Biodiesel Production Processes and Sustainable Raw Materials

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Abstract: Energy security and environmental concerns, related to the increasing carbon emissions, have prompted in the last years the search for renewable and sustainable fuels. Biodiesel, a mixture of fatty acids alkyl esters shows properties, which make it a feasible substitute for fossil diesel. Biodiesel can be produced using different processes and different raw materials. The most common, first generation, biodiesel is produced by methanolysis of vegetable oils using basic or acid homogeneous catalysts. The use of vegetable oils for biodiesel production raises serious questions about biodiesel sustainability. Used cooking oils and animal fats can replace the vegetable oils in biodiesel production thus allowing to produce a more sustainable biofuel. Moreover, methanol can be replaced by ethanol being totally renewable since it can be produced by biomass fermentation. The substitution of homogeneous catalyzed processes, nowadays used in the biodiesel industry, by heterogeneous ones can contribute to improve the biodiesel sustainability with simultaneous cost reduction. From the existing literature on biodiesel production, it stands out that several strategies can be adopted to improve the sustainability of biodiesel. A literature review is presented to underline the strategies allowing to improve the biodiesel sustainability.
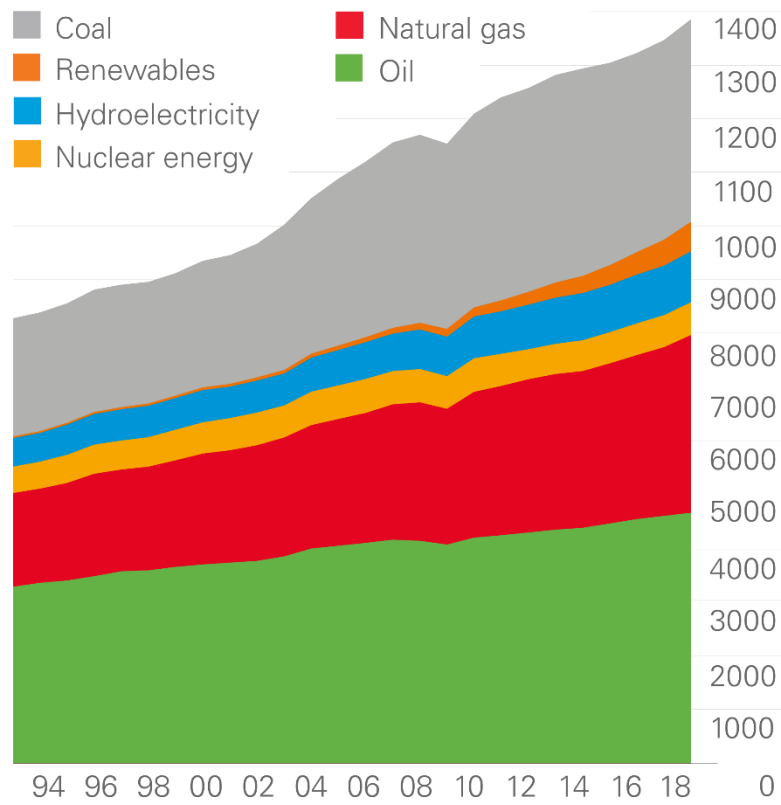
Keywords: biodiesel; sustainability; vegetable oils; animal fats; methanolysis; ethanolysis

1. World Energy

Worldwide energy demand has been growing in the last decades (Figure 1a). According to the U.S. Energy Information Administration (EIA) report, this trend will carry on, with an estimated growth in energy consumption of 28% between 2015 and 2040 [1]. Only in 2018, the world primary energy consumption grew 2.9% [2].

World use of petroleum and other fuels has been growing as well, being the largest growth in the transport and industrial sector. In the transportation sector, fossil fuels continue to supply most of the energy consumed despite the shortage of their reserves [1].

In Africa, Europe and Americas the oil remains the dominant fuel, while natural gas dominates in the Commonwealth of Independent States (CIS) and the Middle East. In the Asia Pacific region, coal is the dominant fuel (Figure 1b).
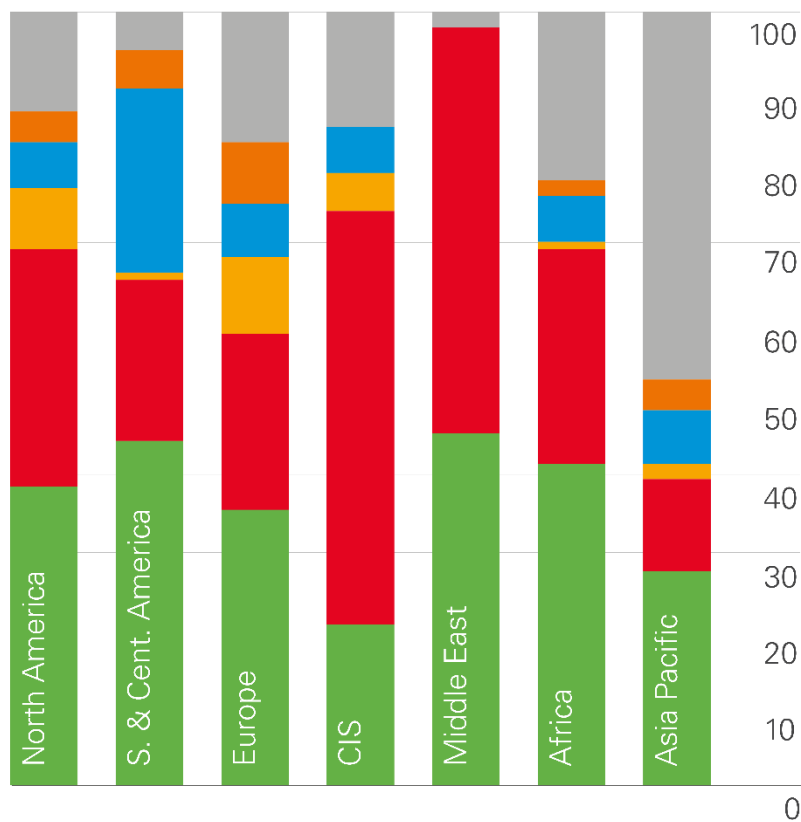
Figure 1. World Consumption by fuel from 1994 to 2018. (**a**) (million tones oil equivalent) and Regional Consumption by fuel 2018; (**b**) (% of different fuels, color legend in Figure 1a) [2].

Replacing fossil fuel with more sustainable energies, maximizing the use of renewable ones, is increasingly important, not only to reduce the emissions of greenhouse gases (GHG) but also to improve energy supply security [3]. These concerns have led to changes in global environmental policy.

In 2007 the European Union launched a climate and energy policy to fight climate change and increase energy security but reinforcing simultaneously its competitiveness. The 2020 package was enacted in legislation in 2009 (Renewable Energy Directive) and sets targets for the year 2020 [4]:

✓　20% cut in greenhouse gas emissions (from 1990 levels)
✓　20% of EU energy from renewable sources in the energetic mix
✓　20% improvement in energy efficiency

The EU also sets binding national targets of minimum energetic incorporation of 10% for the share of energy from renewable sources consumed by all modes of transport in 2020 [5]. One way to achieve the proposed targets is the increase in the use of biofuels as an alternative energy source. Figure 2 shows the share of renewable energy in transport in 2014, 2015 and 2016 for EU countries.
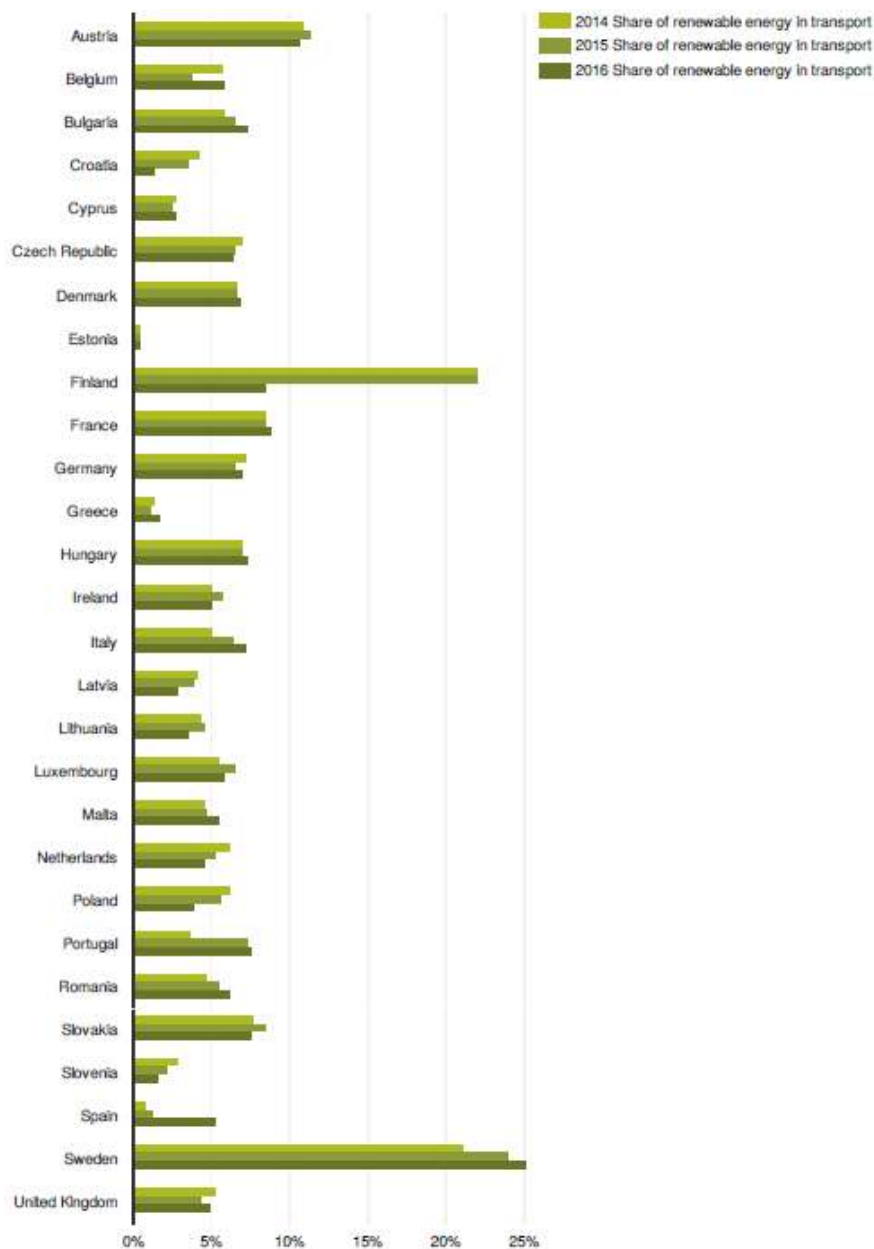

Figure 2. EU share of renewable energy in transport in 2014, 2015 and 2016 [6].

