Review

The Catalysed Transformation of Vegetable Oils or Animal Fats to Biofuels and Bio-Lubricants: A Review

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Abstract: This review paper summarizes the current state-of-the-art of the chemical transformation of oils/fats (i.e., triacylglycerols) to the use of biofuels or bio-lubricants in the means of transport, which is a novelty. The chemical transformation is necessary to obtain products that are more usable with properties corresponding to fuels synthesized from crude oil. Two types of fuels are described— biodiesel (the mixture of methyl esters produced by transesterification) and green diesel (paraffins produced by hydrogenation of oils). Moreover, three bio-lubricant synthesis methods are described. The transformation, which is usually catalysed, depends on: (i) the type and composition of the raw material, including alcohols for biodiesel production and hydrogen for green diesel; (ii) the type of the catalyst in the case of catalysed reactions; (iii) the reaction conditions; and (iv) types of final products. The most important catalysts, especially heterogeneous and including reaction conditions, for each product are described. The properties of biodiesel and green diesel and a comparison with diesel from crude oil are also discussed.

Keywords: oils/fats; transesterification; biodiesel; hydrotreating; green diesel; bio-lubricants

1. Introduction

The world's energy consumption is ceaselessly rising from the industrial revolution in the 18th century. In the last several decades, world energy consumption increased by about 5% per year [1,2]. Many scientists worldwide are trying to find new sources of renewable energy which could replace fossil fuels [3]. Non-renewable resources, including fossil fuels (coal, oil, natural gas, among others), are found in limited reserves and can be depleted, unlike renewable resources, which cannot be depleted. Renewable energy belongs to the natural resources that can naturally recover in a human time-scale. They provide several key objectives: (i) security of energy supply, (ii) the reduction of greenhouse gases, (iii) the reduction of energy prices, and (iv) the possibility of new jobs and general economic growth [4]. This kind of energy can be obtained from sunlight, wind, geothermal resources, oceans, hydropower, and so forth. The definition of renewable resources could be as follows: Renewable natural resources can recover partially or entirely from their consumption, either alone or with human contribution [5]. Humans have used renewable resources (wood) since prehistoric times, but population growth has increased the need for deforestation. Paradoxically, this big issue was resolved by fossil fuels, which allowed to gain energy in other ways than from growing crops, which requires a large area of land.

The first-generation biofuels (mainly produced from food crops) have a limited ability to replace fossil fuels, reduce climate change, and encourage economic growth. Biofuels include bioethanol (produced from grain, sugar beet, sugar cane, corn, starch, etc.), rapeseed oil methyl ester, and fatty acid methyl ester (FAME) (produced from pressed oil plants–palm oil, sunflower oil, soybean oil, etc.) [6]. Bioethanol is widely used in the USA and Brazil, which utilize the excess of sugar cane. In Europe, biodiesel is primarily used

as biofuel [7]. In the European Union, the importance and consumption of biofuels are constantly growing, as currently, 7 wt% has to be blended into diesel by producers [8]. The main associated problems are the following: (i) not enough growing land to replace crude oil, (ii) large amounts of raw material, (iii) ability to compete with food production, and (iv) the use of fertilizers or pesticide for growing.

Problems related to first-generation biofuels have increased for developing biofuels produced from non-edible food crops and forest biomass, including mining residues, agricultural waste (straw, hay, corn, and others), and fast-growing grasses and wood or biological waste from households. These so-called second-generation fuels include bioethanol, diesel oil as a product of Fisher–Tropsch synthesis, biobutanol from bioethanol, and so forth. The second-generation energy crops have a greater potential to replace crude oil than those of the first generation. The main issue is that the technological process is more complicated than for the first generation. Although significant progress has been made, many technical problems still have to be eliminated and overcome so that these crops can be used commercially [9,10]. The second generation requires less land than the first, but the required land for production is still substantial.

The problems associated with production and using first-generation fuels can be solved by third-generation biofuels, which use fast-growing microorganisms (algae, cyanobacteria). This category of biofuels includes microalgae and various types of bacteria that can produce hydrocarbon-based fuel from CO_2 and sunlight [11,12].

In line with the ambitious new European Union, targets related to the use of renewable energy have increased to 12% of renewable sources consumption in 2030, which is an increase in the amount of biomass used [13]. The consumption of renewable energy is also increasing in the USA [14].

The novelty of the review consists in the description and comparison of the ways of transforming oils/fats to biofuels (biodiesel and Green Diesel) and biolubricants used in the means of transport. Other reviews are focused on one product only, one type of oil [15], one method of transformation, one aspect of biodiesel, or one type of catalyst [16]. The review gives a general overview of oils/fats transformation.

2. Raw Material—The Vegetable Oils and Animal Fats

The main raw materials for producing biodiesel and green diesel are triacylglycerols (also called triglycerides), which are contained in vegetable oils and animal fats. The oils/fats are usually sorted into (i) edible oils (such as rapeseed, soybean, sunflower, palm, etc.), (ii) nonedible oils (such as *Jatropha curcas* L., *Pongamia pinnata*, *Ricinus communis*, etc.) [17], (iii) waste cooking oils [18], (iv) animal fats, or (v) oil formed by microalgae, which are rapidly expanding raw materials, such as algae and cyanobacteria (oil extracted from them) [19].

The oils/fats usually contain approximately 98% of triacylglycerols (chemically, esters of higher fatty acids and glycerol). Other chemical matters are mono- and diacylglycerols, free fatty acids, water, dyes, and so forth. The profile of higher fatty acid, bonded in triacylglycerols, determines physical-chemical properties such as viscosity, iodine number, and oxidative stability [20,21]. The concrete composition of oil, including the FA profile, depends on the type of oils/fats, and the type of cultivar, the condition of storing and growing (for vegetable oils)—for example, the content of oleic acid in rapeseed oil (RSO) can range from 45% to 61% [22]—therefore, only the average contents of the major common fatty acids are shown in Table 1. The composition of the other oil is stated in [1]. The fatty acids were sorted by (i) saturated (the most abundant are palmitic and stearic) and (ii) unsaturated (mainly represented by oleic, linoleic, and linolenic acids). The composition of oils/fats is important because they influence the reaction conditions of the following processes.

The free fatty acids (FFA) are not bound through glycerol, and their content is very variable from almost 0 to 90 wt%, for example, RSO contains usually 0.5–1.0 wt% of FFA, and tropical oil usually contains 2–5 wt%. However, some vegetable oils contain more than 90% of the FFA (e.g., tall oil fatty acid (TOFA) [23]).

Table 1. The content of fatty acids in various types of vegetable oils and animal fats [22,24].

Oil/Fat	The Content of Major Fatty Acid, %				
	Palmitic (16:0) *	Stearic (18:0)	Oleic (18:1)	Linoleic (18:2)	Linolenic (18:3)
Palm	45	8	38	10	0.5
Soybean	10	4	21	56	8
Rapeseed	4.5	1.5	56	21	10
Sunflower	6.5	5	24	63	0.3
Olive	11.5	2.5	74	9.5	1.5
Jatropha oil	15.4	5	37	42.2	0.3
Camelina sativa	8.3	0.5	19.5	46.5	25.1
Lard	24	14	44	10.7	0.4
Beef tallow	26	20	40	4.5	0.5
Mutton tallow	27	32	32	1.6	0.2

* The fatty acids are abbreviated: the first number indicates the number of carbon atoms and the second number is the number of double bonds.

The concrete sources of oil/fat depend on the area—rapeseed oil is mainly used in Europe, soybean oil in the USA, and palm oil in Malaysia. The price of biodiesel and green diesel strongly depends on oil/fat (approximately 80–85% of biofuel prices consist of the price of oil). Therefore, newer and cheaper sources are searched for, such as jatropha and TOFA. However, their use is disputable because they usually contain more impurities, especially free fatty acids and water, which complicate further usage.

The vegetable oils can be obtained in various ways, either from the pulps of fruits (palm, olive), from seeds of vegetables (rapeseed, sunflower), or also from beans (soy). The pulp oil is obtained by pressing, which has to be carried out in the place of planting because of the meagre shelf life of the fruit pulp. By contrast, oilseeds and beans can be stored and transported almost unlimitedly. There are two technologies which are mostly widespread in the industry worldwide: (i) pressing with continuous screw presses [25] and (ii) extracting of hydrocarbons (usually fraction C6) [26]. A combination of pressing followed by solvent extraction is used to obtain large volumes; it is possible to achieve a yield of 98% of the oil contained in the raw materials. On a local scale, the producers mainly use a pressing technology to obtain 85% of the contained oil in the raw materials.

The first step for waste cooking oils and animal fats is decantation and filtration to remove food scraps and frying waste. This operation is commonly done by local waste managers, which are in charge of collecting this residue from houses and restaurants. For the preparation of esters, the phospholipids and slime components are removed by degumming. The crude oil is also necessary to refine (at least partially) for the production of FAME [27–29]. Moreover, vegetable oils usually contain natural gums (phosphatides) and other ashes, which are removed throughout oil refining and transesterification. For Green diesel, the high content of metals in the raw material is problematic because it can destroy the catalyst—it has to be reduced by raffinate.

Vegetable oils or animal fats are possible to use directly in an engine, but engine modifications are necessary. The main problems of using oils/fats are (i) high kinematic viscosity (in the range of 30–40 mm^2 s^{-1}), (ii) a low cetane number, and (iii) a lower flash point than fuels formed from crude oil. However, to solve problems with high viscosity, it is necessary to transform the oil/fat into fuels with lower viscosity—esters of low molecular alcohols (biodiesel) or green diesel.

3. The Properties and Comparison of Biodiesel and Green Diesel

Biodiesel is formed by transesterification (usually catalytic), while green diesel (also known as hydrotreated vegetable oil–HVO) is formed by catalytic hydrotreating of oil. The comparison of the properties of biodiesel, HVO and standards for diesel in the European Union countries is stated in Table 2, and details about the production are in the following Sections 4 and 5.

Table 2. Properties of biodiesel, HVO, and fossil diesel (including minimal and maximal standard values for diesel) [1].

