

Review

Biodiesel at the Crossroads: A Critical Review

Rafael Estevez ¹, Laura Aguado-Deblas ¹, Felipa M. Bautista ¹, Diego Luna ^{1,*} , Carlos Luna ¹ , Juan Calero ¹ , Alejandro Posadillo ² and Antonio A. Romero ¹ 

¹ Departamento de Química Orgánica, Universidad de Córdoba, Campus de Rabanales, Ed. Marie Curie, 14014 Córdoba, Spain; q72estor@uco.es (R.E.); lauraaguado8@gmail.com (L.A.-D.); qo1baruf@uco.es (F.M.B.); qo2luduc@uco.es (C.L.); p72camaj@uco.es (J.C.); qo1rorea@uco.es (A.A.R.)

² Seneca Green Catalyst S.L., Campus de Rabanales, 14014 Córdoba, Spain; seneca@uco.es

* Correspondence: qo1lumad@uco.es; Tel.: +34-957-212-065

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Abstract: The delay in the energy transition, focused in the replacement of fossil diesel with biodiesel, is mainly caused by the need of reducing the costs associated to the transesterification reaction of vegetable oils with methanol. This reaction, on an industrial scale, presents several problems associated with the glycerol generated during the process. The costs to eliminate this glycerol have to be added to the implicit cost of using seed oil as raw material. Recently, several alternative methods to convert vegetable oils into high quality diesel fuels, which avoid the glycerol generation, are being under development, such as Gliperol, DMC-Biod, or Ecodiesel. Besides, there are renewable diesel fuels known as “green diesel”, obtained by several catalytic processes (cracking or pyrolysis, hydrodeoxygenation and hydrotreating) of vegetable oils and which exhibit a lot of similarities with fossil fuels. Likewise, it has also been addressed as a novel strategy, the use of straight vegetable oils in blends with various plant-based sources such as alcohols, vegetable oils, and several organic compounds that are renewable and biodegradable. These plant-based sources are capable of achieving the effective reduction of the viscosity of the blends, allowing their use in combustion ignition engines. The aim of this review is to evaluate the real possibilities that conventional biodiesel has in order to success as the main biofuel for the energy transition, as well as the use of alternative biofuels that can take part in the energy transition in a successful way.

Keywords: biofuel; biodiesel; straight vegetable oils; selective transesterification; interesterification; gliperol; DMC-Biod; ecodiesel; green diesel; fatty acid glycerol carbonate esters

1. Introduction

Over the last three decades, through a series of international treaties it has been decided to address, in a global way, a process of replacing fossil fuels by alternative energy sources of renewable nature. In this way, the world's governments have negotiated, for the first time in history, a treaty that envisages climate action by many countries, the so-called Paris Agreement [1]. In this connection, many countries have determined the development of its own internal climate and energy policy framework for 2030 and beyond, advancing in decarbonization and fostering low-carbon innovation towards a new climate economy [2]. Among these strategies to reduce anthropogenic greenhouse gas (GHG) emissions, those measures adopted for reducing the high consumption of fossil fuels play a fundamental role. Thus, an unprecedented effort is being made to implement alternatives (photovoltaic, wind, hydrogen, and nuclear energy) [3,4] that allow the gradual replacement of natural gas, coal, and fossil fuels in the field of electricity generation. However, there is no such equivalent in transport, since vehicles capable of using fuel cells or electric motors cannot yet compete with spark ignition (SI) engines or compression ignition (CI) engines, especially in the field of heavy trucks [5], aviation [6,7], or the shipping sector [8].

Consequently, regardless of the growing effort in the introduction of vehicles that incorporate electric or hydrogen engines, the gradual incorporation of biofuels as fossil fuels substitutes continues being an imperative necessity for reducing GHG emissions [9,10]. In this line, considerable challenges for the transport sector in the coming decades must be assumed in order to increase the energy security [11,12].

The transport sector, including road, air, and waterborne transport, which contributes about 20% of the global emissions of greenhouse gases [11,13] is currently carried out by engines developed at the end of the 19th century, which were thought to work with ethanol or vegetable oils as fuels. These engines are usually known by the names of their inventors, Otto or Diesel, as well as by the two different ignition procedures, by spark, spark-ignition engines [1] or by internal compression ignition engines [14]. These engines were improved and adapted for application with fossil fuels during the last century, using various fractions obtained from the distillation of crude oil (or mineral oil) [15]. Thus, gasoline and diesel engines based on these fossil fuels are employed worldwide. Gasoline is the lighter fraction obtained from crude oil at distillation temperatures below the boiling point of water, whereas Diesel is obtained at higher distillation temperatures. Today, the problem arises since there is a necessity to keep using the current fleet of vehicles designed to work with fossil fuels, without modifying these engines, which surpassed a billion-units in the year 2010 [16].

