,241	2,152	2,060
Spain	1,017	1,103	1,319	1,721	2,008	1,835	1,550	1,450	1,350
Poland	786	861	985	1,019	1,001	1,091	1,081	1,138	1,160
Netherlands	1,056	795	638	1,112	1,010	1,081	1,124	1,136	1,140
Italy	531	558	386	353	508	616	618	620	620
Belgium	568	535	521	511	511	568	568	568	570
Other	1,641	1,022	484	547	853	1,522	1,123	1,117	1,140
Total	11,793	11,245	11,029	12,043	12,495	13,339	12,180	12,100	11,90
HDRD production									
Netherlands	1,013	1,192	1,154	1,218	1,218	1,218	1,218	1,218	1,220
Italy	323	323	323	323	323	328	797	750	800
Spain	377	262	418	465	482	549	480	460	460
Finland	438	533	135	383	354	424	381	397	410
France	-	-	-	-	128	150	476	385	370
Sweden	-	-	-	-	160	205	205	231	255
Portugal	-	-	-	32	37	44	45	45	45
Czech Republic	-	-	-	-	3	3	3	3	4
Total	2,151	2,310	2,029	2,421	2,705	2,921	3,604	3,490	3,560

r = revised / e = estimate / f = forecast

As a renewable and alternative energy source, biodiesel production is promoted and encouraged by several countries with the regulations and policies [83].

The EU is the world's largest biodiesel producer and hosts the largest biodiesel market in the world. Biodiesel account for about three-quarters of the total transportation biofuel market by volume [84]. Biodiesel (FAME) was the first biofuel to be developed and used in the EU and was adopted by the transport sector in the 1990s. EU biofuels goals set out in former Renewable Energy Directive (RED) Directive 2003/30/EC (indicative goals) and in the REDII 2009/28/EC (mandatory goals) further pushed the use of biodiesel (FAME and later commercialization of HDRD: hydrogen-derived renewable diesel) [84].

The production of biodiesel (FAME/HDRD) by EU countries are presented In Table 13. The structure of the EU biodiesel sector is quite diverse. Plant sizes range from an annual capacity of 2.3 million liters owned by a group of farmers to 680 million liters owned by a large multi-national company [84]. FAME production facilities exist in every EU member state, except for Finland, Luxembourg, Croatia, and Malta. In contrast, HDRD production is concentrated in only eight countries (Table 13). The majority of HDRD capacity consists of dedicated HDRD plants, of which the main producers are Finland's Neste, Eni of Italy, and Total Energies of France. Repsol and Cepsa in Spain and Portugal co-process HDRD with conventional fuel at their oil refineries [84].

The consumption of biodiesel (FAME/HDRD) by EU countries is presented In Table 14. The main consumers of biodiesel in the EU are France, Germany, Spain, Sweden, Italy, and Poland. Together they accounted for 72 % of the total EU biodisel (FAME/HDRD) consumption [84].

Table 14 EU27 biodiesel (FAME and HDRD) consumption main consumers (million liters) [84]

Year	2014	2015^{r}	2016^{r}	2017^{r}	2018^{r}	2019^{r}	2020^{e}	2021^{r}	2022^{f}
France	2,931	3,254	3,267	3,276	3,208	3,173	3,097	3,494	3,420
Germany	2,752	2,483	2,498	2,522	2,669	2,621	3,583	3,072	2,900
Spain	1,036	1,091	1,293	1,546	1,979	2,275	1,900	1,920	1,940
Sweden	568	720	1,468	1,756	2,248	1,744	1,596	1,691	1,730
Italy	1,340	1,709	1,362	1,388	1,322	1,257	1,366	1,374	1,380
Poland	730	641	367	551	951	1,025	1,076	1,091	1,100
Belgium	375	436	452	568	625	625	454	625	740
Netherlands	317	229	175	261	426	534	387	505	560
Austria	708	710	641	572	529	578	444	452	470
Romania	172	190	268	278	254	386	384	431	420
Portugal	391	404	337	358	387	385	369	413	415
Others	2,255	1,652	1,057	1,632	1,897	2,110	2,434	2,544	2,535
Total	13,575	13,519	13,185	14,709	16,495	16,712	17,090	17,611	17,610

r = revised / e = estimate / f = forecast

Around 70–95% of biodiesel production cost originates from feedstock cost [70]. In most EU member states, official data on biodiesel/HDRD feedstock use is not available. In Germany, the Ministry of the Environment proposes to reduce the maximum level of biofuel blending in German fossil fuels from 4.4% in 2023 to 2.3% in 2024 and 2.1% in 2025 to zero in 2030 [84].