Properties	Biodiesel	HVO	Fossil Diesel	Standard Min.	Standard Max.
Chemical composition	ester	hydrocarbon	hydrocarbon	-	-
Oxygen, wt%	11	0	0	-	-
Density (15 °C), g cm^{-3}	0.86–0.90	0.77–0.83	0.85	0.80	0.845
Kinematic viscosity (40 °C), mm^2 s^{-1}	4.0–5.5	2.5–3.5	2.7–5.5	2.0	4.5
Cloud point, °C	−13 to 10	>20	−6	−5	+6
Sulphur content, mg.kg^{-1}	<0.01	<10	10	-	10
Caloric value, MJ kg^{-1}	37.5–38	44	44.7–46.7	-	-
Flash point, °C	96–188	68–120	52–136	60	170
Pour point, °C	−15 to 16	−3 to 29	−21	−13	10
Cetane number	50–65	50–105	52–136	60	170

Note: the exact properties of biodiesel and HVO depend on the type of raw material and the conditions of preparation.

The carbon balance of the products of renewable fuels is zero because carbon dioxide, released during its combustion, is removed from the atmosphere by the photosynthesis of plants and converted back into oil. However, it should be noted that the whole process, that is, seed sowing, plant growth, harvesting, extracting of oil from crops, transesterification, finishing, and final product preparation and transport of all substances, significantly influences the carbon balance (increased carbon dioxide emission). There has been extensive discussion about its environmental benefits [30–32].

The oils/fats formed by biofuels are evaluated by many properties, such as the cloud point (°C), which is the temperature when wax begins to form (the first turbidity appears); the pour point (°C), which is the minimum temperature when the sample has the ability to pour down from a beaker (high pour point is generally associated with a high paraffin content); the flashpoint (°C), which is the lowest temperature when an external source can ignite the vaporized sample; the fire point (°C), which is when the sample is combusted for at least five minutes; the cetane number, which is the indication of the combustion speed of fuel and compression needed for ignition; the acid value (mg KOH g^{-1}), which reflects the acidity of samples; oxidative stability (h), which is an important parameter that indicates the susceptibility of the fuel to its degradation; and iodine value (mg I$_2$ g^{-1}), which reflects the number of double bonds.

The HVO is chemically composed of paraffinic hydrocarbons, that is, without oxygen and double bonds in the molecules, which is more similar to fossil diesel and can be used or added to fossil diesel without significant technical limitations to engines. Biodiesel is composed of low alkyl esters of higher fatty acids, containing oxygen and double bonds between atoms of carbonates (they do not contain sulphur or aromatic hydrocarbons). The double bonds are sensitive to humidity and oxygen in the air, which can cause hydrolysis and oxidation during long-term storage (ketones and acids are formed [33]) and so decrease oxidative stability. The low oxidative stability is solved by adding of antioxidants such as sterically hindered phenols, secondary aromatic amines, or butylated hydroxytoluene (Baynox®).

The HVO has a higher cetane number (almost no content of aromatic hydrocarbons) and lower density (Table 2) than biodiesel [34]. Biodiesel density is about 2–7% higher than diesel and increases with an increasing number of carbon in the alcohols chain [35]. On the other hand, the low-temperature properties of HVO are worse than those of biodiesel because of the high content of paraffin [36]. This fact determines the limit of HVO content in diesel blending or implies the addition of additives [37]. The viscosity of biodiesel is comparable to diesel [38,39]. However, the biodiesel viscosity also depends on the profile and conformation (cis or trans) of fatty acids and increases with the increasing length of FA and decreases with the increasing number of double bonds [40].

Biodiesel usually has a lower caloric value than diesel, which causes lower performance and higher consumption [41]. Conversely, biodiesel burns better than diesel fuel, thus reducing engine smoke. It was found that biodiesel has lower emissions of carbon dioxide, sulphur, and air pollution [42–44]. On the other hand, the emissions of NO$_2$

are significantly higher, but the emissions of NO are lower compared to diesel fuel. For biodiesel, combustion of the total amount of NO_x is slightly higher than for diesel fuel combustion [45,46]. It should be mentioned that the emissions depend on the oxygen amount during combustion. Biodiesel has a higher lubricity than diesel and therefore reduces engine wear [47,48]. It is a good solvent, so it can dissolve the dirt from the engine, which can plug a fuel filter, and it can damage parts of rubber in some engines [49]. The exact chemical composition and properties also depend on biodiesel generation [8].

For biodiesel, the biodegradable in water is significantly shorter than diesel (95% of biodiesel degrades compared to 40% of diesel after 28 days). In water, it does not cause a microbiological load up to a concentration of 10 g L^{-1} [50].

The disadvantage of HVO consists in the conditions of production; the temperature is usually between 300 and 370 °C and has a pressure of 2 and 10 MPa, which requires more demanding reaction equipment for biodiesel production. Another disadvantage of HVO is the consumption of hydrogen, which is usually produced from fossil sources and has to be purified before use. On the other hand, the production is insensitive to the quality of vegetable oil (the high content of free fatty acids is not problematic). Biodiesel is most frequently produced by quite undemanding reaction conditions: a cheap, commonly available catalyst (KOH or NaOH), alcohol (methanol), 60 °C and standard pressure. However, the production is more sensitive to the quality of the vegetable oil, which strongly influences the method and conditions of transesterification (refer to Section 4.2). Biodiesel can be easily produced by small local companies without advanced technical knowledge, which is not possible for HVO. The disadvantages are the economic cost of the production process, where the most expensive input is vegetable oil (accounts for 85–90% of the biodiesel cost).

One of the main side-products of HVO is propane (C_3H_8), which can be used as a biogas component. For biodiesel, the main side-product is glycerol, which has wide usage in the chemistry, food, and pharmaceutic industries [51]. A detailed description of the production of biodiesel and HVO is in the following section.

4. The Ester Production—Transesterification

The main transesterification product is biodiesel—the methyl esters of unsaturated and saturated fatty acids of vegetable/animal origin. It is produced by transesterification: triacylglycerols (TG) (Equation (1)) react with alcohol (A), and the products are esters (E) and glycerol (G). Transesterification is usually catalysed.

$$TG + 3\,A \leftrightarrows G + 3\,E \tag{1}$$

This reaction proceeds in three consecutive steps during which undesirable compounds, such as diacylglycerols (DG) and monoacylglycerols (MG), are formed (Equation (2)). Note: The abbreviations MG, DG, TG, and E do not mean a pure chemical substance, but the mixture of various acylglycerols or esters of higher fatty acids.

$$TG + A \leftrightarrows DG + E \quad DG + A \leftrightarrows MG + E \quad MG + A \leftrightarrows G + E \tag{2}$$
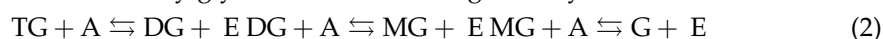
As an equilibrium reaction, the transesterification is performed with an excess of alcohol to shift the direction towards the products (the excess depends on the type of catalyst and alcohol) [52]. Two partially miscible phases, which have to be separated, are obtained after transesterification (Section 4.3).

4.1. Alcohols

Other raw materials necessary for biodiesel production are low molecular alcohols, such as methanol, ethanol, and butanol, which are mostly published (Table 3). Methanol is mainly used due to its lower cost and its appropriate physical and chemical properties. Methanol, as well as ethanol, are immiscible with oil and form a heterogeneous two-phase system. The reaction proceeds at the interface, and intense stirring is necessary [53]. The heterogeneous system can be "removed" by the addition of another liquid (co-solvent), such as tetrahydrofuran, acetone, hexane [54], which forms one phase. The second most frequently used alcohol is ethanol, especially for homogeneous catalysts. Ethanol can be

easy to produce from renewable sources, and transesterification usually processes at a lower temperature (25–30 °C) because, at a higher temperature, saponification is easily processed [55–57]. The higher number of carbons in the alcohol chain means lower reactivity but a higher boiling point—that is, under the same pressure, the transesterification could be carried out at higher temperatures. Ethanol forms azeotrope with water, and to gain pure ethanol without water is quite expensive. Simultaneously, increasing the carbon number slightly increases the caloric value of the esters [58,59].

Table 3. Properties of alcohols are the most often used for transesterification.

Alcohols	Number of Carbons	Boiling Point, °C	Miscible with Oil	Reactive	Hygroscopic	Bio-Source	Price
methanol	1	65	no	++	+	−	++
ethanol	2	78	no	+	−	++	+
butanol	4	118	yes	−	−	+	−

Note: sign + means positive for transesterification.

Butanol is hydrophobic, less corrosive, and miscible with oil, and the reaction occurs in the whole volume. Due to the higher boiling point (Table 3), a higher reaction temperature can be used, but the higher temperature supports saponification. Therefore, transesterification is carried out at lower temperatures (25–30 °C) [59,60]. Butanol is possible to use as a co-solvent [61]. On the industrial scale, only methanol is used because it is the most active. The other alcohols are used only in a laboratory scale.

4.2. The Types of Catalysis

The transesterification can be conducted without a catalyst at high temperatures and pressures (alcohol in the supercritical stage [62]). Otherwise, it is necessary to use a catalyst [63,64]. Generally, the catalysis of transesterification can be either chemical or enzymatic. The chemical catalysts are classed as homogeneous or heterogeneous, which are further classed into an alkali or acid. The disadvantage of homogeneous catalysts is the possibility of being recovered from the reaction mixture and reused. The properties of each type of catalyst are shown in Table 4.

Table 4. Overview of the catalysts used in transesterification.

| Type of Catalyst	Advantages	Disadvantages
Homogeneous alkali	- mild reaction conditions and less energy required - easy availability of catalyst - the high reaction rate (4000 times faster than acid ones) - high yields of reaction (99%)	- using only quality oils (if the FFA content in the oil is more than 2 wt%, the saponification occurs) - irreversible loss of catalyst and decreasing of ester yield - produces more wastewater from purification
Heterogeneous alkali	- environmentally friendly - reusable - easy to separate from the reaction mixture - the possibility of continuous production	- increases the energy requirements for the reaction (temperature, pressure) - challenging catalyst synthesis - catalyst instability - lower activity in comparison with homogeneous ones
Homogeneous acid	- insensitive to FFA and water content in the oil - esterification and transesterification occur simultaneously - easy availability of catalyst - saponification can be avoided	- low reaction rate - can lead to equipment corrosion - irreversible loss of catalyst

Table 4. *Cont.*

Type of Catalyst	Advantages	Disadvantages
Heterogeneous acid	- insensitive to FFA and water content in the oil - esterification and transesterification occur simultaneously - recyclable	- low reaction rate - high reaction conditions and longer reaction times - higher energy requirement - catalyst instability
Enzyme	- mild reaction conditions - environmentally friendly and non-polluting - reusable	- very slow reaction rate - high cost - sensitive to alcohol (methanol can deactivate the enzyme)

Nowadays, enzymatic catalysis is getting a lot of attention [65]. Various types of lipases are used as a catalyst. Moreover, lipases are very often immobilized on different carriers. Their main advantages are a lower reaction temperature (usually 25–40 °C), that is, lower energy consumption, and the immobilized enzyme can be reused. Enzyme catalysts are insensitive to the content of FFAs and water in the input oil, that is, there can be used oil with a high content of FFAs and water. Another great advantage is an easy recovery of glycerol from esters because the saponification reaction does not proceed. The enzymatic catalyst also has some limitations, such as the high cost of the enzyme, prolonged reaction time (up to 10 h), low yield, and the possibility of the enzyme being deactivated by alcohol, especially methanol [66,67]. The enzymatic catalysts are not further discussed because this is not the aim of this paper.