The Renewable Energy Directive was reviewed in 2015 (Directive (EU) 2015/1513) limiting to 7% biofuel production from agri-food-cultures such as cereal and other starch-rich crops, sugars and oil crops used in transport sector [7].

Biofuel production from wastes and residues was also encouraged due to double contribution by double counting for the purpose target. In addition to the current list of raw materials that can be used to produce double counted biofuels (Directive (EU) 2015/1513) it is possible to use raw materials not included in the list but considered as wastes by the national authorities before the adoption of the amendment [7]. Not all countries apply double counting and the definition of waste differs between them.

For example, Portugal is one of the countries that apply double counting, and biofuels produced from animal fats categories I & II and waste cooking oils, among others, are counted twice. The EU targets for the year 2030 (from 2021 to 2030) had been already established [8]:

✓ At least 40% cuts in greenhouse gas emissions (from 1990 levels)
✓ At least 32% share for renewable energy (upwards revision by 2023)
✓ At least 32.5% improvement in energy efficiency

The EU has also set a new binding national target of minimum energetic incorporation of 14% for the share of energy from renewable sources consumed in transport until 2030. The 2050 long-term strategy, instead of set targets, creates a vision and defines directions that the EU must take to achieve climate neutrality as well as the Paris Agreement, which established keeping the temperature increase well below 2 °C compared to pre-industrial levels and the pursuit of efforts to keep it to 1.5 °C, by 2050. Several strategic areas such as energy efficiency; deployment of renewables; clean, safe and connected mobility; competitive industry and circular economy; infrastructure and interconnections; bio-economy and natural carbon sinks; carbon capture and storage to address remaining emissions would have to be worked together to achieve the climate neutrality. In the transport sector an increase in biofuels production due to all alternative fuel options is predicted, which will be required achieving deep emission reductions [9].

2. Biofuels

Biofuels are fuels made from biomass, a renewable alternative to fossil fuels. Many of them can be used in the transport sector, like [10]:

■ bioethanol: ethanol produced from biomass and/or the biodegradable fraction of waste;
■ biodiesel: a methyl-ester produced from vegetable or animal oil, of diesel quality;
■ biogas: a fuel gas produced from biomass and/or from the biodegradable fraction of waste, that can be purified to natural gas quality, to be used as biofuel, or wood gas;
■ biomethanol: methanol produced from biomass;
■ biodimethylether: dimethylether produced from biomass,
■ bio-ETBE (ethyl *tert*-butyl ether): ETBE produced based on bioethanol. The percentage by volume of bio-ETBE that is calculated as a biofuel is 47%;
■ bio-MTBE (methyl *tert*-butyl ether): a fuel produced based on biomethanol. The percentage by volume of bio-MTBE that is calculated as a biofuel is 36%;
■ synthetic biofuels: synthetic hydrocarbons or mixtures of synthetic hydrocarbons, which have been produced from biomass;
■ biohydrogen: hydrogen produced from biomass, and/or from the biodegradable fraction of waste;
■ pure vegetable oil: oil produced from oil plants through pressing, extraction or comparable procedures, crude or refined but chemically unmodified, when compatible with the type of engines involved and the corresponding emission requirements.

In this sector, the most widely used biofuels around the world are bioethanol, as a substitute for gasoline, and biodiesel, as a substitute for diesel. Other biofuels are also used, although with more limited market access.

2.1. Biodiesel

Biodiesel, a mixture of alkyl esters produced of fatty acids is highlighted out as a feasible renewable and low carbon substitute of fossil diesel for the transportation sector [5]. Biodiesel can be used pure or blended with petroleum diesel due to its complete miscibility. Biodiesel blends are referred to as Bxx, where the xx indicates the amount of blend. Thus, B100 corresponds to pure biodiesel, and a B80 blend is 80% biodiesel and 20% petroleum diesel by volume.

Worldwide Europe is the main producer of biodiesel as a result of the environmental policy (Figure 3). Diverse feedstocks can be employed in biodiesel production. Nowadays biodiesel worldwide production is still dominated by vegetable oils: soybean, rapeseed, and palm oil. In the USA the main raw material used is soybean oi, with a 52% share of total biodiesel feedstocks, followed by canola oil and corn oil with 13% each [11]. In Europe, rapeseed oil was the major feedstock used, with 45% of the total production in 2017, followed by used cooking oil (UCO) with 21% and palm oil with 18% [12]. For example, in Portugal, rapeseed is the main vegetable oil used, followed by soybean oil. Table 1 presents Portugal's biodiesel production in the last years.
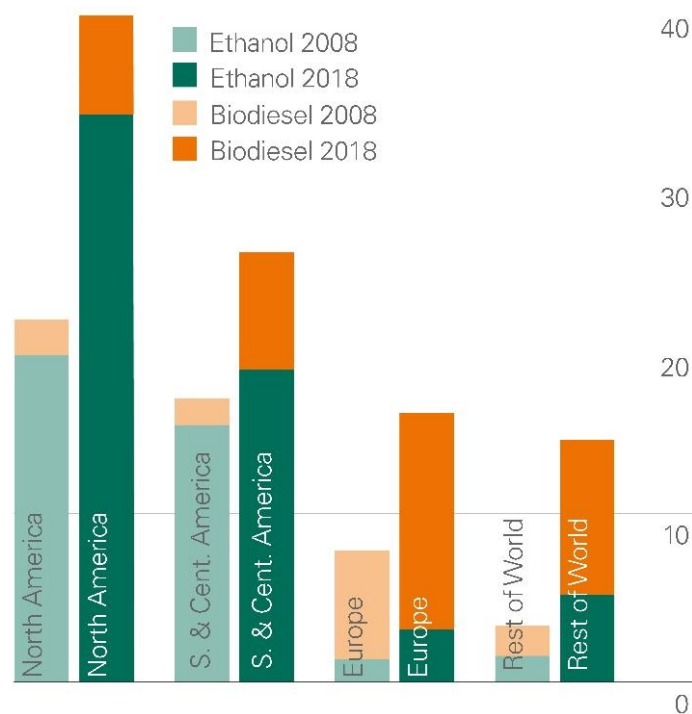

Figure 3. World ethanol and biodiesel production from 2008 to 2018 (vertical axis in million tonnes oil equivalent) [2].

Table 1. Biodiesel production from different feedstocks in Portugal (adapted from [13]).

	Biodiesel Production (ton); Year								
Feedstock	**2010**	**2011**	**2012**	**2013**	**2014**	**2015**	**2016**	**2017**	**2018**
Fresh oils	316,507	365,622	304,190	299,404	324,200	287,329	205,594	175,954	151,078
WCO+ animal fat	4810	4639	4869	11,044	16,906	75,737	131,226	179,875	176,023
Total	321,317	370,261	309,059	310,448	341,106	363,066	336,820	355,828	327,101

2.2. Advantages and Disadvantages

The major benefits of using biodiesel as a replacement for diesel fuel are [14–17]:

- Biodegradability;
- Non-flammable and low toxicity;
- Safer to handle;
- Higher combustion efficiency, portability, availability, and renewability;
- Higher cetane number and flash point;
- Lower emissions such as CO_2, CO, SO_2, particulate matter (PM) and hydrocarbons (HC) compared to diesel;
- May be blended with diesel fuel at any proportion;
- No required engine modification up to B20;
- Excellent properties as a lubricant.

There are also some disadvantages of using biodiesel that must be taken into consideration:

- Lower calorific value;
- Higher pour and cloud point fuel;
- Higher nitrous oxide (NOx) emissions (in some cases);
- Higher viscosity and less oxidative stability;
- Biodiesel is corrosive to copper and brass;
- May degrade plastic and natural rubber gaskets and hoses when used in pure form;
- Biodiesel causes excessive engine wear.

The main restriction for biodiesel commercialization is its higher cost in comparison to petroleum fuel. Raw materials price represents 70–95% of the total production cost [18].

