

Biodiesel and green diesel generation: an overview

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Abstract. First, second, third, and fourth-generation biofuels are continuously evolving as a promising substitute to petrodiesel catalyzed by energy depletion, economic and environmental considerations. Bio-diesel can be synthesized from various biomass sources, which are commonly divided into FAME and renewable biodiesel. FAME biodiesel is generally produced by the transesterification of vegetable oils and fats while renewable diesel is produced by hydro-deoxygenation of vegetable and waste oils and fats. The different generation, processing technologies and standards for FAME and renewable biodiesel are reviewed. Finally, the life cycle analysis and production cost of conventional and renewable biodiesel are described.

1 Introduction

Unstoppable growth in the global population is estimated to hit 12 billion by 2030, which would increase the annual energy needs of the resource limited countries [1]. Energy demand in developing countries is expected to rise by 90%, and approximately one-third of this energy would come from renewable sources, such as biofuels.

Biofuel from harvested biomass is considered as the only available alternative to fossil fuels worldwide. Figure 1 represents the evolution of biodiesel [2].

Biofuels are categorized into four different generations based on their biomass feedstock. This sequence of developments of biodiesel ranges from the processing of edible oils until genetic modification of algae. Food sources are essential feedstock for first-generation biofuels and can also contribute to the competition of food [3]. While only 5% of the world's arable land is used to produce renewable resources in the form of first-generation biofuels, it has made a substantial impact on higher food and feed prices [4]. However, the existing effects of biofuels on the increase in food price remain uncertain in research or news reports. Biofuels produced from food and plantation waste, or non-food crops could solve the crisis [5]. Although the concept of first-generation biofuels had long emerged, it received considerable interest in the late 1990s.

Biofuels from second-generation lignocellulosic biomass, such as waste straw, grass and wood also require land with food and fibre processing compounds. However, energy returns from these crops are more favourable than first-generation biofuels or their products [6]. The search for alternative sources has continued to reduce competition in food crops to the extent that algae are used as a renewable and rich supply of biofuels known as third-generation biofuels [7]. Algae are not in a competitive environment with food or other crops and may be planted in shallow lagoons on marginal land or in enclosed wetlands [8].

Besides, algal biofuel feedstocks may be produced throughout the year unless there is a decrease in the availability of solar irradiation. The oil yields may be much higher than those of the best oilseed crops. For example, compared to neem, karanja, pine and eucalyptus, algae biodiesel contains 45% oil by weight which is significantly higher [9]. However, biofuels from the above sources are limited in geographical distribution; therefore, their carbon impact and economic aspects, are ineffective in replacing fossil fuels [10]. Table 1 shows the advantages and disadvantages of various biodiesel generations.

Fourth generation biofuel research has been carried out between 2000 and 2020 [11]. It is clear from the published research papers that the third-generation biofuels have received the highest emphasis in the last three years [12].

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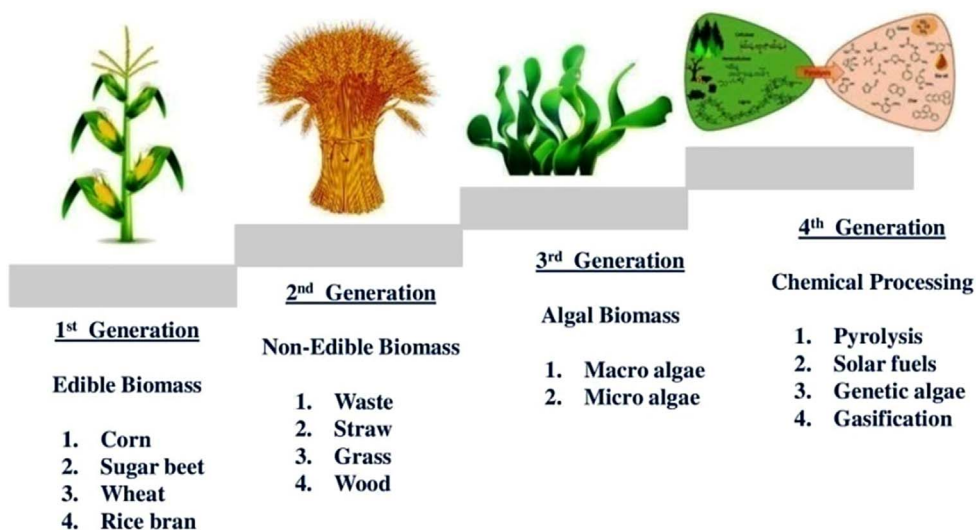


Fig. 1. Evolution of biodiesel [3].

Table 1. Advantages and disadvantages of various biodiesel generations [12].

Biodiesel generation	Advantages	Disadvantages
1st generation biodiesel	<ol style="list-style-type: none"> 1. Low emission of greenhouse gas. 2. Easy and low-cost technology for conversion. 	<ol style="list-style-type: none"> 1. Yield is inadequate to meet the demand. 2. Causes food shortage. 3. High land footprint.
2nd generation biodiesel	<ol style="list-style-type: none"> 1. Using food waste as a feedstock. 2. Use of non-agricultural land to grow a limited amount of crops. 	<ol style="list-style-type: none"> 1. Costly pre-treatment. 2. Sophisticated technology is used to transform biomass into fuel.
3rd generation biodiesel	<ol style="list-style-type: none"> 1. Simple to grow algae. 2. No competition for the use of food crops: wastewater, seawater can be used. 	<ol style="list-style-type: none"> 1. More resources usage for algae cultivation. 2. Low lipid level or biomass accumulation in algae.
4th generation biodiesel	<ol style="list-style-type: none"> 1. High biomass and production yield. 2. More capability to eliminate CO₂. 	<ol style="list-style-type: none"> 1. The cost of the bio-reactor is higher. 2. At the early stage of research, the high investment needed.