Rapeseed oil remains the dominant biodiesel feedstock in the EU, accounting for 40% of total biodiesel (FAME/HDRD) feedstock consumption in 2021 [84]. The popularity of rapeseed oil is based on its domestic availability as well as the higher winter stability of the rapeseed methyl ester (RME) derived from it compared to other feedstocks [84].

Used cooking oil which is a second-generation feedstock for biodiesel production, was the second most important feedstock in 2021, accounting for 22 percent of the total feedstock. The increased use of this feedstock is driven by the fact that its fatty acid composition is better suited for HDRD production than that of rapeseed oil [84].

Palm oil ranked third in commodity use in 2021, with a 17% share [84]. Palm oil was used mainly in Spain, Italy, the Netherlands and Belgium, and to a much lesser extent in Finland, Germany, Portugal Romania and Greece [84]. Palm oil use is projected to decline further by up to 29 percent in 2022 as more EU member state begin phasing out biofuels derived from high-risk indirect land use change (ILUC) crops [84].

Animal fats accounted for 8% of total biodiesel (FAME/HDRD) commodities. It is estimated that Italy is the largest consumer of animal fat for biodiesel (FAME/HDRD) production, followed by the Netherlands and France. Finland, Germany, the Czech Republic, Denmark, Spain, Austria, Hungary, Ireland and Poland [84].

Sunflower oil accounted for only 1.4% of total biodiesel feedstock and is mainly used in Greece, France, Bulgaria, and Hungary, which together account for 59% of sunflower oil-based biodiesel production in the EU [84]. Small amounts of sunflower oil are also used in Romania, Lithuania, and Poland. Sunflower oil use for biodiesel production is declined, due to high prices and limited supply of this feedstock, as Ukraine was a major supplier of sunflower oil to the EU [84].

4.2 Bioethanol

Most bioethanol production today is based on feedstocks from food crops, implementing fermatation process. The most used feedstocks are grains (e.g., corn, other coarse grains, and wheat kernels) and sugar cane. In EU, wheat is grown mainly for bioethanol production - on 0.7% of the EU's agricultural land and 2% of EU 's grain supply [22]. The EU has proposed limiting the share of biofuels from "food crops" in transport energy consumption to 7% due to concerns about the impact on food prices and land use . However, there are conflicting studies and opinions on this issue, and biofuel producers believe that the impact of ethanol production from starch crops may have been exaggerated and that the many benefits of biofuels (security of fuel supply for EU, job and wealth creation, production of valuable by-products, reduction of greenhouse gas emissions) have not been fully considered [85].

Properties of bioethanol

Bioethanol can be directly used in vehicles as it behaves similarly to conventional fuels. The physicochemical properties of bioethanol are summarized in Table 15. Bioethanol is an oxygenated fuel and therefore can reduce particulate emissions from engines. Bioethanol also has a higher octane rating, higher heat of vaporization, and broader fammability limits that improve fuel combustion, increase compression ratio, and shorten ignition timing compared to gasoline and diesel [86].

Table 15 Physicochemical properties of bioethanol [86]

Fuel property	Bioethanol
Density at 15 ^{o}C, kg/m^3	790
Kinematic viscosity at 40 ^{o}C, mm^2/s	1.13
Oxygen, Mass%	34.7
Cetane number, —	5,8
Octane number, —	110
Latent heat of vaporization, MJ/kg	0.91
Lower calorifc value, MJ/kg	25.22, 26.70
Flash point, ^{o}C	13
Auto-ignition temperature, ^{o}C	332.8, 366.0
Water content, mg/kg^{-1}	2024
Stoichiometric fuel/air ratio, —	1/9.01

However, compared to conventional gasoline, the bioethanlo has a low volumetric energy density, which is directly reflected in the fact that vehicles require more bioethanol per kilometer compared to gasoline (up to 50%) [87, 88]. To convert a conventional spark-ignition engine vehicle into a pure bioethanol engine requires adjustment of the timing and the fitting of a larger fuel tank due to the bioethanol's low energy density [89].

When used in pure form (E100 blend), bioethanol is difficult to vaporize at low temperatures and therefore E100-fitted vehicles can be more difficult to start in cold weather [89]. To improve ignition, bioethanol is blended with a small amount of gasoline. Therefore E85 blend is a common alternative. Low percentage bioethanol blends (E10) can be used by most conventional gasoline engines without modification and may even slightly improve their performance [89].