2.3. Transesterification

Biodiesel is produced by transesterification of triglycerides with short-chain alcohols in the presence of a catalyst (Scheme 1). Due to the reversibility of the reaction, it is necessary to use an excess of alcohol to drive the reaction equilibrium [19]. However, the transesterification reaction can be done without a catalyst through supercritical process reactions [20]. This process consists of three consecutive reversible reactions where triglycerides are converted into diglycerides, diglycerides are converted into monoglycerides and finally, monoglycerides are converted into glycerol. In addition, for each glyceride that reacts the formation of an ester (biodiesel) molecule occurs [21].
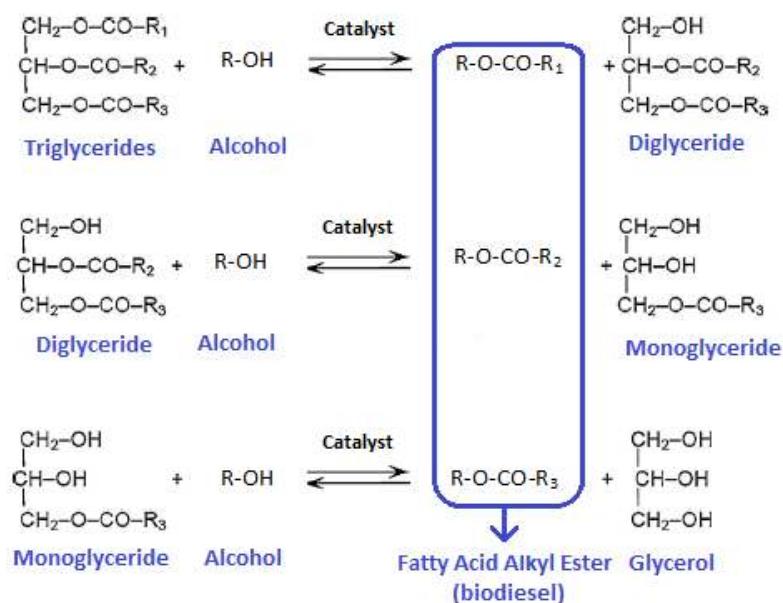
Scheme 1. Transesterification reaction (adapted from [21]).

Various parameters affect the transesterification reaction. In order to produce biodiesel that meets the standard quality parameters, production processes must be optimized [3]. The most relevant, processual and quality, parameters are [3,22,23]:

(1) Free fatty acids, moisture and water content.
(2) Type of alcohol and molar ratio employed.
(3) Type and concentration of catalysts.
(4) Reaction temperature and time.
(5) Rate and mode of stirring.
(6) Purification process of the final product.
(7) Mixing intensity.
(8) Effect of using organic co-solvents.
(9) Specific gravity

Glycerol, also known as glycerin (commercial term, purity > 95%), is a by-product of transesterification reactions. About 1 kg is produced for each 10 kg of biodiesel [24]. Glycerol is a nontoxic, edible and biodegradable compound used as a raw material in different industries, such as pharmaceuticals, cosmetics, tobacco, textiles or foods [24,25]. Due to its commercial value, in transesterification reaction beyond the biodiesel quality it is also important to obtain glycerol with high purity.

2.4. Alcohol Used

In biodiesel production, different alcohols can be used, such as methanol, ethanol, propanol or butanol [26]. The most commonly used are methanol and ethanol, and the reaction product produced when methanol is used is called a fatty acid methyl ester mixture (FAME) whereas if the alcohol is ethanol, the product obtained is a fatty acid ethyl ester mixture (FAEE) [26].

The mild reaction conditions needed, the fast reaction time and the easy phase separation combined with its low-cost and industrial availability make the methanol the most used alcohol in biodiesel production [26,27]. However, the use of this alcohol presents some drawbacks. Methanol is more toxic, volatile and has a lower oil dissolving capacity than ethanol. Although methanol can be obtained from biomass gasification, this alcohol is majorly produced from a fossil sources, about 90% from natural gas. Thus, the biofuel produced by methanolysis is not considered fully renewable biodiesel [28].

Besides, ethanol is made from agricultural products such as potatoes, grain, and corn, allowing this way the production of a renewable fuel [29]. Due to the extra carbon atom, the FAEE produced has a cloud and pour point lower than FAME, which allows the engine to start low temperatures [30]. The combustion heat and the cetane number are higher and the storage properties of FAEE fuel are also improved [27]. The main drawbacks of ethanolysis in biodiesel production are its lower reactivity, compared with methanol, as well as the more difficult separation of FAEE from the coproduced glycerin due to their higher miscibility [31].

Many studies have been carried out to compare the effect of methanol and ethanol on biodiesel production from different feedstocks [32–35]. All achieved results reported that the yield obtained by ethanolysis is lower and more time is needed to complete the reaction than for methanolysis. The separation of FAEE from glycerin is also more difficult. Nevertheless, it allows achieving a completely renewable biodiesel. Although several alcohols can be used to produce biodiesel, so far European Union legislation only covers FAME.

2.5. Feedstocks

As mentioned before several feedstocks can be employed in biodiesel production such as vegetable oils (edible and non-edible), waste cooking oils, animal fats and algae oils [36]. The chemical structure is similar in vegetable oils and animal fats, mainly composed by triglycerides with a smaller fraction of diglycerides and monoglycerides [18]. Triglycerides (Figure 4) are formed by one molecule of glycerol combined with three molecules of saturated or unsaturated fatty acid.
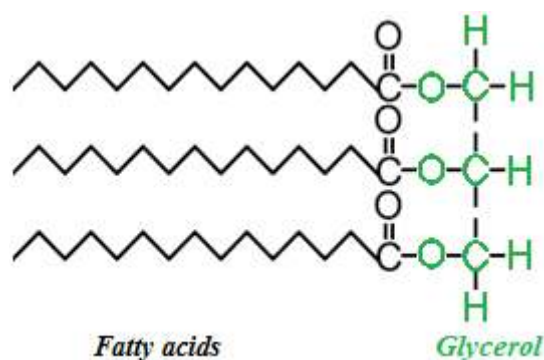
Figure 4. Triglyceride [37].

Both feedstocks are water-insoluble, hydrophobic and soluble in nonpolar organics solvents [18]. The main differences between them are the varied distributions of fatty acids and the high free fatty acids (FFA) content in the fats. The fatty acid profiles of some vegetable oils and animal fats are referenced in Table 2.

Animal fats and greases, at room temperature, tend to be solid due to their high content of saturated fatty acid (carbon-carbon single bond), oils are generally liquids. Refined oils have less FFA, lower acid value, than animal fats, waste grease and waste oils [18].

Table 2. Fatty acid profiles of different feedstocks (minima and maxima weight percentages).

Fatty Acid	Rapeseed Oil [18,38,39]	Soybean Oil [18,38,40,41]	WFO [39,41–43]	Beef Tallow [38,40,44–46]	Lard [18,38, 40,44,47]	Poultry Fat		Fish Oil		
						Chicken Fat [18,38,40,44,48]	Duck Tallow [44]	Catfish Fat [49]	Salmon Oil [50]	Anchovy Oil [51]
Lauric (C12:0)	-	-	nm–0.4	-	-	nm–1.0	-	11.5	0.1	-
Myristic (C14:0)	-	nm–1.0	nm–1.1	2.6–3.5	1.3–1.7	0.5–1.0	-	11.7	5.8	6.7
Myristoleic (C14:1)	-	-	-	0.5–1.3	-	0.1–0.2	-	2.0	-	-
Pentadecanoic (C15:0)	-	-	-	0.5–1.0	-	-	-	1.9	-	-
Palmitic (C16:0)	3.5–4.5	10.5–11.0	8.4–25.8	23.8–27.0	23.2–25.5	20.9–24.7	17.0	28.1	16.9	20.2
Palmitoleic (C16:1)	nm–0.5	-	0.2–4.6	0.5–4.7	2.2–2.7	5.0–7.7	-	-	5.4	6.6
Margaric (C17:0)	-	-	-	1.1–2.5	nm–0.4	-	-	-	-	0.2
Heptadecenoic (C17:1)	-	-	-	0.5–1.7	nm–0.4	-	-	-	-	-
Stearic (C18:0)	0.9–1.5	3.3–4.8	3.7–4.8	12.7–34.7	10.4–17.0	4.5–5.8	4.0	-	4.3	4.2
Oleic (C18:1 cis)	-	22.0–25.4	28.5–52.9	29.9–47.2	40.0–42.8	38.2–48.5	59.4	26.8	19.2	19.7
Linoleic (C18:2)	18.7–22.3	52.3–54.5	13.5–50.5	0.8–2.7	10.7–21.0	17.3–23.8	19.6	6.7	16.1	2.6
Linolenic (C18:3)	7.7–9.0	5.3–7.5	0.6–3.5	nm–0.8	nm–64.7	nm–2.5	-	-	2.8	1.6
Arachidic (C20:0)	0.4–0.5	0.4–0.5	0.1–0.4	nm–0.3	nm–0.2	-	-	-	-	-
Gadoleic acid (C20:1)	1.0–2.0	nm–0.3	0.1–0.8	nm–0.5	0.9–1.0	0.5–1.0	-	2.7	-	-
Eicosadienoic (C20:2)	-	-	-	-	0.5–0.7	-	-	0.8	-	0.2
Eicosatrienoic (C20:3)	-	-	-	-	nm–0.2	-	-	0.5	-	-
Eicosapentaenoic (C20:5)	nm–0.1	-	0.2	-	-	-	-	-	15.6	10.4
Behenic (C22:0)	nm–0.5	0.4–0.5	nm–0.8	-	-	-	-	-	-	-
Erucic (C22:1)	nm–0.1	-	-	-	-	-	-	-	-	-
Docosapentaenoic (C22:5)	-	-	-	-	-	-	-	-	2.5	0.8
Docosahexanoic (C22:6)	-	-	-	-	-	-	-	-	11.4	21.6
Lignoceric (C24:0)	-	nm–0.1	0.04–0.3	-	-	-	-	-	-	-

nm—not measured.

Based on their feedstock, biodiesel can be classified into three categories: first, second and third generation (Table 3):

Table 3. Different generations of biodiesel and their feedstocks (adapted from [3]).