2 Biodiesel production/processing techniques

The following section discusses the various biomass feedstocks and their suitability as substitutes for fossil fuels [13]. Table 2 shows the different processing method for various biofuel generation.

2.1 First-generation biofuel – production

As indicated above, first-generation biofuel feedstocks consist primarily of oleaginous, sugar cane and other food and animal source [14]. Bioethanol of the first generation

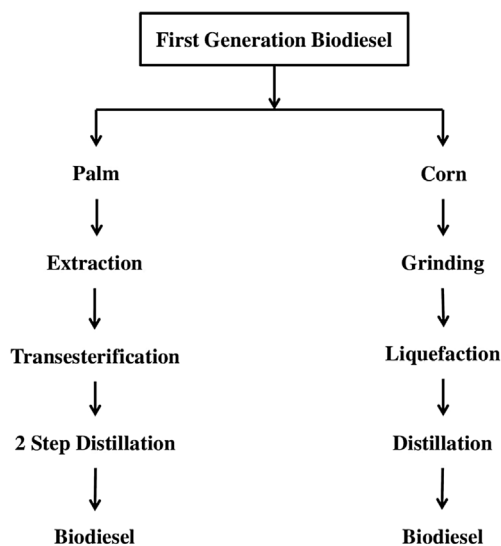
is derived primarily from sugar, which includes plants or cereals. At present, the maximum quantity of biofuel in the form of ethanol has been produced, of which 92% is from corn and sugar cane [15]. Approximately 15% (v/v) of crude corn ethanol with fungal and algae mutants has been studied. The development of sugar cane ethanol is currently at different stages of maturity [16]. Greater yields of ethanol after 300–325 days of planting are also realised. Vegetable oils are often used for the conversion of methyl or ethyl fatty acid esters [17, 18]. Table 3 and Figure 2 represent the processing methods of first-generation biodiesel.

Table 2. Various generations of biofuel with processing technology.

Generation	Biomass used	Processing methodology	Generated fuel	Ref.
1st	Food crops, edible oil/animal fats	Transesterification – Thermochemical processing	Bioethanol, biodiesel.	[16, 18]
2nd	Waste cooking oil, rice/wheat straw, non-edible oils	Pre-treatment – Chemical, biological, physical, fermentation and thermochemical processing	Syngas, biobutanol, biodiesel.	[23, 27]
3rd	Algae and microorganisms	Cultivation – Extraction – Fermentation – Thermochemical processing	Methane, bioethanol, biobutanol, syngas, biodiesel.	[33, 34, 39]
4th	Algae and microorganisms	Metabolic engineering of algae capable of absorbing biomass – Cultivating – Fermentation – Thermochemical processing	Biodiesel, methane, biobutanol, bioethanol.	[45–47]

Table 3. First generation biofuels.

Biomass	Processing method	Ref.
Waste cooking oil	Esterification – Transesterification	[16]
Food crops	Extraction – Transesterification	[17]
Organic oils	Hydrolysis – Distillation	[18]
Animal fat	Hydrolysis – Fermentation	[19]
Bioethanol/biobutanol	Chemical synthesis	[20]

**Fig. 2.** First-generation biodiesel processing [19].

An experiment on cottonseed oil produced 63.4% biodiesel with 35% methane in the presence of 2.6% sodium hydroxide. Reduction of carbon monoxide, particulate matter and exhaust soot emissions have been observed for all biodiesel mixtures [19]. A small increase in NO_x emissions was reported for Karanja biodiesel mixtures. Attempts have been made to test the performance of organic oils,

particularly in diesel engines. However, organic oils were not considered suitable, leaving wax and fluid deposits in engines [20]. Organic sludge, which is produced from the agricultural waste, may be another promising source of biofuel. The cracking response of vegetable oil results in products similar to syngas, liquefied-oil, diesel, light-cycle oil and heavy-cycle oil cracking processes [21].

2.2 Second-generation biofuel – production

Approximately 90% expense of biodiesel production is met from the selected feedstock. The production of low-cost bioethanol from trees, forest residues, wood waste and the organic portion of urban waste is known as second-generation biofuels [22]. With due recognition to its high-octane number, low cetane number and high vaporisation heat, it is capable of replacing gasoline [23]. The production of bioethanol using these materials would no longer need land and would thus have no impact on the production of food and fibre crops. Lignocellulose biomass is plentiful in nature, but only a small part of it can be used. Theoretically, these biomass sources will supply 130 EJ of electricity annually [24].

With all species, such as Southern Blue Gum, Salicaceae and Black Locust, grasses such as Silver Grass and *Panicum virgatum* are becoming increasingly common as they can be cultivated in fertile and degraded land that is not usually suitable for food production and fibre cultivation [24]. The production of ethanol by fermentation from a separate pre-treated cellulose fraction of corn cob with

Table 4. Second generation biofuels.