EU demand for bioethanol

The production of bioethanol by EU countries are presented in Table 16.

Table 16 EU27 bioethanol production, main producers (million liters) [84]

Year	2015^{r}	2016^{r}	2017^{r}	2018^{r}	2019^{e}	2020^{e}	2021^{e}	2022^{f}
France	1,039	987	1,000	1,138	1,299	1,099	1,201	1,248
Germany	870	882	810	799	676	700	747	759
Hungary	591	633	633	646	689	695	704	722
Netherlands	519	443	519	519	519	481	519	519
Spain	494	328	377	522	547	487	487	481
Belgium	557	570	620	646	620	620	633	633
Poland	214	241	258	259	286	276	338	348
Austria	223	224	235	251	254	222	234	234
Total	4,989	4,748	4,813	5,035	5,047	4,891	5,190	5,354

r = revised / e = estimate / f = forecast

From 2015 to 2017, EU bioethanol production fluctuated between 4.75 and 5.0 billion liters. In 2018 and 2019, production exceeded 5.0 billion liters, but fell in 2020 as a result of the COVID-19 crisis [84]. In 2021 and 2022, EU bioethanol production has been recovered. Main producers are France, Germany, Poland, Hungary, Belgum, Netherlands and Spain. Total EU ethanol production capacity, for fuel, industrial, and food uses, is estimated at roughly 6.4 billion liters in 2022 [84]. Further expansion of first-generation bioethanol is expected to be limited. Expansion of cellulosic bioethanol production remains constrained due to high costs and a lack of certainty in the EU policy making process [84]. The consumption of bioethanol by EU countries is presented In Table 17.

Table 17 EU27 bioethanol consumption, main consumers (million liters) [84]

Year	2015^{r}	2016^{r}	2017^{r}	2018^{r}	2019^{e}	2020^{e}	2021^{e}	2022^{f}
Germany	1,485	1,485	1,465	1,491	1,435	1,378	1,453	1,456
France	833	885	989	1,084	1,231	1,062	1,115	1,225
Netherlands	278	237	253	335	366	430	480	500
Poland	323	329	329	299	372	359	361	361
Belgium/Luxembourg	63	63	208	228	228	215	234	241
Spain	375	253	277	319	328	190	205	213
Sweden	263	215	172	224	178	187	196	203
Hungary	123	129	133	138	189	167	180	194
Total	4,530	4,432	4,677	5,029	5,227	5,159	5,443	5,570

r = revised / e = estimate / f = forecast

From 2019, consumption of bioethanol continued to rise and production stagnated, which had influence on bioethanol import increase. This growth was a result of a gradual increase in blending targets towards the 2020 mandate, the improved competitiveness of bioethanol versus gasoline, and increasing imports, predominantly from the USA [84]. The COVID-19 outbreak, and the resulting lockdowns and reduced transport had only a limited effect on the EU's bioethanol use [84]]. Bioethanol consumption had limmited decrise due to EU member states support measures to reach the national blending mandate of 10%. The main consumers of bioethanol in the EU are Germany, France, Netherlands, Poland, Spain and Sweden. The increasing mandates and the introduction and further market expansion of higher ethanol blends, mainly in Germany, France, and Sweden, played an important role in the recovery of bioethanol consumption for road vehicle transport [84].

Fossil fuel and feedstock prices as well as associated biofuel prices surged due to Russia-Ukraine conflict [84]. However, gasoline increased prices have increased the competitiveness of bioethanol. As a result, EU bioethanol consumption is forecast to increase in next years [84]. This growth is mainly driven by the introduction and/or higher sales of high blends such as E10 and E85.

4.3 Biogas

Biogas which is produced at most biological treatment plants has been considered as one of the most important renewable energy sources. The biogas is mainly mixture of methane, carbon dioxide and other trace gases. Environmental pollution from hazardous secondary pollutants produced by the use of a raw biogas is important issue. Therefore, the utilization of biomass requires removal of impurities, such as removal of CO_2, H_2S, NH_3, siloxanes etc. [64]. The thermal heating value of biogas varies between 15 and 30 MJ/m^3, close to that of natural gas [64]. Table 18 presents composition of biogas originates from various sources. Possible biogas utilization pathways are conceivable in all areas of consumption [79], with three main distinctions [90]:

1. using the biogas in a CHP unit for production of electricity and heat,
2. using the biogas directly, for example, in machines or facilities in agricultural operations, and
3. upgrading the biogas to a gas of a higher value.