1st Generation Edible Oils	2nd Generation		3rd Generation Microalgal Oils
	Non-Edible Oils	**Animal Fats**	
Soybeans (*Glycine max*)	Jatropha (*Jatropha curcas* L.)	Pork lard	Bacteria
Rapeseed (*Brassica napus* L.)	Mahua (*Madhuca longifolia*)	Beef tallow	Microalgae (*Chlorella prothecoides*)
Safflower (*Carthamus tinctorius* L.)	Coffee grounds	Poultry fat	Microalgae (*Chlorella vulgaris*)
Rice bran oil (*Oryza sativa* L.)	Camelina (*Camelina sativa*)	Fish oil	Microalgae (*Botryococcus braunii*)
Barley (*Hordeum vulgare* L.)	Cottonseed (*Gossypium hirsutum*)	Chicken fat	Microalgae (*Chlorella sorokiana*)
Sorghum (*Sorghum bicolor*)	Tall fescue (*Festuca arundinacea*)		
Wheat (*Triticum aestivum*)	Neem (*Azadirachta indica*)		
Corn (*Zea mays*)	Jojoba (*Simmondsia chinensis*)		
Coconut (*Cocos nucifera*)	Passion seed		
Canola (*Brassica napus*)	Moringa (*Moringa oleifera*)		
Peanut (*Arachis hypogaea*)	Tobacco seed (*Nicotiana tabacum*)		
Palm (*Arecaceae*)	Rubber tree seed (*Hevea brasiliensis*)		
Sunflower (*Helianthus annuus*)			
Palm kernel (*Elaeis guineensis*)	Nag champa (*Plumeria*)		

First generation refers to biodiesel derived from edible vegetable oils. The most commonly used are rapeseed, palm, soybean, coconut, peanut, and sunflower [52]. The vegetable oils are widely available and relatively easier to convert into biodiesel. However, the use of edible vegetable oils in the production of biofuel raises several ethical issues. Edible vegetable oils come from food crops. The use of arable land, water, and fertilizer in "growing fuel" instead of food not only affects the food price but also sustainability issues [52].

Furthermore, even if the total amount of edible oils available was used in the production of biodiesel, it was not enough to meet today's diesel requirements. These concerns ally with the double counting of biofuels produced from wastes, which have led to an increasing search for more sustainable feedstocks.

Second generation biofuels are biodiesels derived from non-edible crops or feedstocks that have already fulfilled their food purpose such as waste oily streams from the oil refinery, waste cooking oils (WCOs), greases and waste animal fats (WAFs) [53]. The non-edible crops can be grown on lands that cannot be used for arable crops that have a lower necessity of water or fertilizer to grow, making their plantation more economic [53]. The WCO refers to vegetable oils or animal fats that had been heated and used for cooking different types of food. During this process, various chemical reactions occur such as hydrolysis, polymerization, and oxidation modifying the physical and chemical properties of oil/fat [54]. Recycled fats, based on their FFA level, can be divided as yellow or brown grease. The yellow greases have a FFA level of less than 15% while, brown has more than 15% [54]. The second generation also includes WAFs or rendered animal fats, this topic will be explored in the next chapter. The use of these less expensive feedstocks (Table 4) reduces the production costs and reuse wastes, without competing with the food market [47]. The prices of feedstocks are unstable.

Third generation are the biodiesels derived from algal biomass.

Independently of the feedstock category used, the physical and chemical properties of the biodiesel are the same [41].

Table 4. The prices of the feedstocks [55,56].

Type	Price
soybean oil	728 USD per ton [1]
rapeseed oil	827 USD per ton [1]
palm oil	535 USD per ton [1]
WCO	610 USD per ton [2]
tallow (category 1)	400 € per ton [2]

[1] December 2018 price; [2] October 2018 price.

Animal Fats

Biodiesel production can be also done with animal fats as raw materials such as tallow, lard, poultry fat and fish oils (Figure 5) [18]. Animal fats are wastes or by-products that came from animal meat processing industry and carcasses of livestock, with relatively low prices.
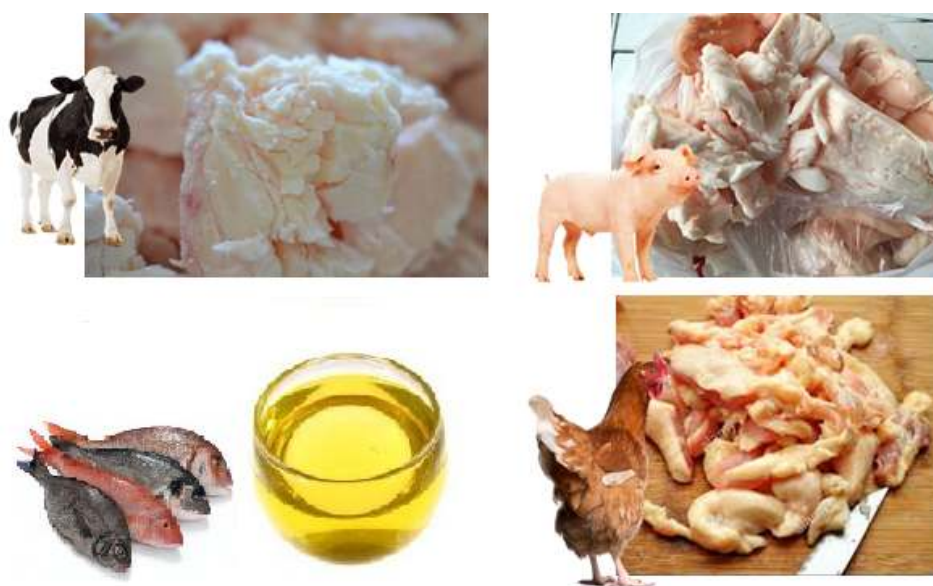
Figure 5. Tallow, lard, fish oil, and poultry fats.

In the European Union the regulation (EC) No 1069/2009 and No 142/2011 lays down health rules as regards animal by-products and derived products not intended for human consumption. These materials can be categorized into three specific categories considering the perceived level of risk to public and animal health [57]:

Category 1 (high risk):

✓ Specified Risk Material (SRM) linked with the transmission of TSEs (Transmissible Spongiform Encephalopathies), this includes the spinal cord and brain.
✓ Fallen stock with SRM
✓ Catering waste
✓ Anything handled with Category 1

Category 2:

✓ Material not fit for human consumption and posing a risk to animals and humans
✓ Fallen stock without SRM

Category 3 (lowest risk):

✓ Fit for human consumption at the point of slaughter

Fats are recovered from waste fat tissues by the rendering process. This process depends on the risk category and to prevent contamination between different categories of waste and different species, all processing is done on separated lines [57].

Many types of rendering are used in the industry. All of them involve the application of heat, the extraction of moisture, and the separation of fat [58]. The fat can mainly be recovered from wet or dry rendering. In wet rendering (Figure 6), the fat is recovered by heating in the presence of water. Boiling in water and/or steam at a high temperature can be employed [58,59]. The color of the fat produced by this process is clearer. The free fatty acid content increases due to the long contact with water [58].
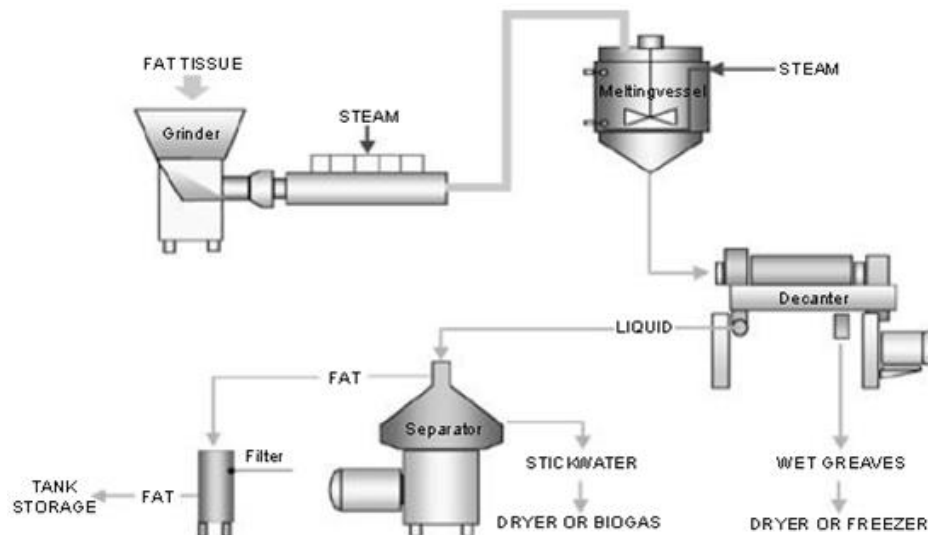
Figure 6. Wet rendering [59].