Biomass	Processing method	Ref.
Cellulose	Advanced fermentation	[22]
Hemicelluloses	Hydrolysis	[26]
Lignin	Gasification	[27]
Tannins	Biological synthesis	[28]
Vegetable oil/animal fat	Hydrogenation	[31]

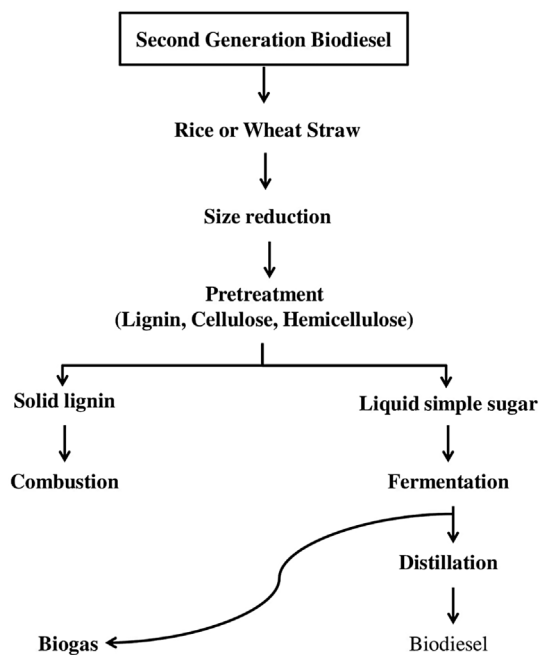
Pachysoletia tannophilus and yeast was studied [25]. It was found that 60–90% of hemicellulose and 52–70% of cellulose could be converted into ethanol by different fractionation processes in corn cobs [26]. Recently, the use of ceiba-pentandra, pineapple, waste paper and coffee residues has been listed for the production of bioethanol. The processing of bioethanol from waste materials can also be combined with the production of biogas [27].

Biodiesel from raw *Jatropha* and *Karanja* oils can be blended with diesel for applications in engines [28]. The biogas is produced from de-oiled neem and pine seedcake. Genetic engineering can be a valuable tool for producing fast-growing low-input energy crops with lower insecticide, fertiliser and water requirements in order to minimise overall biofuel costs [29]. Genetically modified wheat and barley have been found to have hydrolyzed biomass without compromising its composition and losing agricultural productivity [30]. Table 4 and Figure 3 represent the processing methods of second generation biodiesel.

Advanced biofuels such as isopropanol, butane, isobutane and farnesol have recently become more desirable in addition to ethanol due to high energy density and hygroscopic nature [31]. Biochemical engineering of biosynthetic pathways leading to the production of alcohol will boost efficiency [32]. Aldehyde/alcohol dehydrogenase expressions in *Clostridium tyrobutyricum* increased butanol production by approximately 25–35%, but also increased its resistance to butanol [33]. Changing the mechanism of amino acid biosynthesis in *E. coli* resulted in an increased development of 1-butanol and 1-propanol.

2.3 Third and fourth generation biofuel – production

Due to their increased photosynthesis and rapid growth, algae have recently had a major interest in renewable biofuel feedstock compared to other terrestrial plants [34]. On a dry weight basis, algae can generate up to 64% lipid and can grow on a liquid medium from multiple wastewater sources, resulting in lower demand for freshwater [35]. Recent research efforts have focused on finding the best combination of high lipid and optimum algal organism growth conditions [36]. Several algae species, such as Trebouxiophyceae, Chaetocerotaceae, numerous single-cell green algae, Haptophyta, Eustigmatophyceae, Aurantiocytrium limacinum and Scenedesmaeaceae, have been identified as potential biofuels [37]. The highest average lipid and biomass content of chlorophytes was obtained, but the triglyceride content was low. As an alternative, some algal species can produce 10–50% triglycerides, 25–65%

**Fig. 3.** Second-generation biodiesel processing [25].

and 40–80%, respectively, of dry cell weight, such as Botryococcaceae, Ochrophyta and Thraustochytrids, although biomass yields are low in each case [38].

Fast-growing algae are generally found to have low oil content, whereas high lipid algae are slow-growing species. It is, therefore, essential to identify the correct species with high biomass and high lipid concentrations for the marketing of algal biofuels [39]. Biomass and lipid yield of the same strain of microalgae are also affected by the cultivation process. In this context, genetic modification/metabolic engineering may be promising alternatives to the production of lipid levels and algal biomass [40]. Researchers are searching for an acceptable method of culture to increase lipid content and make it more cost-effective and sustainable. Failure to activate ADP-glucose pyrophosphorylase in a pseudomonas starch-free mutant resulted in triacylglycerol being 10 times higher, indicating that sharing of photosynthetic carbon partition from starch to triacylglycerol synthesis may be more successful than lipid synthesis pathway manipulation against triacylglycerol overproduction [41]. The *Synechococcus elongatus* is capable of producing butanol directly from CO₂ by altering the coA-dependent 1-butanol process pathway to cyanobacterium [42, 43]. Figure 4 represents the processing methods of third/fourth generation biodiesel [44].