4.2.1. Homogeneous Catalysis

The homogeneous catalysts for transesterification are strong alkaline or acid matters that are well-soluble with alcohol. The alkaline homogeneous catalysts are the most common because of their low cost and high efficiency [68]. The most popular are NaOH and KOH or their alcoholates (especially $NaOCH_3$). They are the only ones used on an industrial scale [14].

In the case of alkaline catalysis, the reaction particle is the alcoholate of the corresponding metal formed by the dissolving of strong hydroxides in the alcohol (e.g., methanol and KOH (Equation (3)).

$$CH_3OH + K^+OH^- \leftrightarrows CH_3O^-K^+ + H_2O \tag{3}$$
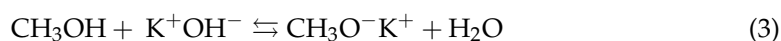
This is an equilibrium reaction, and therefore it is suitable to use the feedstock with the lowest water content since water shifts the equilibrium towards alcohol and hydroxide, which leads to saponification. A simplified reaction scheme of alkali catalyzed transesterification (Figure 1A). Since transesterification is a reversible reaction, it is mostly conducted in excess alcohol to the stoichiometric amount (methanolysis 2×, butanolysis 4×). The microemulsion (caused by formed soaps) is formed throughout transesterification [69].

The usual use of alkaline catalyst is 0.9–1.2 wt% to oil [70], which depends on the type and composition of oil and the type of the catalyst. The low-quality triacylglycerols resources with a high content of FFAs (up to 3 wt%) [71] and water [72] cannot be used for alkaline catalysts because the presence of water causes hydrolysis of oils to the FFAs [73]. The catalyst is lost (i) by neutralization of the FFAs contained in the oil (D) and (ii) by the side reaction: saponification of acylglycerols (B) or esters (C). Reactions are shown in Figure 1, where R_i is a chain of higher fatty acids.

During the removal of unreacted alcohol, a reverse reaction may occur (from the esters and glycerol, there are successively formed MG, DG, and TG), and therefore the reactions have to be finished [74] (the catalyst is not possible to reuse). The reaction can be finished by stopping the mixing and subsequent separation of the formed EP from the glycerol phase (GP), whereby the catalyst as a polar substance passes into the GP, and the

reaction does not proceed further. The obtained EP is usually known as crude biodiesel, which contains many impurities, such as remaining acylglycerols, glycerol, FFAs, methanol, vegetable dyes, soaps, and salts. The glycerol phase is usually of low quality because it also contains (besides glycerol) many organic and inorganic impurities, such as water, soaps, esters, vegetable dyes, and remaining catalysts or products of catalyst neutralization. Both phases have to be purified, that is, further technological treatment is necessary, increasing biodiesel production's energy consumption. This approach is traditionally used in the industry [52].
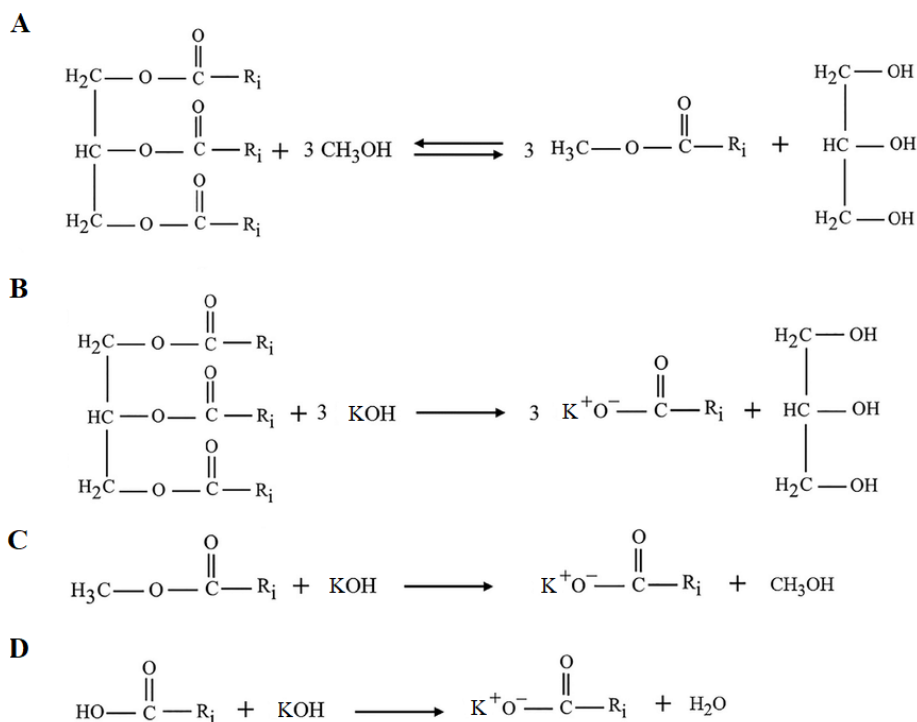
Figure 1. Simplified scheme of the chemical reaction process through alkali catalysed transesterification–transesterification (**A**), saponification of triacylglycerols (**B**), and esters (**C**), and neutralisation of FFA (**D**).

Another approach is to stop transesterification by neutralization of the catalyst because approximately 60% of the catalyst is unreacted [75]. The weak acid (e.g., gaseous CO_2) or inorganic acids (e.g., H_3PO_4 and HCl) can be used for neutralization. The carbon dioxide added into the reaction mixture has the advantage that it behaves as a weak acid and neutralizes only alkaline catalysts (KOH), and cannot convert the formed soaps into FFAs, that is, it does not increase the acid number. Conversely, the amount of potassium ions and free glycerol in the EP is mostly higher than that allowed by the European standard EN 14214. Moreover, the separation of the EP from the GP usually takes longer than 24 h. Therefore, after removing excess alcohol from the whole reaction mixture, it is possible to add a defined amount of water into the reaction mixture (determined according to the photometric titration [76]), which accelerates product separation and improves the properties of the EP. The added water as a polar substance passes into the GP and dilutes it, that is, it decreases the glycerol content in the GP [77].

The application of inorganic (strong) acids for transesterification stopping is usually for the kinetics study, that is, this procedure is not part of biodiesel production [78]. However, inorganic acids, such as HCl and H_3PO_4, are also possible to use for stopping. Two options for acid addition have been described: (i) addition into the whole reaction mixture until the pH falls to 2–3, which means that soaps are converted into FFAs (increases the acid number of the EP), and it is necessary to remove the formed FFAs from the EP [79], and

(ii) precisely, only then are the catalytically active methoxide ions neutralized, the FFAs are not formed, and the acid number remains almost zero [80].

The homogeneous acid catalysts are a suitable alternative for transesterification with raw materials with a high content of FFAs, which are usually waste cooking oils. Moreover, the waste cooking oil usually contains other impurities, such as water and solid particles [81,82] and is degraded by the thermal process, which causes lower oxidation stability and polymerization of oil. As homogenous acid catalysts are used, Brønsted acids can be sulphuric, sulfonic, hydrochloric, and so forth. [83–85].

Freedman et al. claimed that the use of acid catalysts is much more effective than the use of basic ones if the sources of triacylglycerols contain more than 1 wt% of FFAs [86]. The acid catalysts also have higher levels of resistance to other impurities in comparison with the basic ones. The mechanism of using acid catalysis in transesterification differs from the case of using an alkaline one. In the case of acid catalysis, the proton attacks the carboxylic oxygen group, and the subsequent steps are electron transfer and the release of glycerol from the ester. Therefore, acid catalysts are suitable for oils with a high content of FFAs, as they can simultaneously transesterify oils and esterify the FFAs, but their reaction rates are slow. Acid catalysts are almost 4000 times slower than alkaline catalysts. The use of acid catalysts provides a high yield of esters because the saponification reaction does not occur, but requires a high temperature (usually above 100 °C) and high molar ratio of alcohol/oil (more than 6:1 alcohol/oil) and longer reaction time (3–48 h) in comparison with the alkaline ones. [87,88]. The residues of acid catalysts are necessary to eliminate the esters because they can attack the metallic parts of the engine and cause corrosion. The molar ratio of alcohol/oil is an important factor that significantly influences the transesterification performance. An increasing excess of alcohol supports the formation of products, but conversely, the increasing excess of alcohol makes the separation of glycerol difficult. Therefore, it is necessary to establish an optimal molar ratio of alcohol/oil for each acid catalyst according to the optimization of experiments.

Due to the reaction rate limitation, a two-step reaction is used, where firstly the FFAs are esterified, and subsequently, transesterification is carried out with an alkaline catalyst. This approach could provide a high biodiesel conversion (up to 98%) [40].

4.2.2. Heterogeneous Catalysis

Heterogeneous catalysts can solve the problems with the separation of catalysts and their reuse. The heterogeneous catalysts are solid matters (dissoluble in alcohols) with alkaline [89,90] or acid properties, which can be in the form of powders, monoliths or supported on some material. It can be impregnated materials, metallic oxides (alkaline earth metals, transition metals) [91], various types of mixed oxides (Ca-Al, Mg-Al, Mg-Fe, etc.) [92–95], supported metal oxides [96], CaO from food waste [97,98], NaX zeolites, heteropolyacid, coated ZnO, a biomass-derived catalyst [99], and so forth. (Table 5).