In dry rendering (Figure 7), in either batch or continuous processes, the fat tissues are cooked in their "own juices" with dry heat [59].
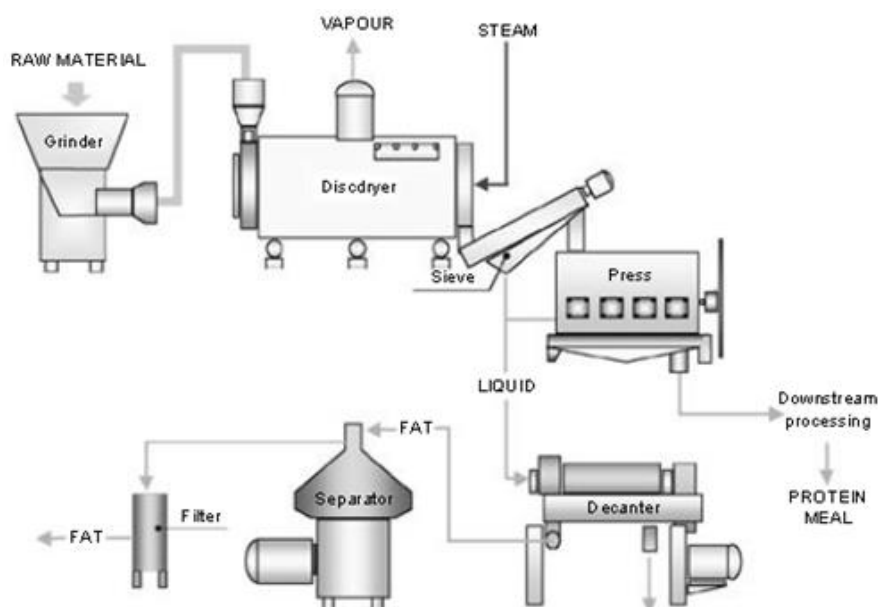

Figure 7. Dry rendering [60].

There is no rule when and where wet or dry rendering is ideal, but it can be observed that the lard and tallow from wet rendering are better than from dry rendering [59]. The rendering process may also be done using an organic solvent.

Usually, fats are further used in food, pet foods, feed applications but can also be transformed into soaps and oleochemicals (Figure 8), depending on the risk category [61]. All fats can be employed as feedstocks in biodiesel production.
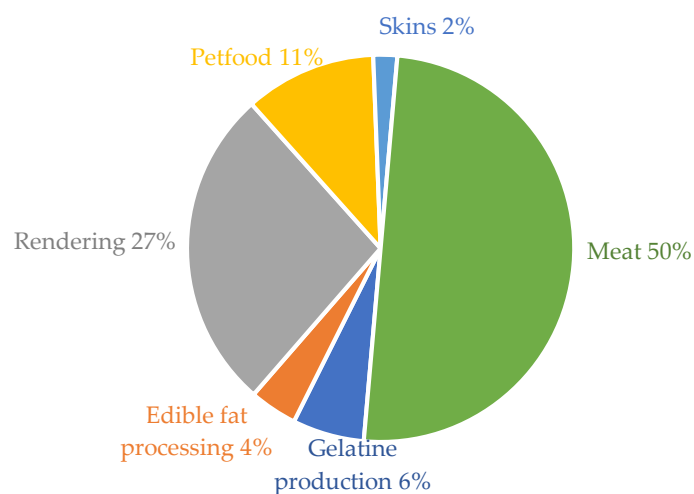

Figure 8. Estimated utilization of slaughtered animal (by % weight) [60].

2.6. Biodiesel Production from Animal Fats Versus Vegetable Oils

In terms of emission of pollutant gases, the advantages of replacing diesel with biodiesel produced from animal fats or obtained from vegetable oils are similar, since the emissions from burning generate similar results. However, Wyatt et al. have reported that three animal fats-based B20 biodiesel blends obtained from lard, beef tallow and chicken fat had lower nitrogen oxide (NOx) emission levels than B20 blend produced from soy oil [40].

In comparison with biodiesel from vegetable origin, biodiesel from animal fats has several advantages. Due to its lower content of unsaturated fatty acids, biodiesel produced from animal fats has a higher cetane number than biodiesel from the most vegetable oils and diesel fuel [18,36]. The cetane number increases with the increment of fatty acid carbon chains and the increase in degree of saturation [62]. A higher cetane number is recognized to lower NOx emissions [36]. Biofuel from animal fats has also a higher calorific value [36]. A nonconsensual issue is the oxidative stability of animal-based biodiesel. Some authors claim that animal fat-based biodiesel is less stable for oxidation due to the absence of natural oxidants as compared to biodiesel from vegetable oil [63–65]. On the other hand, others, claim that from the content of saturated fatty acid, the addition of animal fat improves the oxidative stability of biofuel [36,66,67]. Feedstocks rich in polyunsaturated fatty acids are more susceptible to oxidation, due to the presence of double bonds in the chains, than feedstocks rich in saturated or monounsaturated fatty acids [68].

Pereira et al. evaluated the effect of blending vegetable with animal-based biodiesel on the oxidative degradation of this biofuel. The authors reported that blends of soybean/beef tallow biodiesel presented a higher oxidative stabilities in comparison with soybean biodiesel [67]. Wyatt et al. also reported that the oxidative stability of biofuel from lard, beef tallow, and chicken fat is equivalent or better than soybean biodiesel [40]. However, Sendzikiene et al. [69] showed that biofuel from animal fats such as lard and tallow is less stable for oxidation than rapeseed and linseed oil. Fuel produced from fats has also some disadvantages, such as the higher cold filter plugging point (CFPP) due to a significant content of saturated fatty acids [63–65]. The CFPP refers to the lowest temperature at which a given volume of liquid fuel will still flow through a specific filter in a specified time when cooled under certain conditions [70]. This is an important property to cold temperature countries.

2.7. Catalysts for Biodiesel Production

In order to increase the reaction rate, the transesterification reaction needs to be catalyzed [20].

The catalyst is a substance that increases the reaction rate without being consumed. If the catalysis acts in the same phase as the reaction mixture is a homogeneous catalyst. However, if the catalysts acts in different phase it is classified as a heterogeneous catalyst [26]. In this case, the chemical reaction occurs at the interface between the two phases [71]. Figure 9 shows the different types of catalysts that can be used in the transesterification process.
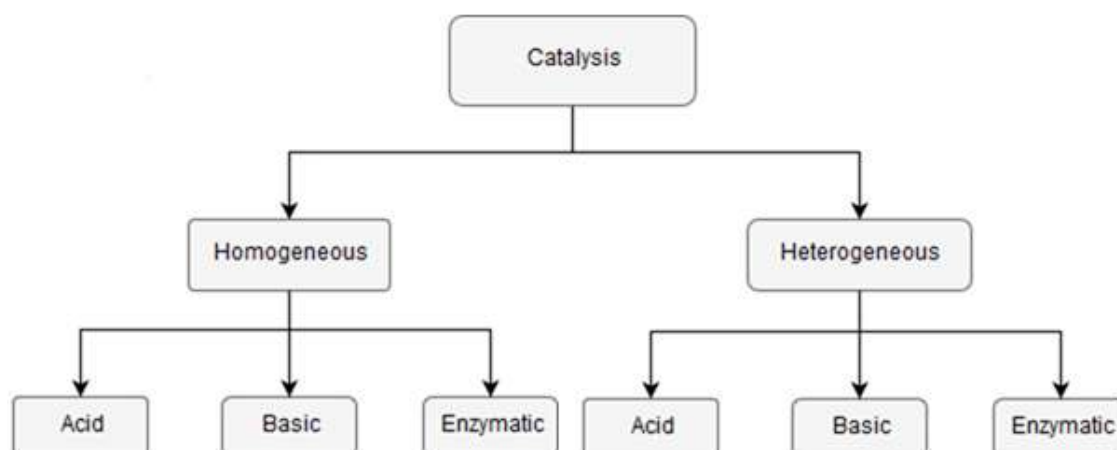
Figure 9. Different types of catalysis employed in the transesterification process.

Homogeneous catalysts have the main advantage of acting in the same phase of the reaction mixture, so the mass transfer resistance is minimized. Depending or their nature they can be basic, acid or enzymatic. These catalysts requires less time for a higher yield and conversion than the heterogeneous one [72].

Currently, the most common catalysts employed in the biodiesel industry are the homogeneous basic ones, such as sodium hydroxide (NaOH) and potassium hydroxide (KOH) that are easily soluble in methanol [22]. Homogeneous basic catalysts, having a higher reaction rate than homogenous acid ones, have the advantage of high biodiesel yield achieved in short reaction time under mild operating conditions. However, high purity feedstocks are essential and such catalytic systems should not be used with low grade fats feedstock which contains a high concentration of FFA and moisture. The FFA reacts with the basic catalyst forming soaps (Scheme 2), which leads to the losses of catalyst and reduced the biodiesel yields.
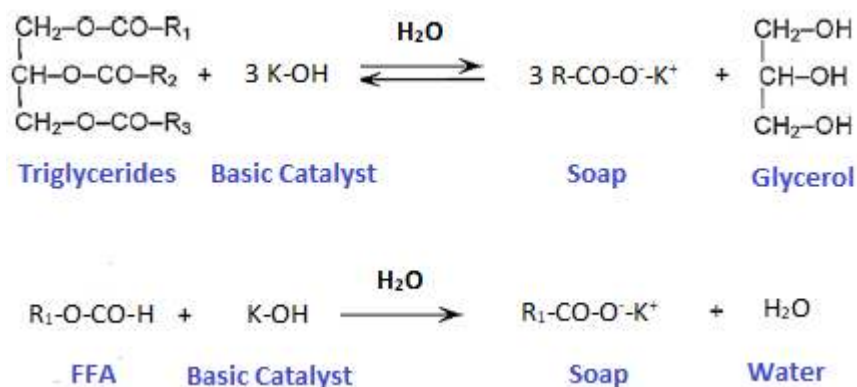
Scheme 2. Saponification reaction of triglycerides and Neutralization reaction of FFA (adapted from [26]).