3 Hydrogenated Vegetable Oil – production

Renewable diesel is derived by refining organic oil/animal fat, extracted in a procedure termed as hydro-treatment of fatty acids. In comparison to the glycerin-based esterification reaction of organic oils/animal fats, the diesel produced in this step is known as renewable diesel in order

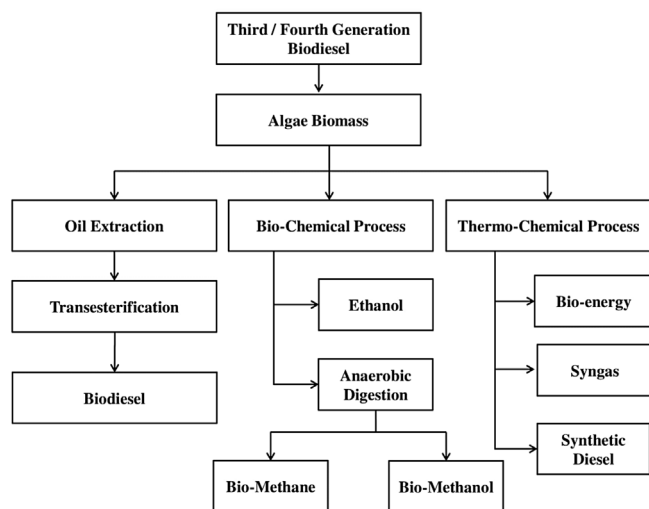


Fig. 4. Third/fourth generation biodiesel processing [36].

to differentiate it from conventional biodiesel [45]. Sustainable diesel is generally referred to as “green diesel”, and can be extracted from fatty acids or vegetable oils using conventional hydro-treatment technology [46]. Any biodiesel or green diesel may be similar to the original biomass oils. Hydro-treated oil is a high-quality, sulphur-free diesel with a very large proportion of Cetane 88–95 [47]. As glycerine is a co-product of the latter process, the net yield of hydrolysed organic oils is much higher than that of the esterification reaction. Oil refiners use hydrolysis to eliminate impurities through the treatment of gaseous hydrogen feed [48]. Conversion temperatures ranging from 800 °C to 950 °C and pressures ranging from 30 to 90 atm are included in hydro-processing and reaction times ranging from 15 to 80 min. Some chemical reactions are improved by the use of solid catalysts, product selectivity is improved and total hydrogen consumption is optimised [49].

Hydrolysis process involves heat and pressure and ultimately reduces the molecular weight of the feed [50]. In triglyceride-containing oils, four hydrocarbon molecules, for example, are reduced by propane molecules and three hydrocarbon molecules under hydrotreatment [51] in the range C12–C18. Green diesel processing includes the hydrogenation of triglycerides for the removal of metals, oxygen and nitrogen compounds by the current refinery [52]. These diesels which can be used for production by dedicated hydro-treatment plants do not use conventional fuel. As a result, the investment cost of developing this renewable diesel is relatively lower than the process of transesterification that produces biodiesel [53].

Renewable fuel may be used as a partial solution or combination with any percentage of petroleum-based diesels, without altering the engines or vehicle fuel tank design [54]. The low carbon intensity of renewable diesel produced from organic waste oils/animal fats is also attributed to the enhanced fuel quality [55]. The simplest form of hydrocarbon molecules with combination of straight chain and branched paraffin in renewable diesel, is considered to be safe fuel based on complete combustion perspective.

Standard carbon numbers are C12–C18 [56]. Paraffin, which contains a large amount of aromatic and naphthenic substances, is often present in diesel oil. Aromatic materials are not ideal for safe combustion and those organic hydro-treated oils/fats are scarce [57]. The EN 14214 petrol diesel fuel standard is suitable for different types of diesel engines. This specification has seven different grades and No. 2D complies with sustainable diesel, the objective of which is to use diesel in low-sulphur applications that are ideal for varying speeds and load conditions [58]. Figure 5 provides a comparison of FAME and Hydrogenated Vegetable Oil (HVO) processing technique.

4 Difference between biodiesel and Hydrogenated Vegetable Oil

Biodiesel is a mono-alkyl ester produced from the long-chain, carbonic fatty acid. It is formed by transesterification of oil-rich fats or biomass. It is possible to convert triglycerides to esters with more gasoline-like properties [59]. Triglycerides react with alcohol, such as methanol and ethanol, in the presence of alkaline catalyst, such as potassium hydroxide and at certain temperatures [60]. It produces methyl or ethyl esters and is a co-product of glycerine. Table 5 shows the comparison between FAME and HVO.

Renewable diesel is a similar process, except that vegetable oil is processed at high pressure and high temperature in the presence of hydrogen and strong catalyst [61]. As a simple and vibrant fuel called green diesel, propane, CO or CO₂, vegetable oil or/and animal fat is converted to diesel. This process can also be carried out with any crude oil. Palm oil, pine oil, potato oil, corn oil is the most common vegetable oil [62]. However, renewable diesel can be generated from a broader variety of feed stocks than biodiesel. Two key reasons why this is supported are as follows:

- The level of unsaturation of feedstock molecules is not considered as the effects as hydrotreatment result in fully saturated paraffin hydrocarbons that are not sensitive to oxidative instability throughout the biodiesel containment of unsaturated methyl esters [63]. Thus, the production of Hydrogenated Vegetable Oil does not rely on the free fatty acids of the feedstock [64].