Table 18 Biogas composition originates from various sources [64]

Parameter, component	Biogas from wastewater	Househol waste	Agricultural waste	Landfill sites	Natural gas (Danish)	Natural Gas (range comp.)
CH_4, mol %	60-70	50-60	60-75	35-65	89	85-92
CO_2, mol %	30-40	34-38	19-33	15-50	0.67	0.2-1.5
C_2+hydroc.	0		-	0	9.4	9
H_2S, ppm	0-4000	72-648	2160-7200	0-100	2.9	1.1-5.9
NH_3, ppm	100	-	72-144	~5	0	-
H_2, mol %	0	-	-	0-3	0	-
N_2, mol %	0.2	0.5	0-1	5-40	0.28	0.3
O_2, mol %	0	0-1	<0.5	0-5	0	-
H_2O, mol % (40°C)	1-5	<6	<6	1-5	-	-
Total Cl, mg/m^3	100	100-800	-	5	-	-
Aromatics, mg/m^3		0-200	-		-	-
Heating value(lower), MJ/m3	23		-	16	39.5	39

Biogas and Biomethane production in EU

Biogas is one of the very important sources of renewable energy worldwide, and particularly in the EU countries [32]. The evolution of biogas and biomethane production in EU for the period 2011 to 2021 is depicted in Figure 13. This graph shows the overall growth in energy generation, as well as the increasing portion of biogas being upgraded to biomethane. Combined biogas and biomethane production in 2021 amounted to 196 TWh (or 18.4 bcm) of energy, representing an estimated 4.5 % of gas consumption within the European Union.

Figure 13 Combined biomethane and biogas production in EU (TWh) [38]

Due to the current geopolitical conflict that has disrupted the international flow of fuel gas and cereals, more European countries are shifting incentives from biogas production to biomethane production encouraging a sustained drive for growth of the biomethane industry. The fact that existing AD-biogas plants can be upgraded and converted to AD-biomethane plants highlights the flexibility of this biogas technological sector. Germany takes the lead with 84 TWh of energy production, followed by the UK (26 TWh), Italy (26 TWh) and France (10 TWh) [38], as it is shown in Figure 14.

The ratio of biomethane in proportion to the total biogas - biomethane production differs significantly between the EU countries. This shift very often depends on the availability of national funds, development of the technology and availability of biomass and land, all very variable aspects amongst the EU countries. Nonetheless, more European countries are taking a clear direction towards biomethane production in recent years. Denmark, Sweden, Norway and Estonia are the countries that are currently reporting more production of biomethane then biogas. Countries such as France, the Netherlands, Italy, Switzerland and the United Kingdom are, indeed, tending also in this direction [38].

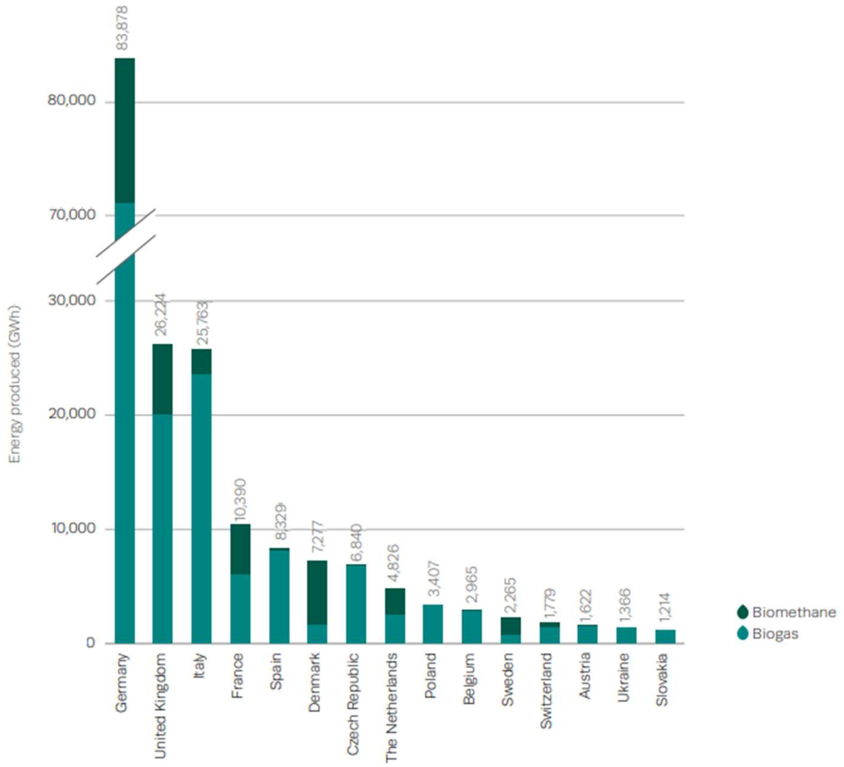


Figure 14 Combined biomethane and biogas production per country in descending order (GWh), top 15 countries [38]