These catalysts are considered environmentally friendly due to decreasing water usage during the separation of esters from glycerol and especially ester purification, because they are easy to recover from the reaction mixture. Another indisputable advantage is their reusability, which could make biodiesel production a continuous process [100]. The main disadvantage of the heterogeneous catalyst is lower activity than the homogeneous one because the reaction proceeds only on the active centres. This is the reason that the transesterification usually proceeds at (i) a higher molar ratio of alcohol to oil, (ii) a higher catalyst amount, and (iii) a higher temperature than the boiling temperature of alcohol at atmospheric pressure (the pressure reactor is necessary). These are the main reasons for not using a heterogeneous catalyst on an industrial scale. Moreover, the synthesis of the catalyst can be quite difficult and time-consuming. An important parameter is also the high stability of the catalyst, that is, almost no leaching of metals into the reaction products is necessary [101,102].

Table 5. The list of heterogeneous catalysts used in transesterification.

Type of Catalyst	Feedstock (Oil/Alcohol)	Operating Conditions (Temp./Amount of Catalyst/Molar Ratio Alcohol to Oil)	Yield, %	Ref.
La-Ca/halloysite	palm oil/MeOH	150 °C/7 wt%/18:1	97.5	[103]
quicklime	mustard seed oil/MeOH	60 °C/9.8 wt%/6.1:1	96.5	[104]
kettle limescale	UCO/MeOH	60 °C/14 wt%/2.15:5 (*v/v*)	97.2	[105]
GO5.0Al(HSP)	sunflower oil/MeOH	120 °C/1 wt%/30:1	97	[106]
Fe/Ba/Al_2O_3	UCO/MeOH	65 °C/6 wt%/18:1 (wt/wt)	84.2	[107]
Ce/dolomite	palm oil/MeOH	65 °C/0.05 wt%/15	97.2	[108]
CaO/wollastonite	palm oil/MeOH	65 °C/8 wt%/15:1	97.6	[109]
Mg/clinoptilolite	UCO/MeOH	70 °C/4 wt%/16:1	98.7	[110]
K/kaolinite	UCO/MeOH	70 °C/15 wt%/14:1	94.8	[111]
Zn/CaO	UCO/MeOH	65 °C/5 wt%/20:1	96.7	[112]
Al_2O_3/Fe_3O_4	UCO/MeOH	100 °C/5 wt%/30:1	77	[113]
S-La_2O_3/NaY	castor oil/EtOH	70 °C/10 wt%/15.1:1	84.6	[114]
TiO_2-CaO	palm oil/MeOH	65 °C/0.5 wt%/5:3	95	[115]
MgO-Al_2O_3	castor oil/BuOH	80 °C/5 wt%/6:1	97	[116]
Cu/Zn/Al_2O_3	UCO/MeOH	65 °C/10 wt%/20:1	89.5	[117]
sulfonated active carbon	soybean oil/EtOH	75 °C/20 wt%/6:1	88.7	[118]
modified graphene	RSO/MeOH	130 °C/1 wt%/12:1	80	[119]
Ca-Al mixed oxide	RSO/MeOH	65 °C/4 wt%/24:1	90	[92]
Mg-Fe mixed oxide	RSO/MeOH	117 °C/4 wt%/24:1	70	[120]
Mg-Al mixed oxide	RSO/MeOH	117 °C/4 wt%/24:1	75	[121]

One of the possible methods of catalyst synthesis is the impregnation of various alkali materials to the convenient support, such as Al_2O_3, TiO_2, MgO, and so forth, with the aim of increasing the number of basic sites. Sulaiman et al. studied the influence of various concentrations of Ba, Ca, Mg, Sr, and Fe oxides impregnated on Al_2O_3 on the activity of catalysts in the transesterification of refined UCO (used cooking oil) with methanol. The type of active species affected the specific surface area and basicity of the catalyst. The activity positively correlated with the basicity; the highest level of activity was achieved for BaFe/Al_2O_3 (0.4 wt% of Fe and 1.4 wt% of Ba) calcined at 800 °C [107]. Abukhadra et al. used the zeolite (clinoptilolite) as the support, which is characterized by the high specific surface area. The impregnated alkali metals, such as Na, K, Mg, and Ca increased the basic properties. The significant differences in the ester yield (UCO with methanol was used) for different metals were not observed. The reusability was tested for Mg/clinoptilolite for five cycles: the ester yield only insignificantly decreased from 98.4 to 94.5% [110]. The potassium impregnated on kaolinite was studied: the presence of potassium positively affected the yield of the ester until 30 wt% (potassium in kaolinite), where 94.8% of the ester yield after 3 h was achieved. A higher amount did not significantly affect the transesterification. If the concentration of potassium was 40 wt%, a slight drop of ester yield was observed, which was explained by the decreasing of basicity (the partial exchange of Al–O–H group for Al–O–K groups). The reusability was tested; the decreasing of ester yield was from 94.8% in the first cycle to 83.3% in the fifth cycle due to potassium leaching [111].

The impregnation of Al_2O_3 by MgO increased the basicity and surface area of the catalyst. The transesterification of castor oil with butanol was carried out at 80 °C with a 6:1 butanol-to-oil molar ratio and 5 wt% of the catalyst with a yield 97% after 6 h [116]. The Al_2O_3 as the support of $CuNO_3$ and $ZnNO_3$ was used for the preparation of the catalyst for transesterification of UCO with methanol. The highest basicity was observed for Cu/Zn/Al_2O_3 catalysts with 2.8 wt% of Cu and 7.1 wt% of Zn calcined at 800 °C. The transesterification was carried out at 65 °C, a 20:1 molar ratio of methanol to oil, and 10 wt% of a catalyst with the highest ester yield of 89.5% after 2 h. The yield slightly reduced to 83.3% after five cycles [117]. As the support, the hierarchical microspheres γ-Al_2O_3 were prepared. The reason was to increase the pore size because the triacylglycerides

comprise quite large molecules (which reduces the inter-diffusion). The support was impregnated by graphene oxide for increasing the acid-based properties. The impregnation of 5 wt% of graphene oxide significantly increased the basicity to 12.3 mmol g^{-1} (without 0.4 mmol g^{-1}). On the other hand, the acidity decreased from 5.6 to 1.7 mmol g^{-1}. The catalyst was tested in transesterification of fresh and used sunflower oil with methanol. The stability was influenced by the larger amount of free fatty acids in the oil. After six cycles, the conversion decreased from 97 to 95% for fresh, and from 93 to 81% for used oil [106].

Calcium oxide, which is a widely studied metal as the basic catalyst, can be (i) impregnated on some support or (ii) used as bulk. The CaO impregnated on wollastonite (calcium inosilicate) and calcined at 750 °C was studied in transesterification of palm oil with methanol. The stability was studied by catalyst reusing: the ester yield decreased from 97.6 to 87.3% (after 3 h) observed for one and five cycles [109]. Borah et al. studied the CaO impregnated with Zn (1 wt%) in the transesterification of UCO with methanol. The transesterification with 1 wt% of Zn on CaO catalyst was carried out at 65 °C, 5 wt% of the catalyst, and 20:1 molar ratio of methanol/oil, and we observed a 96.7% ester yield after 4 h. The ester yield significantly decreased to 64.4% after five cycles, which was caused by zinc leaching. Unfortunately, the authors did not analyze the content of Ca and Zn in the reaction mixture [112]. The TiO_2-CaO catalyst prepared by the impregnation method showed good catalytic performance in the transesterification of palm oil with methanol under UV radiation. The TiO_2 promoted the catalytic activity due to eased cation generation from CaO, which were easily inserted into vacant sites on the surface of TiO_2. The highest ester yield (95%) was observed at 65 °C with only 0.5 wt% of the catalyst and 5:3 methanol-to-oil molar ratio after 150 min. However, the ester yield was decreased for five cycles, where the ester yield was only 60% [115]. The halloysite nanotube functionalized by La-Ca bimetallic oxide with a 1.5 molar ratio of La_2O_3/CaO showed good catalytic properties in the transesterification of palm oil with methanol because the lanthanum promoted the methanol adsorption, which increased activity. The yield of ME was 97% after two hours at 150 °C with 7 wt% of catalyst. [103]. The bulk CaO calcined at 500 °C was used as the catalyst in the transesterification of white mustard seed oil with methanol. The ester yield of 96.5% was reached for 9.8 wt% of catalyst and molar ratio of methanol to oil between 6.1 to 11.6:1 after 50 min [104]. The kettle limescale ($CaCO_3$) calcined at 900 °C was used as a source of CaO. The reaction was carried out with co-solvent (acetone) and various reaction conditions. The highest yield (97.2%) was observed at 60 °C, 14.0 wt% of catalyst, and 2:15:5 volume ratio methanol to oil. The calcium was leached during the transesterification, which caused catalyst deactivation and the formation of calcium soaps [105].

Niu et al. studied the effect of cerium on the activity and stability of the catalysts prepared from dolomite calcined at 800 °C. The CaO and MgO were formed after calcination, and cerium (0.6 wt%) was wet-impregnated. Good stability was observed in the transesterification of palm oil with methanol during five cycles, where the ester yield decreased from 97.2 to 88.6% (2 h transesterification). The reusability was compared with oxides without cerium, where the ester yield decreased from 95.1 to 83.5%. The increase of the catalyst stability was explained by the synergistic effect between CaO and formed CeO_2 [108].

The mixed oxides (most often synthesized by calcination from hydrotalcites of various metals, such as Ca, Mg, Al, Fe, and Zn usually synthesized by co-precipitation) are other possible catalysts. The Ca-Al mixed oxides showed good catalytic activity in the transesterification of RSO oil with methanol (at 65 °C, 24:1 molar ratio of methanol to oil and 4 wt% of catalyst). It was found that the Ca-Al mixed oxides are stable in ester, oil, and methanol. However, the additional phase CaO, founded in Ca-Al mixed oxides, was soluble in the water present in the feedstock. Therefore, the CaO caused the instability of the catalyst [121]. Other types of mixed oxides are Mg-Al/Fe, which were also tested in the transesterification of RSO oil with methanol. The molar ratio Mg to Al influenced the

catalyst properties: the basicity was decreasing, but the specific surface area, as well as ester yield, were increasing with Mg/Al molar ratio. The highest ester yield (75%) was observed for Mg/Al molar ratio 7.2 (at 117 °C, 24:1 molar ratio of methanol/oil, 4 wt% of the catalyst after 8 h) [121]. On the other hand, the highest ester yield (70%) was observed for Mg-Fe mixed oxides with a Mg/Fe molar ratio of 6:1 under the same reaction conditions [120]. The Mg-Al and Mg-Fe mixed oxides were stable because the concentration of Mg, Al, and Fe in the products was negligible.