5 Properties and standards of bio-fuel

5.1 Properties and standards of conventional biodiesel (FAME)

Some of the key physical/chemical characteristics of biodiesel (FAME) extracted from the six feedstocks are detailed in Table 6. The fatty acid methyl esters are tested based on ASTM standards [65]. Multiple studies argued that the prices of FAME are very different. This variation in properties, as with the fatty acid profiles, is primarily due

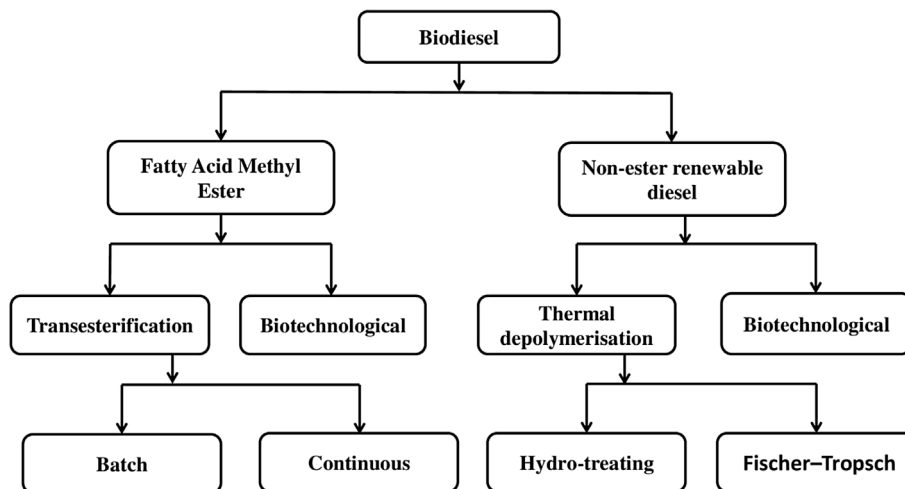


Fig. 5. FAME and HVO processing comparison [52].

Table 5. Comparison between FAME and HVO [60].

Properties	FAME	HVO
Feedstock	Food corps, seeds and non-edible oils	Vegetable oil/animal fats
Catalyst	Ethanol, methanol	Hydrogen
By products	Glycerol, wax, soap	Water
NO _x pollutants	Emission increased to 15%	Emission decreased
CO ₂ contaminates	20–32% ppm	12–15% ppm

to the use of various analytical techniques and varying degrees of performance. [66]. All sources of uncertainty are the chemical method used for the production of FAME, the cleaning and washing process used for raw FAME and the storage period prior to the testing [67].

The oxidation stability of FAME is a key property of biodiesel, but this review has not been taken into account, as the cleaning and storage activities of FAME strongly influence the same [68]. In addition, some of the biodiesel samples included antioxidant additives which had altered the inherent stability of FAME. There are some other FAME for which standards have been developed, but which also rely mainly on production and handling practises and not on FAME itself [69]. These include water, sediment, methanol content, ash, metal, acid count, glycerin and cold soak filtering.

The method used to evaluate the biodiesel properties reported in the literature was close to that used for the above fuel [70]. Initially, without a prior judgement on the validity of the data, all recorded values were recognised. The mean and standard deviations for each FAME are determined from this raw data [71]. Careful inspections were then carried out, in particular for values which varied significantly from the average. In some cases, viscosity values have been observed to be measured at temperatures other than the 40 °C standard [72]. Since the viscosity varies significantly with the temperature, the non-normal temperature values have been omitted when deciding the mean and standard deviations [73]. Energy quality is

another important FAME property, as no requirements are set for this by the U.S. and European biodiesel standards [74]. However, several authors have recorded energy content values, but the measurements used are very contradictory. For example, lower heating, higher heating value, gross energy content and net energy content were all noted, usually without specific measurements [75]. Some sources have not suggested the exact metric. In these cases, the authors’ opinion credited values either to a lower heating value or to a higher heating value.

5.2 European standards of conventional biodiesel (FAME)

The biodiesel properties shown in Table 7 have been determined on the basis of the FAME types:

- Average chain length.
- Average unsaturation.

The average chain length was determined by multiplying the mass fraction of the FA portion by the corresponding carbon number, and then adding the entire component [76]. Similarly, the mean degree of unsaturation was determined and summarised by multiplying the corresponding amount of carbon double bonds by the mass fraction of each FA component [77].

Table 6. Properties of various FAME biodiesel [67].

Properties	Corn	Neem	Palm	Sunflower	Rapeseed	Pine
Specific gravity	0.881	0.001	0.874	0.016	0.003	0.007
Cloud point, °C	−2	3.3	5	4	−1	13
Flash point, °C	124	143	122	114	136	159
Cetane value	50.4	33.8	58.9	53.8	51.8	49.6
CFPP, °C	13	2	−1	6	8	−3
Kinematic viscosity, mm ² /s	1.60	3.78	0.56	4.45	0.23	3.87
Pour point, °C	3	−6	4	2	10	3
Sulfur, ppm	1	3	8	4	6	5

Table 7. FAME biodiesel European standard [75].

Properties	EN 590:2004	EN 14214:2012
Density, kg/m ³	815–834	EN ISO 3575
Total contamination, mg/kg	30	EN ISO 12668
Flash point, °C	58	EN ISO 12716
Cetane value	51.5	EN ISO 5163
CFPP, °C	13	EN ISO 112
Kinematic viscosity, mm ² /s	1.0–3.2	EN ISO 3206
Water, mg/kg	250	EN ISO 13024
Sulfur, mg/kg	10–50	EN ISO 8763

Biodiesel properties can differ considerably from one feedstock to another [78]. However, the characteristics of conventional diesel are also useful for a brief comparison of some critical properties of biodiesel fuels as shown in Table 7.

5.3 Properties and standards of Hydrogenated Vegetable Oil

Renewable diesel is as clear and bright as water with high heating value. The energy content of renewable diesel is higher than that of biodiesel in MJ/kg, *i.e.* the mass and volume required to meet the test specifications of renewable diesel [79]. Low sulphur and metal-free content make it suitable for various applications. The impurity that causes precipitation over the cloud point makes it a clear fuel. The aromatic linearity makes it almost equivalent to the stability of diesel oil [80]. The renewable diesel is similar to diesel water solubility and the sustainability of the fuel is not the major concern [81]. The cloud point is less than −40 °C for renewable diesel, which provides a high mixing order throughout the year, except in winter. Density also remains almost constant at a low cloud point [82].