The combined number of biomethane and biogas plants in EU is shown in Figure 15.

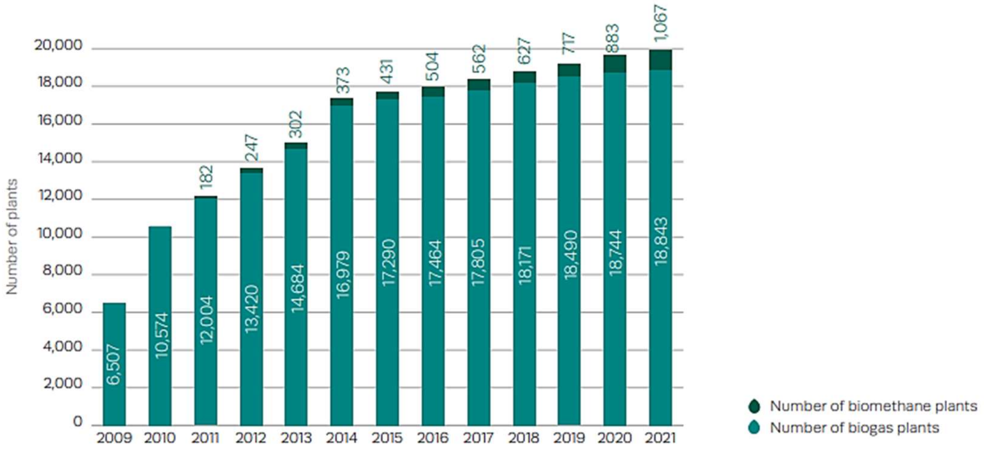


Figure 15 Combined number of biomethane and biogas plants in EU [38]

It can be seen that biomethane plants are larger in size than biogas plants, as the share of biomethane production from anaerobic digestion (19%) is larger than the portion of biomethane plants in the total number of anaerobic digestion plants (5%) [38]. A biogas plant produces on average 8 GWh per year, a biomethane plant produces an average of 35 GWh per year. In 2021, there were 1,067 biomethane-producing facilities in total in EU, an increase of 178 plants relative to 2020, making 2020 the year with the biggest increase in biomethane plants. As for biogas, a period of rapid growth occurred between 2009 and

2014 that was followed by a period of modest increase in plant numbers from 2014 and 2021. The total number of biogas and biomethane plants in the European Union was 19,910 at the end of 2021 [38]. Germany led the development of EU's biomethane market for almost a decade (2008 – 2015) but was overtaken by France in 2017 [38].

Opportunities of Anaerobic Digestion Technology within a European context

1. Reliable Technology

The Anaerobic Digestion (AD) Technology is a well-established readily available off the shelf technology capable of processing a variety of biomass that are very prone to biological degradation. This technology has been applied worldwide to generate biogas from organic materials. Biogas is the main energetic component derived from this process, a clean fuel the produces fewer emissions on burning. Also as a side-stream, the process supplies a product known as digestate that has a high fertilizer values with the capacity of replacing chemical fertilisers.

2. Economic Security

Not every country has large reserves of crude oil. For them, having to import the oil puts a huge dent in the economy. If more people start shifting towards biofuels, a country can reduce its dependence on fossil fuels. In return, Biofuel production increases the demand for suitable biofuel crops, providing a boost to the agriculture industry. More jobs will be created with a growing biofuel industry.

3. Utilization of Renewable carbon neutral feedstock.

The feedstock biomass sources are renewable home-grown energy crops. The release of carbon dioxide is mitigated by the fact that it is used during photosynthesis by the crops that will be used as feedstock biomass, hence creating somewhat of a self-sustaining system within a carbon neutral context.

4. Methane emission reduction when treating animal manure

This technology can also be utilized to valorize livestock manure. Anaerobic digestion is a process that converts cow manure into biogas rich in methane, reducing indirectly GHG emissions from animal waste storage and distribution and from the replacement of biogas with non-renewable energy sources [91].