The basic catalyst, zeolites and mixed with surfactants and kaolin were studied in the transesterification of castor oil with ethanol. The specific surface area decreased with the increase of the calcination temperature (600–1000 °C) from 369 to 2 m^2 g^{-1}. The addition of surfactant slightly increased the specific surface area and basicity. The basicity decreased with the increase of the calcination temperature from 12.7 to 7.5 mmol g^{-1}. The optimized reaction conditions were determined: 70 °C, 15:1 molar ratio ethanol/oil and 10 wt% of catalyst to oil, where the ester yield was 84.6% after 50 min. Moreover, the decrease to 75% of the ester yield was presented after five cycles [114].

The heterogeneous acid catalysts were developed for (trans)esterification of oil with a high content of FFA (usually contained in the used UCO). The magnetic catalysts Al$_2$O$_3$/Fe$_3$O$_4$ with a mass ratio of oxides 0.5 were prepared by incorporation of Al$_2$O$_3$ on the Fe$_3$O$_4$ nanoparticles. A strong acid was mainly present in the catalysts. The catalysts were tested in the transesterification of UCO with methanol, and the 77% ester yield after 2 h was observed [113]. Another type of catalyst is the sulfonated active carbon prepared by impregnation of active carbon by 4-benzenediazoniumsulfonate. The catalyst was used in the transesterification of soybean oil with ethanol (75 °C, 6:1 molar ratio ethanol to oil and 20 wt% to catalyst). The reaction mixture was stirred by a microwave for better mass transfer. The highest ester yield (88.7%) was observed after 20 min [118]. The modified graphene by diazonium cation showed suitable catalytic activity in the transesterification of rapeseed oil with methanol. Although the catalyst had a lower concentration of acid sites (1.46 mmol g^{-1}), it showed the best catalytic activity, which was explained by the formation of a unique two-dimensional sheet structure with good dispersion of -SO$_3$H groups. The 80% ester yield (130 °C, 12:1 molar ratio methanol/oil, and 1 wt% of catalyst to oil after 24 h) was determined. However, the ester yield was only 60% after four cycles [119].

4.3. The Separation and Purification

The separation of the final product from other matter and its purification is an essential part of biodiesel production. After transesterification, the first step is separating the ester phase from the glycerol phase by gravity field or using centrifugation, which is the most popular method in the industry [3]. These phases have different polarity and density—the EP (containing nonpolar ester) has a lower density than GP, which contains especially polar matters. However, the separation is not completed, and some glycerol remains in the EP (known as free glycerol), and some esters remain in the GP (ester losses). Moreover, the ester content in the GP depends on the type of oil [122] and alcohol used: in the range 6–15 wt% for methanol [123] and in the range 13–29 wt% for ethanol [124]. The ester content in the GP corresponds to ester loss during transesterification and decreases the methyl esters yield [125].

The glycerol phase is an integral part of biodiesel production and is mainly neglected and not further analysed because it is considered a waste product of transesterification. The exact composition of the GP generally depends on the transesterification process and on the method of separation and purification of the obtained esters. The GP usually contains 30–60 wt% of glycerol and other kinds of matter: soaps, water, salts, alcohol, glycerides, remaining catalyst, and esters [126]. The GP can be treated by the addition of acids, which neutralise the alkali matter [127]. The formed glycerol is used in many areas of the industry [128,129].

The quality of fatty acid methyl esters has to conform to the values given by the European standard EN 14214. The standard specifies a total of 23 different parameters,

for example, density, viscosity, flash point, acid number (free fatty acids content–FFAs), methanol content, water content, the content of reaction components: free glycerol (the content of pure glycerol in the ester phase–EP), MG, DG, TG, the content of group I metals (Na, K), group II metals (Ca, Mg), phosphorus content, and so forth, which as the final product have to conform and are necessary to determine. The standard methods for analysing parameters are recommended [130].

## 5. The Green Diesel Production–Co-Processing

Another process for the transformation of oils/fats to biofuels is the catalytic hydrotreating of triacylglycerols at high temperatures (300–400 °C) and pressure (5.0–7.0 MPa). The formed biofuel, known as Green diesel or hydrotreated vegetable oil (HVO), is composed mainly of paraffins (n- and iso-paraffins) in the range of 15–18 carbon atoms and is free of aromatics, oxygen, sulphur, nitrogen, or metals [34]. In terms of volume production processes, the hydrotreatment of vegetable and animal oils to paraffins (in diesel or jet fuel range) is considered as one of those with higher current commercial capacity, behind the biorefineries focused on the fermentation of sugars and starches to ethanol and the transesterification of vegetable and animal fats to FAME. In this way, some of the most representative companies of the sector have developed commercial triglycerides, FFA and tall oil hydroprocessing installations with a capacity value higher than 70,000 BPD during recent years (Figure 2). This fact is especially noticeable in the case of the Neste company with NExBTL technology for green diesel as the main product [131].
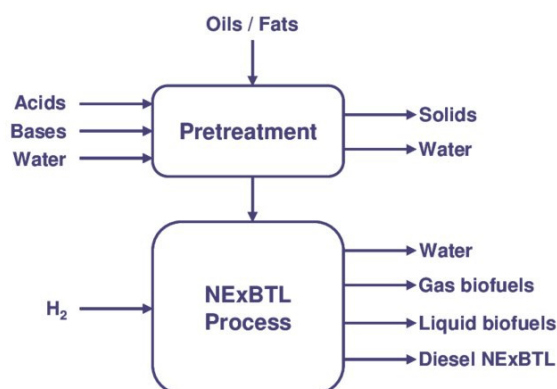
Figure 2. NExBTL catalytic hydrotreating of oils/fats technology for biodiesel production (Neste® 2021) [132].

The co-processing of middle distillates (e.g., straight-run gas oil) with vegetable oils (rapeseed oil, sunflower oil or even waste cooking oils) seems to be the most promising way to produce HVO on an industrial scale. In this way, the co-processing approach allows using the infrastructure already available in the existing refineries [133], that is, hydrotreating units, commonly used for sulphur compound elimination (among others) from diesel fractions. Moreover, using waste oils (using cooking oils or animal fats) also offers an efficient way of managing residues [134], obtaining a valuable biofuel integrated with the petroleum fraction [135].

Several studies have already been published relating to the co-processing of different crude oil feedstocks (heavy gas oil, vacuum gas oil, and atmospheric gas oil) with vegetable oils (including using cooking oil and animal fats) [136–138]. These works have shown the viability of the co-processing approach. A percentage of 5–10 wt% looked to be optimal to not affect the regular activity of the hydrotreating units in terms of hydrogen consumption and catalyst deactivation. Figure 3 shows a schematic representation of the co-processing of triacylglycerols at current refinery hydrotreating units, taking into account the main products obtained during the process.
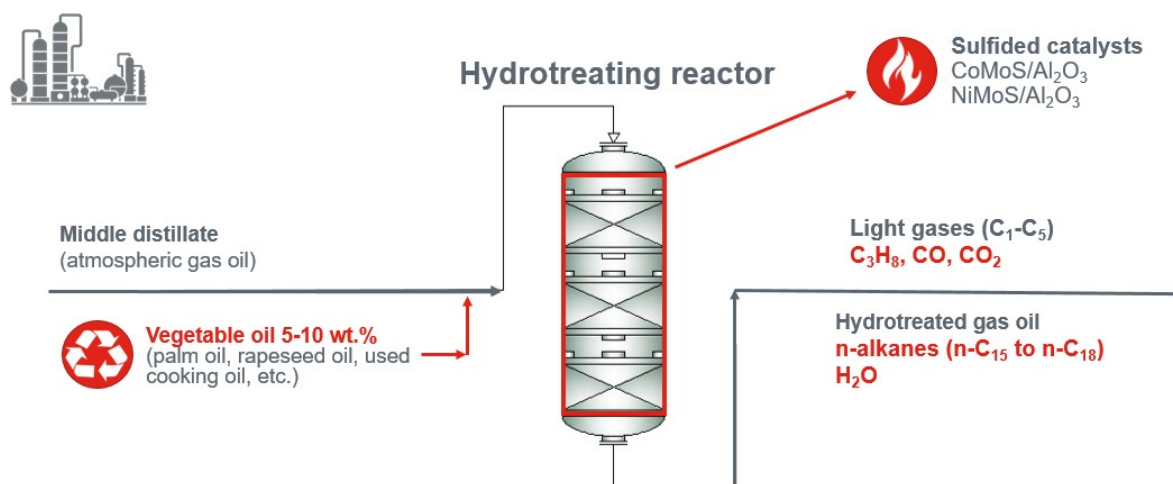
Figure 3. Co-processing of vegetable oils in hydrotreating units of current refineries.

5.1. Reaction Pathways of Triacylglycerols Hydrotreating

During co-processing, hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) of the middle distillate occurs, as well as catalytic deoxygenation of the triacylglycerols of the vegetable oil. Figure 4 shows a scheme of the chemical reactions that occurred during triacylglycerol deoxygenation. In this way, the hydrogenation of double bonds of the alkyl chains is the first step. After this step, the hydrogenated molecule is broken, producing three free carboxylic acids and one C_3H_8 molecule. Then, the reaction continues via three possible pathways [139,140]: hydrodeoxygenation (HDO), producing paraffins with an even number of carbon atoms (usually nC_{16} or nC_{18}) and two molecules of water; and (hydro)decarboxylation (HDC), producing paraffins with an odd number of carbons (nC_{15} and nC_{17}) and one molecule of CO_2 and (hydro)decarbonylation, leading paraffins with an odd number of carbons as well, but with one molecule of H_2O and CO as side products. In the presence of H_2, the gaseous side products (CO/CO_2) could react to CH_4 by methanation.
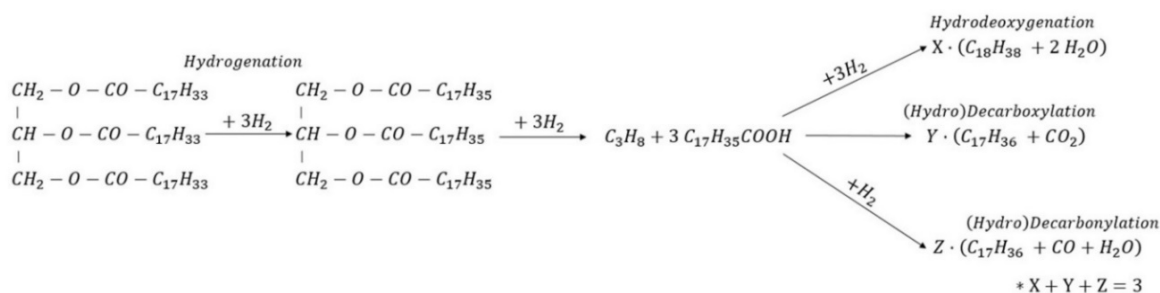
Figure 4. Reaction pathways in the hydrotreatment of triacylglycerol (triolein).