As with conventional bio-diesel, some precipitation of paraffins from the renewable diesel may take place if the temperature is below cloud point for a long period. It is recommended to store all diesel fuels above cloud point [83]. Due to the influence of high cetane and low density, CI engines are more widely used. The Cetane index also shows a linear increase with the mixing ratio [84]. Mixing

of medium HVO concentrations of more than 60% affects the cetane number of fuel. Direct blending limitations could not be applied to other fuel properties such as density, viscosity, the concentration of water. In contrast, reductions in density may result in some fuel savings and flexibility in the refinery process [85]. They are safe for storage and transport as renewable diesel flash points are above diesel. There is no microbial development of renewable diesel [86]. They can be combined with diesel fuel in refining or/during fuelling. Green diesel and diesel oil are highly compatible [87].

Without impacting fuel processing, engines and exhaust emissions, treatment of vegetable oil is a new way of producing high-quality bio-based diesel fuel. Instead of “biodiesel” reserved for fatty acid methyl esters, these oils are often referred to as “renewable fuel” [88]. Vegetable oils that are chemically hydrolyzed are paraffin hydrocarbon blends that are free from sulphur and fragrance. By changing the process intensity or further catalytic processing, the cold characteristics of HVO may be modified in accordance with local specifications [89]. The amount of Cetane is very high and the other properties of liquid and biomastic-liquid diesel fuel are very similar to Fischer–Tropsch synthesis gas. Table 8 shows the properties of Hydrogenated Vegetable Oil.

As HVOs are hydrocarbons, they comply with conventional diesel fuel requirements (EN 590), with the exception of a low-density value. The criteria of FAME ester (EN 14214) do not refer to HVO [90]. The lower heat output of HVO is significantly higher than ethanol. One litre or

Table 8. Hydrogenated Vegetable Oil properties [80].

Properties	Hydrogenated Vegetable Oil
Density, g/mL	0.852
Oxidation stability, hr	>25
Net heat value, MJ/kg	55
Viscosity, cSt	6.5
Flash point, °C	125
Nitrogen, mg/kg	2.6
Sulfur, mg/kg	3.5
Cetane index	82

one gallon of HVO will drive the vehicle almost twice as long as ethanol-based fuel, such as E60, compared to spark ignition engines, where greater efficiency is also considered [91].

When examining the properties of biodiesel extracted from different feedstocks, it is necessary to take into account the essential requirements laid down by the various organisations of the basic fuel institutions, in particular the European Committee for Standardization (CEN) [92]. At present, only the B100 standard, EN 14214, has been established by CEN, but not for mixtures such as B50. Mixtures of B15 and below are permitted under the European Standard Conditions for conventional diesel fuel (EN 275) and negotiations are on-going to increase the volume of B20 [93].

6 Environmental impact of biofuels

Emissions of GreenHouse Gases (GHG) from biofuels depend not only on the gas produced by the combustion of carbon but also on the combined impact of GHG emissions during the various stages of supply, such as biomass processing, transport to the industrial conversion unit and distribution [94]. CO₂, CH₄ and N₂O, are three essential GHGs rendered into CO₂ equivalents of Global Warming Potential (GWP) proposed by the *Intergovernmental Commission on Climate Change*, are researched in recent years. Net fossil fuel GHG emissions include refining/extraction, transport, conversion, storage and end-use pollution [95].

6.1 Impact on land usage

Direct and indirect land use and biomass improvements are well considered in terms of GHG emissions. As bio-energy plants are grown on land previously abandoned for crop cultivation, a direct land-use change takes place [96]. This applies to grasslands, forests, soil or degraded soil. As the development of energy crops changes prior to land operation, indirect land-use changes occur [97]. The transition to land use is the most important one for the development of palm oil biodiesel for net GHG emissions, which could have been reduced by 80% if depleted soil could have been used instead of natural rainforest or converted to tourism

[98, 99]. The land use change results in soil carbon sequestration to increase the mitigation of biofuel. Several studies have shown that, for several decades, converting cropland to grassland for grass cultivation usually raises soil carbon at a rate of 0.5–2.0 t carbon/ha per year [100].

6.2 Environmental concern

In addition to the two main environmental issues referred to above, the production of biofuels will either directly or indirectly affect the supply of water and nutrients [101]. Biomass feedstock farming requires water and nutrients, regardless of the method of biofuel processing [102]. The use of sea water or wastewater for bio-mass cultivation may be a potential option instead of freshwater. Seawater is readily available, but its high salinity in a variety of species precludes its application [103]. Biofuel feedstocks of first and second generation in raw waste water are difficult to produce. However, as described above, with the use of nutrients in waste water and seawater, algae can grow, which reduces the need for freshwater [104]. Algae cultivation thus provides an optimised system for waste water or water use for the production of biofuels.