5. Flexibility of AD/biogas project

The AD technology platform, apart from being a classical process for the conversion of biomass into bio-gas, can also be integrated to compliment other established and up and coming technological process, in order to obtain a wider variety of other product [92].

Challenges of Anaerobic Digestion Technology within a European context

1. Constraints in the adoption of the technology

Although the technology is reliable, robust and readily available, the decision to purchase this technology has to be backed by: availability of capital, availability of trained personnel, and the availability of an appropriately sited location at affordable price. Furthermore, from a feedstock perspective, certain parameters have also got to be met, such as the willingness of framers to cooperate in the cultivation and delivery of feedstock, and the availability of natural resources to sustain the cultivation of the energy crops, such as vast areas of arable land with fertile soils and the availability of irrigation water. The gradual decrease in soil fertility, water availability and in some cases also access to sufficient agriculture land in southern EU as compared to the Northern EU seems to be closely correlated to a similar trend in the establishment of plants focused on first generation feedstock. Furthermore, no AD plants using first generation feedstock are to be found on Mediterranean islands that are members of the European Union.

2. Monoculture

AD Technology utilizes a biological process involving the utilization of micro-organisms to digest a specific substrate. To maximise the efficiency of the technology, the digestive process requires a constant supply of feedstock that is uniform in quality. Hence, a plants efficiency is best maintained when the feedstock originates from one energy crop. This automatically leads to crop monoculture, producing the same crops year after year with no crop rotation. Monoculture is associated with soil degradation and an increase, changes in environment in terms of pest habitat resulting in higher usage of agro-chemicals. Nonetheless, the pest will eventually develop a resistance prompting genetic engineers to develop genetically modified crops that show a higher are resistance to pests. Land Use Change of natural habitats and other ecologically valuable land acquired for biofuel plantations has been linked to loss of biodiversity [93].

3. Production and Use of the Excess Digestate

A secondary end product of the AD technology is the digestate, a residue of the feedstock following digestion. While the carbon component of the substrate is converted to biogas, similarly the nitrogen component, while remains unaltered in terms of quantity, does undergo a transformation process. During the retention period, organically bound nitrogen is mineralized, thereby transforming into a matrix with a high fertilizer value as a soluble compound that is readily taken up by plants. This digestate can easily substitute chemical fertilizer used in the production of the energy crop feedstock, however there has to be enough land available on which to apply all the digestate produced. Excess digestate is very challenging to manage given its liquid nature and the risk of ammonia volatilization. Monoculture of energy crops is in theory a heavy user of fertilisers that can be replaced by digestate. However, similar to conventional fertilisers, precaution needs to be taken to avoid environmental pollution.

4. Food vs. Fuel

The term ‘energy crops’ is often associated with the potential conflict with the use of agricultural land for food thereby the term ‘food vs. fuel’ originated. As early as 1991, David O. Hall noted that the food vs. fuel issue is ‘far more complex than has been presented’. The 2007–08 world food price crisis prompted warnings of sustained high food prices over the next decade as food production and supplies are displaced by biofuel production. On April 2015 the European Parliament approved a reform of the Renewable Energy Directive (RED), which includes a 7% cap on food crop based biofuels for the transport sector.

5. Antimicrobial resistance

Muthaiyan et al. [94] highlighted that the routinely use of antibiotics in fermentation process of ethanol to control contaminants in bioethanol plants. This practice has a potential risk of developing antibiotic resistant bacteria that can have significant repercussions that are not only linked to limiting the effectiveness of antibiotics to treat future bacterial contamination in AD plants, but will also contaminate the substrate, a byproduct of ethanol production. This substrate has a market value as an animal feed supplement and as a potential application in other industries such as bioplastics adding to the financial feasibility of the bioethanol industry. However, since 2005 the EU has legislated against the use of animal feed products containing antibiotics residues.

There is also a very real risk to human health if antibiotics had to enter the food chain through the consumption of crops irrigated by antibiotics contaminated water discharged from ethanol plants as the high use of antibiotic agents in non-human settings that in turn reduces the efficacy of antibiotics important for human medicine, as the antibiotics used are identical or nearly so [95].