It is possible to estimate the catalyst selectivity between these deoxygenation pathways, using Equations (4) and (5) [141]:

$$\text{HDO } [\%] = \frac{\Delta(\text{even paraffins})}{\Delta(\text{total paraffins [even + odd]})} \cdot 100 \tag{4}$$

$$\text{HDC/HDCn } [\%] = \frac{\Delta(\text{odd paraffins})}{\Delta(\text{total paraffins [even + odd]})} \cdot 100 \tag{5}$$

where 'Δ(even paraffins)' and 'Δ(odd paraffins)' represent the paraffins produced from triacylglycerol hydrotreatment that formed according to HDO and HDC/HDCn pathways (wt%), respectively, and 'Δ(total paraffins [even + odd])' represents the total paraffins formed only by the hydrotreatment of triglycerides (wt%) (usually in the nC_{15} to nC_{20} range).

As a result of co-processing, the hydrotreated gas oil increases its paraffin content, which means a higher content of diesel compounds in the product. This co-processing affects some hydrotreated gas oil parameters, such as density, flammability, cetane index, or cold flow properties [142]. The observed effect is significantly positive in density, cetane index, and flammability, obtaining a hydrotreated gasoil with lower density and better ignition quality. On the other hand, increasing the paraffin content could negatively affect the cold flow properties, such as pour point, cold filter plugging point, or cloud point. This effect has been already described in the literature [143]. It is significant in the case of co-processing that more than 10 wt% of triglycerides are in the feedstock. At this point, it would be necessary to add additives to control those parameters in the final product or blend with other desulfurized gasoil to attenuate the paraffin increase. There are not many significant studies studying this fact in detail.

5.2. Hydrogen Consumption Due to Triacylglycerols Co-Processing

As long as vegetable oil hydroprocessing or co-processing have been conceived to perform at similar conditions as middle distillate hydrotreating, an excess of hydrogen is required for the reaction. In this sense, a laboratory or pilot plant scale is commonly used with H_2 with 99.99 vol.% purity from commercial cylinders. However, it is common to use rich hydrogen flows produced in other units, such as platforming or naphtha refining at an industrial scale. These flows are composed of a high amount of H_2 (around 80–90 wt%), followed by other light gases, such as CH_4 and C_3H_8.

In terms of H_2 consumption, the HDC/HDCn reactions are more efficient, with 6–9 molecules of H_2 instead of 12 per triacylglyceride molecule being deoxygenated. However, as a reaction intermediate, the CO_x derived from these reactions continues reacting in the presence of H_2, affecting the catalytic activity. This by-product might increase the H_2 consumed by side-reactions, such as methanation or reverse water gas shift reaction.

In general, the presence of other gases does not represent a significant problem during HVO production. Nevertheless, there is an exception with CO/CO_2 gases produced during the triacylglycerols deoxygenation reactions, in which those are the main products from the HDC/HDCn reactions. In this case, depending on the used catalysts, an inhibition effect of CO/CO_2 has been reported [144,145] due to a decrease of H_2 partial pressure and absorption phenomena of CO on active sites on CoMo catalysts, affecting the hydrotreating activity. Conventional NiMo hydrotreating catalysts look to be more efficient in the top layers of the industrial catalyst bed of industrial hydrotreating units [146].

Except in cases where the gas used for hydrotreating is recirculated, these named effects of CO/CO_2 absorption are not so significant. Hydrogen consumption due to triacylglycerols co-processing is a parameter to consider. It works as a limit to determine the maximum amount of vegetable oil/animal fat possible to proceed, or the proper operating conditions to carry out.

In terms of H_2 consumption, recent works study the hydrotreating of triacylglycerols into n-alkanes using alternative H_2 sources, such as oxalic acid, or under low hydrogen pressure [147]. These studies point to the significant hydrotreating activity of vegetable oils by commercial NiW and NiMo catalysts.

5.3. Suitable Catalysts for Triacylglycerols Co-Processing

Commercial sulfide transition metal-based catalysts, commonly used for hydrotreating, can also be used for co-processing [139]. These catalysts use molybdenum or wolfram as an active phase, promoted by nickel or cobalt in an Al_2O_3/SiO_2 support. The metal composition of the catalysts depends on the reactions which we are interested to promote. In this way, Co-Mo catalysts were mainly used when a high HDS efficiency is required and Ni-Mo ones when HDN efficiency is needed. On the other hand, W-based catalysts were chosen to promote hydrocracking reactions. The list of catalysts is in Table 6.

One of the most important parameters affected during co-processing was the hydrotreating effectiveness (i.e., HDS and HDN efficiencies Equations (6) and (7))

$$\text{HDS (\%)} = \frac{(S_0 - (S_\text{P} \cdot \text{η}))}{S_0} \cdot 100 \tag{6}$$

$$\text{HDN (\%)} = \frac{(N_0 - (N_\text{P} \cdot \text{η}))}{N_0} \cdot 100 \tag{7}$$

where S/N_0 and S/N_P represent the sulphur or nitrogen content of the feedstock and the liquid product, respectively (wt, ppm), and 'η' represents the process yield: the mass ratio between the desulfurized gasoil obtained and the liquid feedstock.

The addition of triacylglycerols to the feedstock during co-processing affects the catalyst activity, that is, hydrotreating efficiency, either to increase heteroatoms to remove from the feed [148] or for the effect of side products [144]. In this way, NiMo/Al_2O_3 [136] looks to be the best option, promoting the HDO pathway instead of the HDC/HDCn reactions and showing more resistance against the CO/CO_2 inhibition effect.

The catalyst selectivity strongly depends on the operating conditions (mainly reactor temperature) and catalyst metal composition during deoxygenation. In this sense, a high operating temperature (more than 350 °C) or high amount of biomass in the feedstock (more than 10 wt%) promote the HDC/HDCn reactions, to the detriment of the HDO pathway. On the other hand, Ni- or Pd-based catalysts promote the HDC/HDCn reactions, while NiMo/Al_2O_3 and CoMo/Al_2O_3 catalysts promote the HDO pathway [149].

Table 6. The list of heterogeneous catalysts used for green diesel.

Catalysts	Feedstock	Operating Conditions (Temperature, °C/Pressure, MPa/L/W-HSV, h^{-1})	Reference
NiMo/Al_2O_3 (commercial)	Heavy gas oil/UCO: 90/10, 70/30	310, 330, 350/8.4/LHSV = 1.0	[150]
NiMo/Al_2O_3 CoMo/Al_2O_3 (both commercial)	Heavy atmospheric gas oil/UCO: 90/10, 70/30	330, 350, 370/5.6/LHSV = 1.0	[136]
NiMo/Al_2O_3 (commercial)	AGO/Used frying oil: 80/20, 50/50	320, 350/5.5/WHSV = 2.0	[141]
NiMo/Al_2O_3 (commercial)	SRGO/UCO: 80/20 SRGO/Animal fat: 80/20 SRGO/Palm oil: 80/20	350/5.5/LHSV = 2.0	[151]
NiMo/Al_2O_3 (commercial)	Light gas oil/RSO: 90/10, 80/20	320, 350, 380/3.0, 5.0/LHSV = 2.0	[36]
CoMo/Al_2O_3 (commercial) NiMo/Al_2O_3 (synthesized)	SRGO/Jatropha oil: 90/10, 80/20, 70/30, 60/40, 50/50	300/5.0	[152]
NiW/SiO_2-Al_2O_3 NiMo/Al_2O_3	Gas oil/UCO: 75/25	340–380/5.0/LHSV = 2.0, 4.0	[153]
NiMo/Al_2O_3 (commercial)	Heavy vacuum gas oil/canola oil: 95/5, 90/10, 80/20	360–395/8.0–10.0/LHSV = 1.0–2.5	[154]
CoMo/γ-Al_2O_3 (commercial)	Gas oil/Palm oil: 95/5, 90/10	330, 350, 365/3.3/WHSV = 0.85, 1.0, 1.4	[155]
NiW/(Pseudoboehmite + SBA-15	LCO/WCO 50/50	365/9.5/75 min	[156]
Mo/Al_2O_3 + NiMo/Al_2O_3-SAPO-11)	SRGO/RSO 70/30	350, 380/4.0–7.0/LHSV = 1.0–1.5	[157]
CoMo/Al_2O_3 (commercial)	Gas oil/cottonseed oil: 90/10	305–345/3.0/WHSV = 5–25	[158]

5.4. Sulphur-Free Catalysts

The increase of oxygen content compounds in the feedstock (more than 20 wt%) significantly promotes sulfur leaching of sulfur from the catalyst surface during hydrotreating [148], which decreases the HDS efficiency during triacylglycerols co-processing. In this way, it is mandatory to find and study new materials that used hydrotreating catalysts and overcome this problem.

The sulphur-free catalysts, such as molybdenum carbide, nitride, and phosphide catalysts, present a promising method of resolving problematic sulphur-leaching due to sulphur not being needed to maintain its activity. Previous studies have shown their suitability for the hydrogenation of middle distillates or vegetable oils [159,160], based on their capacity of adsorbing H_2, and transferring them to the reactant molecules. According to these studies, the MoCx and MoNx looked to be the most active. For the MoCx catalysts, an increase in reaction temperature resulted in decreased deoxygenation activity, favouring hydrocracking behaviour. In the case of MoNx catalysts, they showed a higher tendency for hydrocracking and a higher feed rate effect than reaction temperature.

In the middle distillates hydrotreating, those MoCx and MoNx catalysts showed the significant activity of HDS and HDN, observing values of 75% for HDS and 35–40% for HDN rates with MoCx and MoNx supported on Al_2O_3 and TiO_2. In the case of co-processing, these catalysts also showed significant activity, converting all the triglycerides into paraffin [161]. Table 7 shows a list of sulphur-free carbide/nitride heterogeneous catalysts used for green diesel production.