6.3 Life Cycle Assessment of biodiesel

Engines working with ethanol fuel emit less carbon monoxide than petrol engines. A number of studies have been conducted to reduce net GHG emissions from lignocellulosic ethanol relative to fossil fuels [105]. Authors reported a reduction of 40% and 80% in GHG emissions compared to petrol for E90-fuels derived from ethanol switchgrass and corn Stover ethanol, respectively [106]. The corn stovers had reduced GHG emissions by about 7 and 18 compared to natural gas and coal as a source of heat and energy [107]. Net emissions of GHGs vary by source of biofuel and are correlated with significant volumes of by-products produced during the processing of biofuels, which involves a Life-Cycle Assessment of the treatment of biofuels from multiple sources to quantify the net emissions of GHGs [108]. Biofuel co-products can be used in the Life Cycle Assessment (LCA). LCA analyses on lignocellulosic ethanol from switchgrass and corn stover in Canada have shown that corn stover are more desirable than switchgrass for net GHG emissions when using Cradle-to-Grave analysis for the processes [109]. Compared to ethanol derived from switchgrass, a saving of 40% of GHG emissions from starch-derived ethanol from corn was recorded. Many researchers noted that savings of 80–100% GHG emissions are possible with the use of ethanol compared to fossil-based gasoline. Table 9 represents Life Cycle Assessment of biodiesel [110].

In the proposed LCA model for the conversion of urban solid waste ethanol [111], the authors noted an 82% decrease in switchgrass GHG emissions, followed by hay (75.2%), corn (90%), wheat straw (73%) and corn (47%). The overall GHG emissions from the manufacture of process chemicals and enzymes used for the pre-treatment of lignocellulose biomass, including corneal ethanol GHG emissions, are estimated to be significantly lower than those

Table 9. Life Cycle Assessment of biodiesel.

Biofuel	Net energy ratio	The model used for calculation	Ref
Fossil fuel	6.3	Energy life cycle analysis small farm production	[115]
Soybean biodiesel	4.25	Energy life cycle analysis small farm production	[116]
Palm biodiesel	7.9–8.5	CED, PNAS	[118]
Pine biodiesel	8.36	Energy accounting method	[119]
Algae biodiesel	5.58	Biofuel analysis meta model	[120]
Rapeseed biodiesel	6.71–7.2	Greet model	[122]
Corn biodiesel	4.26–5.12	Energy and Resources Group	[124]

from the manufacture of corn ethanol and petrol/diesel emissions.

In the case of third and fourth generation biofuels, the reduction of GHG emissions can be achieved by recycling CO₂ produced as a carbon source for the production of algae during the fermentation process [112]. The life cycle of the production of chlorellaceae biogas was investigated and compared with first-generation biodiesels. The high productivity of algae allowed the recycling of CO₂ in flue gas [113]. Algae were also able to directly absorb and produce methane, and nutrients were also recycled [114]. Their findings have shown that the production of algae methane can directly mitigate the emissions, whereas further changes could be made by reducing the cost of mixing and by increasing the output of the anaerobic process under regulated conditions [115].

The proposed algal cultivation in conventional raceway ponds should be slightly more environmentally safe than fossil fuel, with a potential production target of 60 tonnes of lipids per year. Biodiesel from algae grown in raceway ponds was 70% lower than fossil fuel. Both algal processing stages had a significantly lower demand for fossil energy and GWP than the cultivation requirements [116].

6.4 Life Cycle Assessment of Hydrogenated Vegetable Oil

Traditionally, LCA has been used to identify the environmental hazards of a number of other biofuels, both diesel and petrol [117]. Three separate feedstocks were studied to assess the Life Cycle Assessment of HVO. The rapeseed oil methyl ester and wheat ethanol marginally enhanced performance in terms of global warming and eutrophication, but the same was true of potential photochemical ozone production and energy consumption. The greenhouse gas emissions and a wide range of environmental impacts with a combination of biofuels (methyl ester, ethanol, biogas, dimethyl ether, etc.) have been studied [118]. Methyl ester from waste cooking oil had low greenhouse gas emissions, but no analysis on acidification and eutrophication have been studied [119]. The life-cycle emission between petrol and E10 was very limited (10% bioethanol and 90% gasoline) in terms of greenhouse gases [120]. Several LCA studies on bio-based ethanol showed, favourable net energy output. Despite the results of several studies, it cannot be inferred that biofuels have a lower impact on the atmo-

sphere than fossil fuels. The importance of integrating additional effects on LCA research, in addition to greenhouse gas emissions are also demonstrated [121–123]. The environmental effects of HVOs combustion in heavy vehicles in Europe, were analysed using LCA research. The standard unit was assumed as 1 kWh from the heavy vehicle (kWh engine) [124]. For the production of HVO, vegetable oils may come from different biological sources. Rapeseed oil, palm oil, and jatropha oil were investigated. Rapeseed oil is expected to be a raw material for the production of HVO from European feedstock [125]. In reality, with the best prices per hectare, palm oil is the cheapest vegetable oil among all vegetable oil feedstocks. It is also currently used in the production of HVO by the Nest Oil feedstock [126]. Jatropha is a plant that is thought to thrive on wastelands and can also be used to replenish the soil. Malaysia's palm oil and India's Jatropha were considered in Germany in this analysis [127]. Hydrotreatment is required for all three feedstocks at the Neste Oil production facility in Greenland. The HVO is considered to be part of the diesel engines in Germany.

Electricity has been modelled as a specific source of electricity used in different countries, rather than as marginal electricity. In this article, all loads were considered using fossil diesel, not HVO or other non-fossil fuels [128]. Production capital, such as construction and transport vehicles, as well as the transport of workers to installations and electricity for offices, have been systematically omitted. Large-scale production has been assumed for all three oil plants [129]. Aspects relevant to land planning for agriculture are not covered. In this was partly due to well-defined methodological problems: the parameters to be considered and the methods to be applied are not stated. In addition to a study of other LCA reports, land use has been omitted [130].