4. Constraints and concerns

As mentioned earlier, first-generation biorefineries are facilities that primarily use food and feed crops as feedstock (e.g., sugar cane, rice, wheat, potato, sugar beet, barley, corn, peanut, soybean, rapeseed, sunflower, olive, oil palm etc.) for the production of biofuels and other bioproducts [96]. While they represent a significant step toward sustainable alternatives to fossil fuels, they also come with some limitations and concerns.

5.1 Competition with food production

Although biogas is produced mostly from waste materials, biodiesel in the EU is mostly produced from the crops (e.g., rapeseed or other oil) that are also used as food and this inevitably raises the 'food or fuel' concerns [32]. Clearly, the raw materials which are also a segment of the food chain supply do not serve a long-term and full-scale solution; therefore, first-generation biofuels will not be able to fulfill the energy requirement in the future [97]. The first generation biofuels can compete with the food sector, either directly when edible biomass feedstock is used as an energy source or indirectly when bioenergy crops[1] are grown on land that would otherwise be used for food production [98]. Both effects can impact food prices and food security if demand for the crops or land is very high [99]. Increased biofuel production could also reduce the availability of water for food production as more water is diverted to biofuel feedstock production [98]. Here are some key points regarding the competition with food production:

- Food Security: The competition for food crops between the biofuel and food industries can have adverse effects on food security, particularly in regions where food availability is already precarious. For an example, crops used to produce 1 TJ of biofuel would be sufficient to feed 110 and 90 people in the case of bioethanol and biodiesel, respectively [100].
- Food Prices: When a substantial portion of the crop supply is diverted from the food market to the biofuel industry, it can lead to reduced food availability and higher prices for essential food items. In addition biofuels received some of the blame for the food price increase mid-2008, resulting in the "biomass: food versus fuel" slogan [101].
- Land Allocation: The allocation of arable land for biofuel crop cultivation may result in less land being available for food production.
- Policy Conflicts: Government policies that promote biofuel production, such as subsidies and mandates, can conflict with policies aimed at ensuring food security and affordable access to food. Balancing these policies is a complex challenge.

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[1] bioenergy crops – not edible feedsctoks (e.g. miscantus etc.)

In order to mitigate the aforementioned concerns, considerable efforts have been made to use non-food feedstock for biofuel production [32]. Therefore, it is essential to replace the first generation biofuels gradually with biofuels from non-food biomass [97].

5.2. Land Use Change (LUC)

Changes in land use, mainly related to deforestation and the expansion of agricultural food production, contribute to about 15% of global greenhouse gas emissions [98]. Currently, less than 3% of the world's agricultural land is used to grow biofuel crops, and land-use changes associated with bioenergy account for only about 1% of total global emissions from land-use change [98]. LUC is a critical consideration due to its potential environmental and ecological impacts. Here are some key points related to land use change:

- **Conversion of Natural Ecosystems:** Land use change often involves converting natural ecosystems, such as forests, grasslands, wetlands, or other natural habitats, into areas for agricultural or industrial purposes. This can have significant ecological consequences, including habitat loss and fragmentation, which lead to declines in biodiversity and threaten endangered or vulnerable species.
- **Deforestation:** One of the most concerning forms of land use change is deforestation, which is the clearing of forests for agriculture, urban development, or other purposes. Deforestation contributes to the release of carbon stored in trees and soil into the atmosphere, increasing greenhouse gas emissions and contributing to climate change.
- **Soil Erosion and Degradation:** Intensive agriculture associated with land use change can lead to soil erosion, reduced soil fertility, and degradation. This can have long-term negative effects on agricultural productivity and the environment.
- **Water Resource Impacts:** Altering land use can affect local water resources by changing the hydrology of an area. For example, converting wetlands into agricultural fields can disrupt natural water flow patterns and impact water quality.
- **Indirect Land Use Change (ILUC):** ILUC refers to the concept that changes in land use in one area can indirectly drive land use changes elsewhere. For example, the expansion of biofuel crop cultivation may lead to deforestation in other regions to meet the demand for food crops, thus contributing to land use change and its associated impacts.
- **Regulatory and Policy Considerations:** Many countries and regions have implemented regulations and policies to address land use change associated with biofuel production. These may include sustainability criteria, land-use planning, and requirements for avoiding deforestation and habitat destruction.

5.3. Resource Intensive

First-generation biorefineries often require large amounts of water, fertilizer, and energy to produce biofuels, which may be environmentally unsustainable and negate some of the environmental benefits.