Table 7. List of Sulphur free carbide/nitride heterogeneous catalysts using for green diesel by vegetable oil hydrotreating or co-processing with petroleum feedstocks.

Catalysts	Feedstock	Operating Conditions (Temperature, °C/Pressure, MPa/L/W-HSV, h^{-1})	Reference
NiMoCx/Al$_2$O$_3$ CoMoCx/Al$_2$O$_3$ NiMoCx/TiO$_2$ CoMoCx/TiO$_2$	AGO/RSO: 95/5, 90/10, 75/25	330, 340, 350/5.5/WHSV = 1.0, 2.0	[162]
Mo$_2$C/Activated carbon	Rapeseed oil and Soya oil	360, 380/2.0–3.0/2 h (batch reactor)	[163]
NiS, NiPx, NiCx	Spent coffee oil	375, 425/2.0–4.0/3 h (batch reactor)	[164]
MoNx, MoCx, MoPx	Rapeseed oil	350, 370, 390/5.5/WHSV = 1.0, 2.0, 4.0	[165]
Mo$_2$C/C and Ru/Al$_2$O$_3$	Canola oil	300/WHSV = 5–25 h^{-1}	[166]
NiMoCx	Soybean oil	400/4.5/LHSV = 1.0	[167]
MoCx/Al$_2$O$_3$ MoCx/TiO$_2$ MoCx/ZrO$_2$ MoNx/Al$_2$O$_3$ MoNx/TiO$_2$ MoNx/ZrO$_2$	AGO/RSO: 95/5, 90/10, 75/25	330, 340, 350/5.5/WHSV = 1.0, 2.0	[161]
PMoCx/Al$_2$O$_3$ (P content 0.0–4.5)	AGO/RSO: 95/5, 90/10, 75/25	330, 340, 350/5.5/WHSV = 1.0, 2.0	[168]

However, in cases where deep desulfurization of middle distillates is needed, the conventional hydrotreating catalysts (NiMoSx/Al$_2$O$_3$ and CoMoSx/Al$_2$O$_3$) seem to be more efficient. A simple means of increasing the activity of sulphur-free catalysts is to add Co or Ni as promotors to the structure of the catalysts. This addition increases the catalyst activity significantly due to the ensemble and ligand effects. The effect of promotor addition has already been described for hydrotreating model molecules [169,170] and industrial feedstocks [162], resulting in a significant increase in HDS activity of the MoCx of up to 80%. This activity is comparable with conventional hydrotreating catalysts, but

the HDN is still low. In this way, other metals, such as phosphorus, promote the HDN efficiency of MoCx catalysts by having a synergistic effect on the catalyst's active sites.

According to current research, the phosphorus addition on MoCx catalysts affects catalyst properties and hydrotreating effectiveness. Figure 5 shows the effect of phosphorus on catalyst activity.
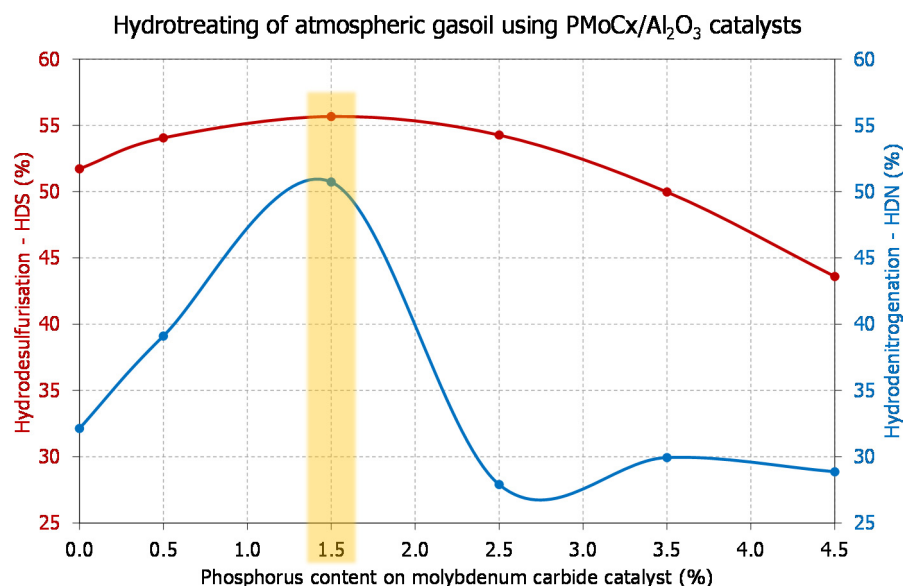
Figure 5. Effect of phosphorus addition on hydrotreating activity of MoCx/Al$_2$O$_3$ catalyst. Red line represents HDS efficiency and it is read at left axis. Blue line represents HDN efficiency and it is read at right axis.

Thus, it was possible to claim that adding up to 1.5% of phosphorus on MoCx catalysts resulted in a moderate increase of catalyst acidity, the formation of strong acid sites, and higher reducibility of catalysts. This fact significantly improves hydrogenation activity, HDS (5–10%), and HDN (10–25%) efficiencies during the middle distillates hydrotreating.

The following research is expected to focus on phosphorus development promoting Co/Ni-Mo carbide and nitride catalysts for co-processing to obtain similar activity as conventional hydrotreating catalysts. In this sense, using these kinds of catalysts represents a suitable alternative for current refineries interested in using their hydrotreating units without significant changes in their schema and a flexible process that allows high-quality biofuel production.

6. The Used Oil as Bio-Lubricants

An attractive way to utilise vegetable oils is their use as bio-lubricants that reduce the wear of machines and decrease friction between two surfaces [171]. The vegetable oils have great potential to replace lubricants produced from petroleum oil, known as mineral-based oils, which are obtained when refining crude oil (distillate fraction from the vacuum distillation). Crude oil reserves are relatively depleting and increasing environmental pollution because they introduce harmful materials (heavy metals, sulphur compounds) into the environment and air by their volatility.

The main advantages of using bio-lubricants are: (i) Less emission due to the high boiling point of esters; (ii) not containing aromatic carbohydrates, meaning over 90% is degradable; (iii) not being harmful to living organisms; (iv) equal or longer tool life due to a higher wetting tendency caused by polar groups of esters reducing friction; (v) the viscosity index not varying much over a wide temperature range; and (vi) being cheaper on account of less maintenance, as well as storage and disposal costs. On the other hand, the disadvantages are (compared to bio-lubricants from crude oils): (i) Less chemical stability,

(ii) being more expensive, (iii) being offered in a smaller range of viscosities than mineral oils; and (iv) being poorly compatible with paints and sealants [172,173].

Generally, lubricants are used in many industries, such as automobile, agriculture, transmission, and others. Mineral-based lubricants are being replaced by bio-lubricants, especially in agriculture, forestry (chainsaw oil), hydroelectric power plants, and so forth, where high biodegradability is the main advantage in the case of release into the environment. The different properties, such as chemical stability, fluidity, chemical stability, flash point, the temperature stability of viscosity, and solubility in water are required for each application. In producing bio-lubricants, we tried to achieve the approximation of the properties of mineral-based oils that are regulated by European and USA standards [174].

The vegetable oils can be used without modification because they have excellent lubricity and a high viscosity index (it gives information about the temperature viscosity behaviour of lubricating oils—a higher viscosity index means higher lubricity at a higher temperature) [175]. Other properties, determined for bio-lubricants, are very similar to those determined for oils/methyl esters, such as cloud point, pour point, flash point, fire point, acid value, oxidative stability, and iodine value (the explanation is in Section 3) [173]. The main limitations of using non-modified oils are (i) the poor properties at low temperature (formation of macro-crystals) and (ii) low oxidative and thermal stability, which are caused by the presence of an acyl group in the molecule of triacylglycerol (contains β-hydrogen that is the cause of instability). Moreover, the presence of unsaturated fatty acids also supports the instability of oils. These limitations can be suppressed by various methods, such as (i) the direct addition of antioxidants into the formed bio-lubricants, such as vitamin E, vitamin C, or citric acid derivates; (ii) the genetic modification of the fatty acid profile (i.e., decreasing of the content of unsaturated fatty acids); (iii) the catalytic transformation of functional groups present in oils, such as acyl (C=O), alkoxy (O–R), and double bonds by different methods, such as epoxidation and esterification/transesterification of vegetable oils (Figure 6) [176]. This method improves stability and low-temperature properties (viscosity and pour point).
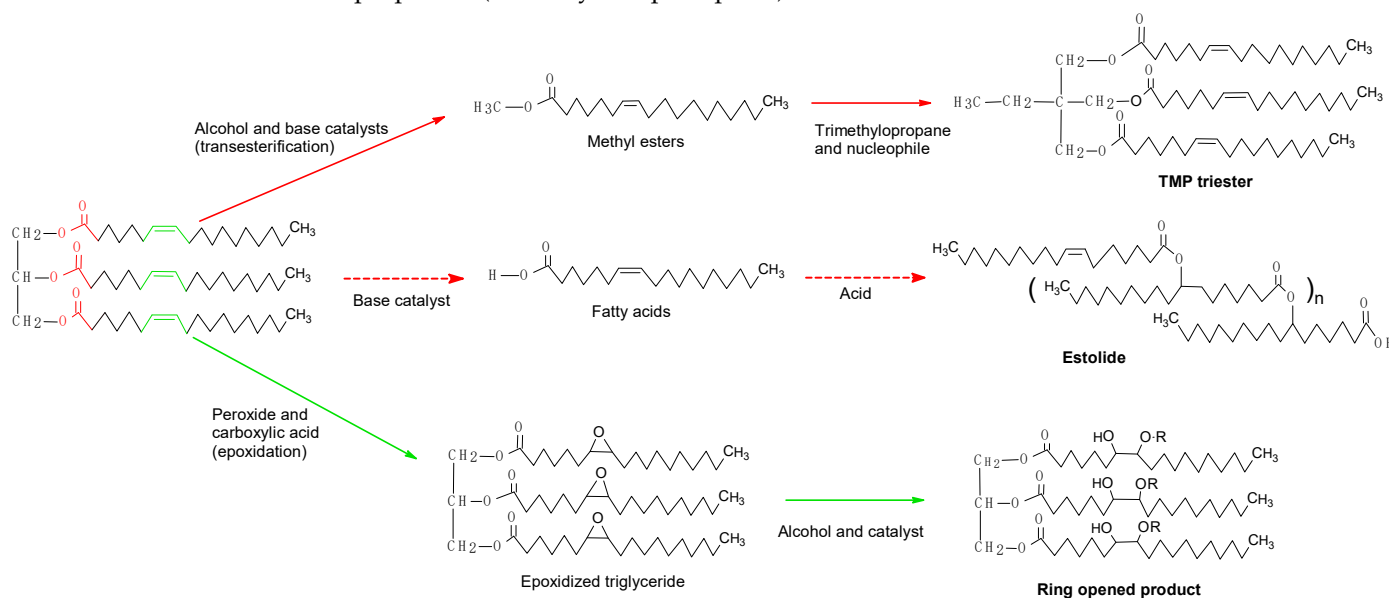
Figure 6. Reaction pathways for preparation of bio-lubricants.