The most important aspects of the biofuel evaluation are potential greenhouse gases and environmental pollution [131]. Global warming potential, acidification potential, eutrophication potential and embedded fossil energy production are the impact categories assessed in the report. Biofuels have emissions that contribute to acidification and eutrophication; input from the supply chain, for example in Rapeseed Methyl Ester, or RME and ethanol studies has shown a substantial effect on overall supply. Notice that the “pound” unit in this analysis also corresponds to the metric tonne, *i.e.* 1000 kg. The sensitivity analysis

investigated the effect of certain parameters on the biofuel which are increasingly common in LCA studies [132, 133].

6.5 Economic assessment of biofuels

Biofuel production costs include the cost of feedstock over time, plus the estimated conversion costs, including resource costs, chemicals and enzymes, electricity costs, operation and maintenance costs, minus the value of the co-product over time [134]. Except for sugar cane ethanol in Europe, the cost of production of all first-generation biofuels is essentially subsidised in all countries. In brief, higher food crop prices make biofuels of the first generation more competitive [135]. For some of its feedstock products, such as corn in European countries, the rapidly increasing demand for biofuel feedstocks has significantly increased prices. In this sense, biofuels are derived from low-cost feedstocks [136]. The minimum cost was estimated for corn ethanol, while the limit was estimated for algal biodiesel. The cost of capital per unit of production capacity decreases as the size of the plant increases for relatively large plants.

Generally speaking, the cost reduction is considered to be sufficient to cover the rising cost of biomass resulting from longer average transport distances associated with higher output sizes [137]. Developed economies are more serious in thermochemical processes, than biochemical conversions but in both situations, commercial development has to face challenges [138]. The economy of first-generation biofuels in Europe is more forward-looking than the exemption from excise duty under current political circumstances. Still, the critical problems of this generation of biofuels are a lack of feedstock land and moderate environmental efficiency. Industrial processing of first and second-generation biodiesel is carried out in several countries [139].

Biomass processing costs are dominant for both algae and rapeseed biodiesel. Important factors are the production of biomass from algae, the supply of carbon, the harvesting and the source of water [140]. While land costs are low for the development of algae biomass, there are higher infrastructure and mixing costs. However, in the case of algae, the high cost of energy recycling offsets much of the gain [141]. In the case of rapeseed biodiesel, the most increased cost is the effect of food prices and GHG emissions. The cost-effectiveness of biomethane production from three separate sources, including the urban fraction of organic waste, household waste and grass/slurry is analysed [142]. Of the three path, organic fraction of municipal solid waste is the cheapest, followed by slaughterhouse waste, grass and slurry [143]. The price of petroleum-derived transport fuel at service stations, while more expensive, focuses on the biomethane produced from grass and slurry. Biomethane, saves about 85% of CO₂ emissions, which is preferable to liquid fuel [144].

According to the *International Energy Agency*, the cost of sugar cane ethanol for EU countries is € 0.50 per litre. The cost of corn, sugar beet and wheat ethanol vary from € 0.9 to € 1.6 per litre without subsidies, whereas the price of lignocellulosic ethanol on a pilot scale is around € 4.0 per litre [145]. Currently, animal fat is the cheapest source of biodiesel, while conventional transesterification costs for vegetable oil are currently about € 0.4 – € 0.9 / lt. New

processes are expected to save more costs from economies of scale [146]. Lignocellulose biomass costs more than € 0.8/L for liquid diesel, with possible reductions to € 0.6 – € 1.2/L. According to the *IEA* study (2013), cost of ethanol, conventional biodiesel, and advanced biodiesel are € 0.6/L, € 1/L and € 1.1/L respectively [147]. Despite substantial attempts, the cost of biofuels has not decreased dramatically in these years. Developing economies would allow biofuels to compete with fossil fuels in the long term [148]. Hassan and Kalam [149] proposed more optimistic lower cost estimates for second-generation biofuels than conventional biofuels. Borowitzka and Moheimani [150] calculated the cost of the production of algal biodiesel to be between € 9 – € 25 and € 15 – € 40 per gallon in open ponds and photobioreactors, based on a wide range of available reports. This high cost is mainly due to advanced processing techniques of algae. Efrogmson *et al.* [151] indicated that the cost of algal biofuels could be significantly reduced by lowering the number of steps in the processing of algal biofuels, as well as the co-production of a better fraction.

7 Conclusion

The present review is to highlight the various biodiesel generation, production, properties, standards, life cycle cost and sustainability assessment. The following are the summary of the analysis:

- First-generation biofuels are almost in decline. Second-generation biofuels which do not displace food production or cause more greenhouse gas emissions are increasingly applied in Europe.
- The third generation of biofuels are having the highest emphasis in the recent years owing to strict environmentally sustainable standards of biofuels.
- The fuel properties and standards for biofuels and Hydrogenated Vegetable Oil have been explored. However, various conversion and upgrading techniques have to be applied to meet the biodiesel standards of EN 14214.
- The requirement of 60% greenhouse gas savings over the entire life cycle of the fuel including cultivation, processing and transport compared to fossil fuels poses lot of challenges in meeting the current state-of-the-art renewable diesel standards.
- The fourth-generation biofuel are quite fairway in meeting the production costs and performance in engines to consider as serious sustainable fuel.

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