The feedstocks moisture, and the water formed in the above reaction (Scheme 2), can also hydrolyze the triglycerides into diglycerides and FFA, increasing the acidity index and decreasing the biodiesel yields, according to the reaction in Scheme 3.
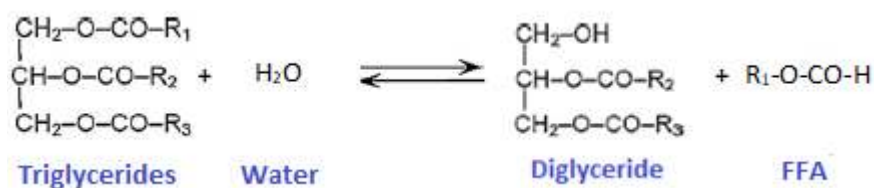
Scheme 3. Hydrolysis of triglycerides in FFA (adapted from [26]).

In order to overcome this issue, the transesterification reaction can be done in two stages. First, FFAs are converted into esters through pretreatment of the feedstock with an acid catalyst, reducing the FFA level (Scheme 4), followed by alkali transesterification. Another possibility is the use of a homogeneous acid catalyst such as sulfuric acid (H_2SO_4) or hydrochloric acid (HCl). Acid catalysts are not affected by FFA or water content due to their simultaneously capacity to catalyze both transesterification and esterification reactions (Scheme 4). Although, the acid catalyzed reaction is slower and thus, severe reaction conditions are needed, such as high reaction temperature, high acid catalyst concentration, and high alcohol:oil molar ratio in comparison with basic catalysts.

Scheme 4. Esterification reaction of FFA (adapted from [26]).

Homogeneous catalysts cannot be separated from the reaction mixtures so they cannot be reused or regenerated, which is their major drawback. Besides that, these are corrosive to reactors and their separation from the reaction mixture is more difficult, requ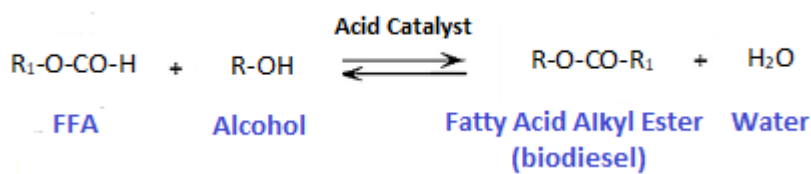iring more complex equipment [73,74]. In the homogeneous catalysis purification process, a large amount of water is needed to neutralize and purify the biodiesel, producing a large quantity of wastewater, and increasing the production costs.

In the last decades, there has been a growing interest in the development and employment of new heterogeneous catalysts for biodiesel production. Heterogeneous or solid catalysts can be easily recovered, regenerated and reused. Depending or their nature they can be basic like alkaline earth metal oxides (CaO, MgO), hydrotalcite, acids like zirconia and alumina-based catalysts or enzymatic, like immobilized lipase [74,75]. Heterogeneous catalysts facilitate continuous reactor operation as they are easily separated from the reaction medium. They also minimize biodiesel and glycerin purification steps. Water consumption decreases because no catalyst neutralization process, and consequent steps, are required [21,74]. Like the homogeneous basic catalysts, the performance of basic solid catalysts is also affected by high FFA and water content, is also more active than solid acid one with mild operating conditions requirements. Mass transfer resistance is an issue when using heterogeneous catalysts due to the presence of three phases (oil/alcohol/catalyst) in the reaction mixture. In comparison with a homogeneous catalyst, solid catalyst presents lower conversions requiring more severe reaction conditions to achieve the same conversions [21,74]. Another issue to consider is the leaching of the active phase into the reaction mixture. The catalyst leaching leads to a homogeneous contribution. The extent of the catalyst leaching affects not only the life expectancy of catalysts and consequently their reuse but also the biodiesel quality [76]. For these reasons the heterogeneous catalyst should not be leaching and must be reused.

Lipases are enzymes that can be used in biodiesel production as catalysts, belonging to the homogeneous if used in its free form or heterogeneous group if immobilized [75]. Compared with other catalysts, enzymes have high selectivity, the products achieved (biodiesel and glycerin) are purer and no soaps are formed. Like acid catalysis (homogeneous or heterogeneous), enzymes have the capacity to catalyzed both triglycerides by transesterification and FFA by the esterification reaction. The main disadvantages are its high costs and the risk of enzyme inactivation by the short chain alcohols and products [75,77]. A literature survey on advantages and disadvantages of both homogeneous and heterogeneous catalysis is presented in Table 5.

Table 5. Advantages and disadvantages of homogeneous and heterogeneous catalysts in biodiesel production.

	Advantages	Disadvantages
Homogeneous	Less time required with a higher yield Mild operation condition Base catalysts are more active than acid Acid catalysts are not affected by the content of FFA or water simultaneously capacity to catalyzed transesterification and esterification reaction	Not separable from the reaction mixture, cannot be reuse A large amount of water is needed to neutralize and purify the biodiesel Base catalysts are affected by high FFA and water content
Heterogeneous	Easily recovered, regenerated and reused Available to batch or continuous fixed bed reactors Requires fewer process units with a simpler separation and purification processes The amount of water is reduced Base catalysts are more active than acid Acid catalysts are not affected by the FFA or water amount, capacity to catalyzed both transesterification and esterification reaction	Lower conversions requiring more severe reaction conditions to achieve the same conversions of homogeneous ones Mass transfer resistance due to the presence of three phases (oil/alcohol/catalyst) in the reaction mixture Base catalysts are affected by high FFA and water content

2.8. Homogeneous and Heterogeneous Catalytic Conversion of Animal Fats

Animal fats can be used as feedstocks to produces biodiesel through homogenously- (Table 6) and heterogeneously- (Table 7) catalyzed processes. Tables 6 and 7 summarize the main characteristics of both types of catalyzed processes.

2.9. Biodiesel Purification

After the transesterification reaction, biodiesel must be purified in order to accomplish the quality specifications (ASTM D6751 or EN 14214) and for further commercialization. In heterogeneous catalysis, in the first step, the solid catalyst can be easily recovered from the reaction mixture by filtration, instead, homogeneous ones will be dispersed and cannot be reused.

Table 6. Review of homogeneous catalysis to process animal fats.

Feedstock	Alcohol Type	Catalyst/ Co-Solvent	Reaction	Alcohol:Oil (Molar Ratio)	Cat. Conc. (wt % Oil)	Temp. (°C) and Impeller Speed	Time (h)	Catalyst	Alcohol:Oil (Molar Ratio)	Cat. Conc. (wt % Oil)	Temp. (°C) and Impeller Speed	Time (h)	Y = Yield; C = Conversion; P = Purity (%)	Ref.
				Reaction Conditions					**Optimized Condition**					
Mix of WFO and pork lard (fat fraction of mix 0–1(*w/w*))	MeOH	NaOH	-	6:1	0.8	60	1	-	6:1	0.8	60	1	Y = 81.7–87.7 P = 93.9–96.3	[47]
beef tallow	MeOH	KOH	-	6:1	1	60 and 60	2	-	6:1	1	60 and 60	2	Y = 90.6	[78]
pork lard													Y = 91.4	
chicken fat													Y = 76.8	
sardine oil													Y = 89.5	
corn oil	MeOH	KOH	-	-	-	60 and 300 rpm	2	KOH	6:1	1	60 and 300 rpm	2	Y = 91	[79]
chicken fat		1st PT: H$_2$SO$_4$					1	1st PT: H$_2$SO$_4$	45 kg oil/40.5 kg alcohol	2.4 kg		1	Y (experiment 1) = 80.4; Y (experiment 2) = 81.5	
		2nd PT: H$_2$SO$_4$					1	2nd PT: H$_2$SO$_4$	40 kg fat/3.1 kg alcohol	0.1 kg		1		
		KOH					2	KOH	6:1	1		2		
fleshing oil		1st PT: H$_2$SO$_4$					1	1st PT: H$_2$SO$_4$	50 kg oil/21.1 kg alcohol	0.62 kg		1	Y (experiment 1) = 81.6; Y (experiment 2) = 82.3	
		KOH					2	KOH	7.5:1	1		2		
beef tallow	MeOH	methanolic KOH	-	-	-	-	-	-	-	-	70-90	65 min.	Y = 96.26	[80]
beef tallow,	MeOH	KOH	-	6:1	0.8	60 and 60	2	-	6:1	0.8	60 and 60	2	Y = 90.8	[81]
pork lard													Y = 91.5	
chicken fat													Y = 76.8	

Table 6. *Cont.*

Feedstock	Alcohol Type	Catalyst/ Co-Solvent	Reaction	Alcohol:Oil (Molar Ratio)	Cat. Conc. (wt % Oil)	Temp. (°C) and Impeller Speed	Time (h)	Catalyst	Alcohol:Oil (Molar Ratio)	Cat. Conc. (wt % Oil)	Temp. (°C) and Impeller Speed	Time (h)	Y = Yield; C = Conversion; P = Purity (%)	Ref.
				Reaction Conditions					Optimized Condition					
Mix of waste fish oil(WFO); palm oil (PO) and WFO	MeOH	1st: H_2SO_4	-	6:1	1	60	1	-	6:1	1	60	1	FAME content (33.3 wt % PO; 66.7 wt % WFO) = 80	[82]
		2nd: NaOH	-	9:1	0.5	60	1	-	9:1	0.5	60	1	Y (33.3 wt % WFO; 66.7 wt % PO) = 98.5	
pork lard blended with *n*-hexane solvent	MeOH	KOH	-	6:1–18:1	0.48–3.05	50–60	2	-	10:1	2.0	60	2	Y (65 wt % solvent) = 98.2	[83]
Cyprinus carpio fish oil	MeOH	KOH; CH_3ONa; NaOH; EtONa/*n*-hexane; pet. ether; acetone; cyclohexane; diethyl ether	-	-	-	-	-	KOH	5:1	0.6	50	0.5	Y (1.5:1 hexane to methanol volume ratio) = 98.55 ± 1.02	[84]
beef tallow	MeOH	KOH	-	6:1	1.5	65 and 400 rpm	180 min	-	6:1	1.5	65 and 400 rpm	180 min	ester content = 95–97	[45]
lard	MeOH	NaOH	-	180 cm³ fat/138 cm³ MeOH	1.4 g	40–70	1.5	-	180 cm³ fat/138 cm³ MeOH	1.4 g	70	1.5	Y = 73	[85]
lard	MeOH	KOH	-	3.48–8.52	0.16–1.84	24.8–75.2	20 min.	-	7.5:1	1.26	65	20 min.	Y = 97.8 ± 0.6	[86]
Silurus triostegus heckel fish oil	MeOH	KOH	single and two-step transesterification	3:1–12:1	0.25–1.0	32–60	0.5–2	-	6:1	0.50	32	0.5	Y KOH = 96	[87]
		NaOH		6:1	0.5	32–60	1							
chicken fat	MeOH	KOH	Sulfuric acid, hydrochloric acid and sulfamic acid with methanol	6:1	-	25–60	1–4	K methoxide	6:1	1	60	1	Y KOMe = 88.5	[88]
		NaOH												
		KOMe (32% in MeOH)												
		NaOMe (30% in MeOH)												