The first modification is the esterification/transesterification of triacylglycerols to form new triesters [177]. This method is similar to the preparation of methyl esters by transesterification reaction (Section 4) because the first step is the preparation of methyl esters by common base-catalysed transesterification. The next step is the reaction of methyl esters with various types of alcohols (trimethylolpropane (TMP), valeric acid,

pentraerythritol, etc.) to form triesters at the acid or base catalyst. As an alternative, metallic or metal oxides are used as heterogeneous catalysts for esterification (Table 8).

Table 8. The overview of catalysts used for biolubricant triesters.

Catalysts	Feedstock	Operating Conditions (Temp./Pressure/Time/Other)	Yield, %	Ref.
Sodium Methoxide	Jatropha oil, TMP	150 °C/10 mbar/3 h	>80	[178]
Sodium Methoxide	Palm ME, TMP	140 °C/25 mbar/25 min/oscillatory flow reactor at 1.5 Hz	94.6	[179]
Calcium Methoxide	Palm ME, TMP	180 °C/50 mbar/8 h	92.4	[180]
Sodium Methoxide	Canolabiodiesel, ME, TMP	110 °C/1 mbar/5 h	90.9	[181]
Dibutyltin dilaurate	Castor biodiesel, TMP	170 °C/0.01 bar	89.7	[182]
KOH	UCO ME, TMP	128 °C/200 Pa/1.5 h	85.7	[183]
Fe-Zn double-metal cyanide	Sunflower oil, octanol	170 °C/8 h	98	[184]
p-Toluensulphonic acid	Rubber ME, NPG/TMP/PE	135–140 °C until theoretical reaction complete	94.5–96.5	[185]
C Antarctica lipase	Rapeseed ME, NPG/TMP/PE	200 °C/50 h	98	[186]
p-Toluensulphonic acid	Thumba ME, xylene, NPG/TMP/PE	135–140 °C until complete	89–95	[187]
1% $NaOCH_3$	Jatropha seed, TMP	150 °C/10 mbar/3 h	47	[188]
$Ca(OH)_2$	Fluted Pumpkin, TMP	160 °C/6 h	81.4	[189]
2% H_2SO_4	Rubber seed, TMP	150 °C/5 h	79	[190]
0.9% $NaOCH_3$	Palm oil, TMP	130 °C/10 mmHg/4 h	97.8	[191]
0.8% o-phosphoric acid	Castor seed, TMP	120 °C/1 h	96.6	[192]

They can be easily separated compared to homogeneous catalysts. However, they are prone to deactivate from coking and are usually more expensive [193]. The formation of triesters significantly improves properties at low temperatures and thermal-oxidative stability [176,185].

Another modification is to form estolides from the acyl group by hydrolysis of triacylglycerols to obtain various esters. In the reaction, a carbocation is formed at the site of unsaturation, which can undergo nucleophilic attack by other fatty acids to form an ester bond. The functional group carboxylic acid is bonded by double bonds to another fatty acid, and the estolides are formed in the presence of catalysts or without catalysts (Table 9). The fatty acids are usually prepared from triacylglycerols by hydrolysis. The bio-lubricants based on estolide treatment improved the oxidative stability, low-temperature properties, and also lubricity [194].

Table 9. The overview of catalysts used for estolides.

Catalysts	Feedstock	Operating Conditions (Temp./Pressure/Time/Other)	Yield, %	Ref.
H_2SO_4, $HClO_4$, or p-Toluensulphonic acid	Sunflower oil	50–100 (depending on catalyst)/3–24	-	[195]
H_2SO_4	Olive oil	100/3–24 h	-	[195]
H_2SO_4, $HClO_4$, or p-Toluensulphonic acid	Ricinoleic acid	50–100 °C (depending on catalyst)	-	[196]
Tin (II) 2-ethylhexanoate	Castor 2-EH ester, lauric acid	130 °C/12–18 Pa/24 h	73	[197]
-	Castor 2-EH ester, estolide, butanethiol	−28 to −18 °C/3 h/photochemical reactor	91	[197]

Table 9. *Cont.*

Catalysts	Feedstock	Operating Conditions (Temp./Pressure/Time/Other)	Yield, %	Ref.
-	Saturated Castor FA ester, capping FA	200 °C/20 Pa/24 h	-	[198]
-	Unsaturated Castor FA ester, capping FA	200 °C/20 Pa/24 h	-	[198]
BF_3	Oleic acid estolide, linear alcohols	60–80 °C until 99% complete	-	[199]
$HClO_4$	Coriander FA, 2-EH, capped with various FA	Estolide: 60 °C/7.5–10.9 kPa/24 h Ester: additional 3–4 h after 2-EH added	65–76	[200]
-	Castor 2-EH ester estolide, butanethiol	−28 to −18 °C/3 h/photochemical reactor	96	[197]

The last modification is epoxidation, which removes the double bonds between two carbons in fatty acids by bonding an oxygen atom, whereby the epoxide (oxirane) functional group is formed. The oils/fats reacted with oxidants (hydrogen peroxide) in the presence of formic or acetic acid, sometimes involving the use of various enzymatic or heterogeneous catalysts, such as Amberlite IR-120H, sulfuric acid, and the sulfated-SnO_2 catalyst (Table 10) [177].

Table 10. The overview of catalysts used for biolubricant synthesis by epoxidation.

Catalysts	Feedstock	Operating Conditions (Temper./Time/Other)	Yield, %	Ref.
-	Oleic acid, formic acid, H_2O_2	4 °C/2 h	-	[201]
-	Passion fruit oil, formic acid, H_2O_2	10 °C then adding H_2O_2 and heating to 60 °C, 7 h	-	[202]
H_2SO_4	Jatropha oil, formic acid, H_2O_2	10 °C for 2 h while H_2O_2 added then 60 °C until complete	96	[203]
Sulfated-SnO_2 Catalyst	Canola oil, acetic acid, H_2O_2	70 °C/6.5 h	-	[204]
-	Methyl oleate, formic acid, H_2O_2	-	97	[205]
H_2SO_4, H_3NSO_3, or CH_4O_3S	Epoxidized mustard oil, 2-EH	120 °C until complete	92–95	[206]
Sulfated Ti-SBA-15	Epoxidized canola oil, acetic anhydride	130 °C/5 h	100	[207]
H_2SO_4	Epoxidized soybean oil, Guerbet alcohols	110 °C/20 h/0.47 mol alcohol	-	[208]
CaO	Epoxidized FA UCO ME, methanol, isooctadecanol	90–140 °C	-	[209]
Pyridine	9,10-hydroxyacyloxy-stearic acid ME, CCl_4, acylchlorides	50 °C/5 h	66–88	[210]
p-toluensulphonic acid	Monoepoxide linoleic acid, oleic acid	70–80 °C oleic acid added over 1.5 h then heated to 90–110 °C over 3–6 h	-	[211]
Amberlyst-15	Epoxidized canola oil, n-butanol	100 °C/15 h	-	[212]
p-toluensulphonic acid	Epoxidized linseed oil, oleic acid, xylene	150 °C/4–5 h	-	[213]

The reason is that oils are non-polar matter, and the change of double bonds to the epoxide group change the polarity (polar matter is formed), which provide better adsorption on the surface of materials in the engine (better lubricity). Moreover, epoxidation increases oxidation stability. On the other hand, epoxidation decreases the viscosity index and increases the pour point. This fact limits the use of bio-lubricants in many applications, mainly due to the pour point [208]. This problem can be solved by opening the epoxide

ring and adding another functional group, such as various fatty acids and acetyl, which also increases polarity. These processes are usually catalysed by acid catalysts, such as p-toluenesulfonic acid, which is homogeneous, or various zeolites, which are heterogeneous. The formed bio-lubricants have better properties than epoxides [206].

7. Conclusions and Prospects

Vegetable oils or animal fats represent an important source of reusable energy. This paper summarised and compared the transformation of oils/fats to biofuels. For biofuels, two main methods were described: (i) esterification or transesterification to biodiesel, and (ii) co-processing or hydroprocessing to green diesel. Biodiesel is a mixture of esters of higher fatty acids and low molecular alcohol (not paraffinic). In contrast, green diesel is a strongly paraffinic biofuel with lower density, higher cetane index, and flammability. A detailed comparison of biodiesel and green diesel properties was introduced. The production of green diesel is compatible with the current petrochemical infrastructure and allows for an efficient transition to a long-term sustainable energy perspective (the industrial scale is possible). The transformations are usually catalysed by many types of catalysts, such as homogeneous (e.g., KOH, H_2SO_4) or heterogeneous (e.g., CaO, mixed oxides, zeolites, heteropolyacids, molybdenum carbide or nitrides). The production of bio-lubricants also decreases the consumption of crude oil. Moreover, biofuels and bio-lubricants are more environmentally friendly than similar products produced from crude oil.

Future research will focus on developing the stable catalyst with a higher yield at lower production costs and looking for a new cheap source of oils/fats, such as waste or non-food oils. For esters, we will be looking for new applications, such as the transformation to bio-lubricants, epoxidation to monomers, or additives to oil.

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Abbreviations

AGO	Atmospheric gasoil
DG	Diacylglycerols(s)
E	Ester(s)
EP	The ester phase
EH	Ethylhexyl
FAME	Fatty acid methyl ester
FFA	Free fatty acid(s)
HDS	Hydrodesulfurization
HDN	Hydrodenitrogenation
HDO	Hydrodeoxygenation
HVO	Hydrotreated vegetable oil
G	Glycerol
GP	The glycerol phase
ME	Methyl esters
MG	Monoacylglycerols(s)
RSO	Rapeseed oil
SRGO	Straight run gas oil
TG	Triacylglycerol(s)
TOFA	Tall oil fatty acids
UCO	Used cooking oil

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