5.4. Water pollution and fouling

First-generation biofuels, have been associated with concerns related to water pollution and fouling. One of the primary reasons for this is the increased use of fertilizers and pesticides in agriculture to grow these crops for biofuel production. Here's how this process can lead to water fouling:

- **Fertilizer Use:** To maximize crop yields, often are used synthetic fertilizers that contain nutrients like nitrogen and phosphorus.
- **Nutrient runoff:** When it rains or when fields are irrigated, excess fertilizers can be washed off the fields and enter nearby water bodies, such as rivers, lakes, and streams.
- **Water Pollution:** Nutrient runoff can lead to water pollution. Excessive nutrients in water bodies can cause a process called eutrophication. In eutrophication, the excess nutrients promote the rapid growth of algae and aquatic plants. As these organisms die and decompose, oxygen levels in the water can decrease, leading to "dead zones" where aquatic life cannot survive.
- **Harm to Aquatic Ecosystems:** Eutrophication and oxygen depletion can harm aquatic ecosystems by disrupting the balance of species and leading to fish kills. It can also affect water quality and make water sources less suitable for drinking.
- **Algal Blooms:** In some cases, nutrient runoff can result in harmful algal blooms (HABs). These blooms can produce toxins harmful to aquatic life and humans. Some types of algae in HABs can produce toxins that can contaminate drinking water supplies.

5.5. Greenhouse Gas Emissions

While biofuels are often promoted as a more environmentally friendly alternative to fossil fuels because they can reduce greenhouse gas emissions, the actual emissions reductions depend on several factors and can vary widely. Here are some key points to consider regarding greenhouse gas emissions in the context of first-generation biorefineries.

- **Carbon Intensity:** The carbon intensity of biofuels depends on the feedstock used and the production processes involved. In some cases, the cultivation, processing, and transportation of biofuel feedstocks can generate substantial greenhouse gas emissions, offsetting the benefits of using biofuels.
- **LUC:** Clearing land for biofuel crop cultivation, especially through deforestation or conversion of carbon-rich ecosystems like peatlands, can release large amounts of carbon dioxide (CO_2) into the atmosphere. This land-use change can have a significant impact on the overall emissions associated with biofuels.

- **Energy Input:** The energy required to grow, harvest, transport, and process biofuel feedstocks can contribute to greenhouse gas emissions. If the energy input is primarily derived from fossil fuels, it can reduce the emissions savings achieved by using biofuels.
- **ILUC:** The concept of indirect land use change considers the potential impacts of biofuel production on land-use decisions worldwide. For example, if the cultivation of biofuel crops leads to increased demand for agricultural land, it may indirectly drive deforestation and carbon emissions elsewhere.
- **Lifecycle Analysis (LCA):** Assessing the greenhouse gas emissions associated with biofuels requires a comprehensive LCA that considers emissions at every stage, from feedstock production to biofuel use. Different biofuels and feedstocks can have varying emissions profiles.

5. Conclusion

This report provides a brief overview of the main characteristics of of first-generation biorefineries.

First-generation biofuels are produced from sugar crops, starch crops, oilseeds, and animal fats. Sugar and starch plants are converted into bioalcohols, including ethanol, butanol, and propanol, through a fermentation process. Oils and animal fats can be processed into biodiesel. Ethanol is the most commonly used bioalcohol fuel. Other most common first-generation biofuels is biogas. Since all the resultant biofuels are mostly of high quality; their production and usage has gained considerable interest during the last few decades. For example, most vehicles can use gasoline-ethanol blends with an ethanol content of up to 10 percent (by volume). Flexible-fuel vehicles can use E85, a gasoline-ethanol blend with an ethanol content of up to 85 percent.

Since the biofuels derived from plant-based biomass are considered as renewable energy source, they have great potential to reduce and replace consumption of fossil fuels. However, the future success of first-generation biofuels is limited due to their social and environmental unsustainability. First-generation biofuels negatively impact greenhouse gas emissions, biodiversity, land use, water usage, and water fouling due to the increased use of fertilizer to grow crops for biofuels.

To address these concerns, there have been efforts to transition from first-generation biorefineries, which rely on food crops, to second- and third-generation biorefineries that use non-food feedstocks like agricultural residues, algae, and waste materials. Additionally, improving the efficiency of biofuel production processes and developing sustainable land-use practices can help mitigate the competition with food production and resolve economic considerations. Sustainable land management and agricultural practices, as well as policies that carefully consider both food and biofuel priorities, are essential for finding a balance between the two sectors and minimizing negative impacts on food security and affordability.

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Weblink: https://wire-cost-eu.ipportalegre.pt/

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