Table 6. *Cont.*

				Reaction Conditions					Optimized Condition					
Feedstock	Alcohol Type	Catalyst/ Co-Solvent	Reaction	Alcohol:Oil (Molar Ratio)	Cat. Conc. (wt % Oil)	Temp. (°C) and Impeller Speed	Time (h)	Catalyst	Alcohol:Oil (Molar Ratio)	Cat. Conc. (wt % Oil)	Temp. (°C) and Impeller Speed	Time (h)	Y = Yield; C = Conversion; P = Purity (%)	Ref.
chicken fat	MeOH	KOH	pre-treatment sulfuric acid and methanol	4:1–8:1	0.75–1.25	45	3–9 min	-	7:1	1	45	9 min	Y = 94.8	[89]
beef tallow	MeOH	NaOH	radio frequency heating	5:1–9:1	0.2–0.6	-	RF heating 1–5 min	-	9:1	0.6	-	RF heating 5 min.	Y = 96.3 ± 0.5	[90]
tallow	MeOH	KOH	-	6:1	0.8	60	2	-	6:1	0.8	60	2	Y = 90.8	[91]
lard													Y = 91.4	
poultry													Y = 76.8	
mutton tallow	MeOH	KOH	pre-treatment sulfuric acid and MeOH	6:1	0.35–0.4 g	60 and 900 rpm	1.5	-	6:1	0.39 g	60 and 900 rpm	1.5	Y = 93.2	[92]
mix of chicken and swine fat residues	EtOH	KOH	animal fats pre-treated	6:1–8:1	0.44–1.32	30–70	1	-	7:1	0.96	30	1	C = 83.5	[93]

PT = pretreatment.

Table 7. Review of heterogeneous catalysis to processes animal fats.

Feedstock	Alcohol Type	Catalyst/ Co-Solvent	Catalyst Preparation	Alcohol:Oil (Molar Ratio)	Cat. Conc. (wt % Oil)	Temp. (°C) and Impeller Speed	Time (h)	Catalyst Preparation	Alcohol:Oil (Molar Ratio)	Cat. Conc. (wt % Oil)	Temp. (°C) and Impeller Speed	Time (h)	Y = Yield; C = Conversion; P = Purity (%)	Ref.
						Reaction Conditions					**Optimized Condition**			
catfish fat (*Pangasius*)	MeOH	barnacle / bivalve clam	900 °C	6:1–15:1	2–7	65	2–8	900	12:1	5	65	4	FAME content = 97.2 ± 0.04 wt % / FAME content = 96.9 ± 0.03 wt %	[49]
waste lard from piglet roasting (compared to heated and unheated lard	MeOH	quicklime and CaO	Pure CaO 550 °C, 2 h Quicklime 550 °C, 4 h	6:1	5	40; 50; 60 and 900 rpm	up to 3	Quicklime 550 °C 4 h	6.1	5	60; 900 rpm	1	FAME concentration waste lard = 97.5%	[94]
chicken fat	MeOH	crab, cockle shells and mix	900 °C, 2 h	-	-	-	-	900 °C, 2 h	13.8:1	4.9% (1:1 crab:cockle)	65	3	P = 98.8	[48]
commercial-grade fat	MeOH	Amberlyst™ A26 OH	-	6:1	1–2.7 mol/L of fat	65	60–500 min	-	6:1	2.2 mol/L	65	6	Y = 90–95	[95]
pork lard	MeOH	CaMnOx	-	9:1–27:1	1:5	40–60	4–8	-	21:1	1	60	8	Y = 99.6	[64]
soybean oil (SBO) and beef tallow (bf)	MeOH / EtOH	Sulfonated polystyrene compounds	- / -	3:1–9:1; 100:1 / 100:1	20 mol % of –SO$_3$H groups in relation to the oil mass	28–64 / 64	3–18 / 18	-	100:1 / -	20 mol % of –SO$_3$H groups in relation to the oil mass	64 / -	18 / -	C$_{SBO}$ = 85 / C$_{Beef\ tallow}$ = 85 and 75	[96]
beef tallow	MeOH	KF/CaO-Fe$_3$O$_4$	-	3:1–12:1	1–6 g	40–65	20–70 min.	-	10:1	5 g	55	1	Y = 94	[97]
beef tallow	MeOH	Cs$_2$O/γ-Al$_2$O$_3$	wet impregnation with aqueous solution of Cs$_2$CO$_3$.	8:1–12:1	4–6 g	55–75	80–160 min.	-	10.5:1	5.3%	66	2	Y = 95.5	[98]

Biodiesel phase can be separated from the glycerin phase in a decanter by sedimentation or centrifugation due to their density difference [99,100]. The excess alcohol used in the reaction can be separated from both phases by evaporation or distillation. The obtained biodiesel still contains free glycerol, soap, residual alcohol, catalyst and mono, di, and triglycerides unreacted, which must be removed. Table 8 summarizes the main consequences of biodiesel contamination on internal combustion engines.

Table 8. Biodiesel impurities and properties effects on internal combustion engines [101,102].

Impurities	Effects	
	Biodiesel	**Engines**
FFA	Low oxidation stability	Corrosion
water	Reduces the heat of combustion Hydrolysis (FFA production)	Corrosion Bacteriological growth (filter blockage)
methanol	Low values of density and viscosity Low flash point (transport, storage, and use problems)	Corrosion of Al and Zn pieces
glycerides	High viscosity	Deposits in the injectors (carbon residue) Crystallization
metals (soap, catalyst)	-	Deposits in the injectors (carbon residue) Filter blockage (sulfated ashes) Engine weakening
glycerin	Decantation storage problem	Increase aldehydes and acrolein emissions

Biodiesel can be purified by several processes. The most used industrial biodiesel purification process is water washing. This method is simple, efficient and allows one to obtain biodiesel with high purity. Distilled water, deionized water, acidulated water, acid and water or water, and an organic solvent can be added to biodiesel [99,102,103]. Due to their water solubility, residual glycerol, methanol, catalyst, and any soap formed during the reaction can be eliminated. Lastly, washed biodiesel need to be dehydrated [99,103]. Biodiesel purification with water is time-consuming and produces large volumes of wastewater which cannot be discharged in watercourses. Wastewater effluent has to be treated, increasing the biodiesel production costs. To overcome this issue, a dry washing purification process, using solid sorbents such as ion exchange resin, silica, activated carbon among other adsorbents, can be adopted. This purification process is fast, easy to integrate in an industrial plant and being water-free, no wastewater is produced lowering the production cost [102]. The main drawback is the purified biodiesel may not meet methanol and glycerin EN 14214 specifications. Therefore, methanol and glycerin should be removed as much as possible before the purification process [101,104]. Also, the adsorbent cost, its recycling, and elimination can be a disadvantage [105].

Inorganic and polymeric membranes can also be employed for biodiesel purification [104]. Membrane works as a selective barrier retaining the biodiesel contaminants [105]. No water is consumed within this process, consequently, no wastewater is produced although the addition of a small amount of water improves glycerin retention. High-quality biodiesel meeting the required specifications can be achieved. This process presents some issues too such as, membrane cleaning, membrane costs and the increase of biodiesel production cost [103].

2.10. Quality Specifications

The quality of biodiesel can be influenced by several factors that may be reflected in its chemical and physical properties. To be commercialized, biodiesel has to accomplish the quality specifications established by institutions like the European Committee of Standardization (ISO) and the American

Society for Testing and Materials (ASTM) (Table 9). These regulations, which are dynamic and must be periodically reviewed, describe not only the quality requirements but also the test methods employed.

Table 9. ASTM D6751 and EN 14214 specifications of biodiesel fuels (B 100) [106,107].

Property Specification	ASTM D6751 Limit	Test Methods	EN 14214 Limit	Test Methods
Ester content (% (m/m))	-	-	96.5	EN 14103
Density at 15 °C (kg/m^3)	880	D1298	860–900	EN ISO 3675/12185
Viscosity at 40 °C (mm^2/s)	1.9–6.0	D445	3.5–5.0	EN ISO 3104
Cetane number	Min. 47	D613	Min. 51.0	EN ISO 5165
Iodine number (g I$_2$/100 g)	-	-	Max. 120	EN 14111/16300
Acid value (mg KOH/g)	Max. 0.50	D664	Max. 0.50	EN 14104
Pour point (°C)	-15 to -16	D97	-	-
Flash point (°C)	Min. 130	D93	Min. 101	EN ISO 2719/3679
Cloud point (°C)	-3 to -12	D2500	-	-
Cold filter plugging point (°C)	Max. +5	D6371	-	EN 116/16329
Copper strip corrosion (3 h at 50 °C)	No 3	D130	class 1	EN ISO 2160
Carbon residue (% (m/m))	Max. 0.05	D4530	-	-
Methanol content (% (m/m))	Max. 0.20	EN 14110	Max. 0.20	EN 14110
Water content (mg/kg)	Max. 500	D2709	Max. 500	EN ISO 12937
Sulfur (mg/kg))	S15 Max. 15 S500 Max. 500	D5453	Max. 10.0	EN ISO 20846/20884
Sulfated ash (% (m/m))	Max. 0.02	D874	Max. 0.02	EN ISO 3987
Phosphorus content (mg/kg)	Max. 10	D4951	Max. 4.0	EN 14107/16294
Free glycerol (% (m/m))	Max. 0.02	D6584	Max. 0.02	EN 14105/EN 14106
Total glycerol (% (m/m))	Max. 0.24	D6548	Max. 0.25	EN 14105
Monoglyceride (% (m/m))	Max. 0.40	D6584	Max. 0.70	EN 14105
Diglyceride (% (m/m))	-	-	Max. 0.20	EN 14105
Triglyceride (% (m/m))	-	-	Max. 0.20	EN 14105
Distillation temperature, 90% recovered (°C)	Max. 360	D1160	-	-
Oxidation stability h (at 110 °C)	Min. 3	EN 15751	Min. 8	EN 14112/15751
Linolenic acid methyl ester (% (m/m))	-	-	Max. 12.0	EN 14103
Polyunsaturated (≥4 double bonds) Methyl esters (% (m/m))	-	-	Max. 1.00	EN 15779
Alkaline metals (Na$^+$ K) (mg/kg)	Max. 5.0	EN 14538	Max. 5.0	EN 14108/14109/14538
Alkaline earth metals (Ca + Mg) (mg/kg)	Max. 5.0	EN 14538	Max. 5.0	EN 14538
Total contamination (mg/kg)	-	-	Max. 24	EN 12662

2.11. Properties of Biodiesel from Different Feedstocks

Biodiesel properties are influenced not only by raw materials but also by transesterification and purity process. Table 10 shows a literature review of biodiesel properties from different feedstocks.

Table 10. Biodiesel properties from different feedstocks.

Property Specification	ASTM D6751 Limit	EN 14214 Limit	Rapeseed Oil [3]	Soybean Oil [3]	Palm Oil [3]	Chicken Fat [79]	Fleshing Oil [79]	Beef Tallow [3,18]	Mutton Tallow [18]	Lard [18]	Fish Oil [108]	WCO [108]
Density at 15 °C (kg/m^3)	880	860–900	882	914	864	867–889.7	875.5–876.7	832–872	856–882	873–877.4	881–890	875–888
Viscosity at 40 °C (mm^2/s)	1.9–6.0	3.5–5.0	4.44	4.04	4.5	4.94–6.25	4.7–4.77	4.89–5.35	4.75–5.98	4.59–5.08	3.82–7.2	3.66–6.8
Cetane number	Min. 47	Min. 51.0	54.4	37.9	54.6	52.3	58.8	60.36	59–59	-	50.9–52.6	41–66
Iodine number (g I$_2$/100 g)	-	Max. 120	-	128–143	54	95.5–130	53.6–61	nm–44.4	40–126	67–77	nm–185	60–125.21
Acid value (mg KOH/g)	Max. 0.50	Max. 0.50	-	0.266	0.24	0.22–0.8	0.28–0.32	0.147–0.2	0.3–0.65	0.04–1.13	0.35–1.32	0.27–1.31
Pour point (°C)	−15 to −16	-	−12		15	−6–12.3		10–15	−5	5–7	−14–4	−2.5–9
Flash point (°C)	Min. 130	Min. 101	170	254	135	169–174	168–175	152–171	-	143.5–147	114–176	70.6–190
Cloud point (°C)	−3 to −12	-	−3.3	0.9	16	−5–14		nm–16	−4	-	−5	−12–13
Cold filter plugging point (°C)	Max. +5	-	−13	−4	12	2–3	10–11	nm–14	-	-	-	−5–12
Copper strip corrosion (3 h at 50 °C)	No 3	class 1		1	1	No 1	No 1	No 1	-	No 1	-	-
Carbon residue (% (m/m))	Max. 0.05	-	81	-	-	nm–0.024	-	-	-	nm–0.21	76.53–80.01	0.0004–77.38
Methanol content (% (m/m))	Max. 0.20	Max. 0.20	-	-	-	0.01–0.06	0.01–0.01	nm–0.1	-	-	-	-
Water content (mg/kg)	Max. 500	Max. 500	-	<0.005 %vol		200–440	326–410	nm–374.2	-	184–1100	-	
Sulfur (mg/kg))	S15 Max. 15 S500 Max. 500	Max. 10.0	-	0.8	0.003	nm–81.5	138.1–141	nm–7.0	-	-	-	0–12.5
Sulfated ash (% (m/m))	Max. 0.02	Max. 0.02	-	<0.005	0.002	-	0.03	nm–<0.005	nm–0.025	nm–0.002	-	-
Phosphorus content (mg/kg)	Max. 10	Max. 4.0	-	0.1	<0.001	-	100	nm–<0.1	nm–16	-	-	-
Free glycerol (% (m/m))	Max. 0.02	Max. 0.02	-	0.012	0.01	0.008–0.02	0.01–0.01	0.008–0.01	-	-	-	-

Table 10. *Cont.*

Property Specification	ASTM D6751 Limit	EN 14214 Limit	Rapeseed Oil [3]	Soybean Oil [3]	Palm Oil [3]	Chicken Fat [79]	Fleshing Oil [79]	Beef Tallow [3,18]	Mutton Tallow [18]	Lard [18]	Fish Oil [108]	WCO [108]
Total glycerol (% (m/m))	Max. 0.24	Max. 0.25	-	0.149	0.01	0.03–0.19	0.10–0.05	0.076–0.33	-	-	-	-
Monoglyceride (% (m/m))	Max. 0.40	Max. 0.70	0.473	-	-	0.02–0.56	0.06–0.27	0.13–0.223	-	-	-	-
Diglyceride (% (m/m))	-	Max. 0.20	0.088	-	-	0.05–0.09	0.02–0.09	0.63–0.12	-	-	-	-
Triglyceride (% (m/m))	-	Max. 0.20	0.019	-	-	0.06–0.12	0.04–0.20	0–0.07	-	-	-	-
Distillation temperature, 90 % recovered (°C)	Max. 360	-	-	-	-	-	-	307–344	-	nm–352.5	-	-
Oxidation stability h (at 110 °C)	Min. 3	Min. 8	7.6	2.1	10.3	nm–6	-	nm–1.6	-	-	-	0.43–15.9
Linolenic acid methyl ester (% (m/m))	-	Max. 12.0	-	-	-	-	-	-	-	0.9–1.4	-	-
Polyunsaturated (≥4 double bonds) Methyl esters (% (m/m))	-	Max. 1.00	-	-	-	-	-	-	-	-	-	-
Alkaline metals (Na+ K) (mg/kg)	Max. 5.0	Max. 5.0	-	-	-	-	5	2–2.63	-	nm–17.2	-	-
Alkaline metals (Ca + Mg) (mg/kg)	Max. 5.0	Max. 5.0	-	-	-	-	-	-	-	-	-	-
Total contamination (mg/kg)	-	Max. 24	-	-	-	-	-	-	-	-	-	-
Heat of combustion (MJ/kg)	-	-	37	39.76	-	39.34–40.17	39.89–39.95	40.23	-	36.5–40.10	37.79–42.24	35.40–43.21

nm—not measured.

3. Conclusions

Biodiesel obtained by alcoholysis of fats is a feasible low carbon fuel to replace the conventional fossil diesel thus helping to mitigate the anthropogenic carbon emissions. First generation biodiesel, obtained by methanolysis of vegetable oils, presents severe sustainability issues related to the use of arable lands to produce energy-dedicated crops (oleaginous crops). Biodiesel sustainability issues can be minimized by using non-edible fats such as animal fats and waste cooking oils. Replacing methanol by ethanol could also contribute to reducing carbon emissions from biodiesel because ethanol can be obtained by biomass fermentation, thus being a renewable alcohol.

Biodiesel production processes can be improved by replacing conventional homogeneous (basic) catalysts with heterogeneous catalysts. Among the huge number of scientific papers on heterogeneous catalysts for biodiesel production, the excellent performances (catalytic activity) of calcium-based catalysts stands out but they have never been tested industrially. The lack of data on the stability of calcium catalysts appears to be a limitation to their industrial testing. Dry-washing purification of biodiesel, instead of the wet process nowadays in use, can also contribute to biodiesel sustainability. Biodiesel dry-washing decreases the large volumes of wastewater generated in the traditional purification method and cuts down the energy required in the biodiesel drying process.

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

ASTM	American Society for Testing and Materials
CFPP	Cold Filter Plugging Point
CIS	Commonwealth of Independent States
EIA	U.S. Energy Information Administration
ETBE	Ethyl *tert*-butyl ether
FAEE	Fatty acid ethyl ester
FAME	Fatty acid methyl ester
FFA	Free fatty acid
GHG	Greenhouse gas
HC	Hydrocarbons
ISO	European Committee of Standardization
MTBE	Methyl *tert*-butyl ether
NOx	Nitrous oxide
PM	Particulate matter
SRM	Specified Risk Material
TSE	Transmissible Spongiform Encephalopathies
UCO	Used cooking oil
WAF	Waste animal fats
WCO	Waste cooking oil

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