In this scenario, the greatest consensus, in order to find a viable energy transition, is using the current fleet of vehicles in the coming decades, and gradually introducing biofuels in mixtures with these fossil fuels. In this way, biofuels can be easily integrated into the logistic of the global transportation system [17]. In this sense, the objectives pursued by the EU are estimated at 20% of biofuel in the mixture with fossil fuels for the year 2020 and 30% for 2030 [18]. However, despite the fact that these objectives are, apparently, not difficult to achieve, the replacement of the fossil fuel with biofuels is currently considered unattainable in these deadlines. The reason is that the most used biofuels, bioethanol and biodiesel, require huge agricultural resources to comply with these energy purposes [19–22], being much higher for biodiesel. To get an idea, the 1.6% of these biofuels in respect the total transport fuel worldwide [19], correspond to an ethanol production of almost 50 billion liters and a world biodiesel production of almost four billion liters [2], i.e., a relation lower than 1/10. Therefore, the incorporation of bioethanol has been, until now, easier and more effective than that for biodiesel. It is commonly accepted that bioethanol, produced from sugarcane, corn, or any other cereal, can easily be mixed in any proportion with gasoline to get liquid biofuels for use in spark ignition engines. This is feasible because the rheological properties of bioethanol are very similar to that of gasoline, being especially decisive due to their similar kinematic viscosity values [23].

However, the use of seed oils as biofuels, for the replacement of fossil diesel, is not as easy to achieve as with bioethanol and gasoline. The problem is that the CI engines are built to operate with viscosity values in the interval of 3–5 cSt, which is the one exhibited by fossil diesel fuel. Since seed oils have higher viscosity values, at least in the range of 30–40 cSt, it is necessary to perform some type of oil treatment to reduce their initial viscosity values, before mixing them in different proportions with fossil diesel. Biodiesel is, to date, the liquid biofuel produced in higher amounts for being employed as a substitute of fossil diesel. Nowadays, it is obtained through chemical conversion, mainly homogeneous alkaline transesterification of vegetable oil or animal fat with methanol, giving rise to a mixture of mono-alkyl esters of long chain fatty acids derived [24–27]. However, the transesterification reaction on an industrial scale has been associated as the main problem, with glycerol being generated in the process (10% by weight of the total biodiesel produced). This glycerol has to be completely removed, since the high temperatures reached in the engines promotes the formation of polymers of glycerol, as well as acrolein, which has a high toxicity. Therefore, to eliminate the glycerol, several washes with water have to be performed, making the process more expensive and tedious.

To solve this existing important barrier that prevents consolidation of conventional biodiesel as a suitable biofuel for the fossil fuel replacement, different alternative methods to convert vegetable oils into high quality diesel fuels while avoiding the generation of glycerol are being investigated. Thus, several oxygenated biofuels that integrate glycerol as soluble derivatives, very similar to biodiesel,

have been described, such as Glycerol, DMC-Biod, or Ecodiesel [28]. Likewise, alternative high-quality diesel fuels, generally known as “green diesel”, have also been obtained by several processes, i.e., cracking or pyrolysis, hydrodeoxygenation, and hydrotreating of vegetable oils. All these biofuels can be considered as “renewable diesel”, although their composition is similar to that of a fossil fuel [29,30].

Finally, aware of the economic barriers that delay the process of replacing fossil fuels in current diesel CI engines, the use of straight vegetable oils (SVO) has been addressed as a possible strategy to make the fossil diesel replacement economically viable. Two alternatives are possible for this task. On one hand, the possibility of modifying the engine designs, as well as the operating parameters. On the other hand, the use of additives that allows for the reduction of kinematic viscosity of the blend. The first option, given the large number of cars existing seems very unworkable. Therefore, some researchers have described biofuels, from various plant-based sources such as alcohols, vegetable oils, and several organic compounds, that are renewable and biodegradable, as well as exhibiting adequate viscosity to be blended with vegetable oils in order to achieve a reduction of their kinematic viscosity. Since these compounds have lower octane index values, these low-carbon biofuels, with low viscosity, are considered as less viscous and lower cetane (LVLC) fuels to be employed in mixtures with oils [31,32].

This review aims to evaluate the real possibilities that conventional biodiesel has to respond to the challenge of successfully carrying out the energy transition, considering the current fleet of diesel vehicles. Likewise, this review overviews the alternative processes to successfully achieve this inexcusable current challenge. In such a case, what possibilities and advantages or disadvantages present each one of the methods described recently, in order to reduce the viscosity of triglycerides to be used as biofuels in mixtures with fossil diesel.

2. Biodiesel: The Current Renewable Biofuel in CI Diesel Engines

Once several international conventions (Kyoto and so on) were approved in the last decade of the last century [33], intending to minimize the anthropogenic effect on climate change, it was practically unanimously assumed that vegetable oils would be the raw material for obtaining the biofuels which will replace the current fossil fuels used in CI diesel engines. This solution was very easy to adopt, given that the first fuel used by Rudolf Diesel was a vegetable oil [34]. But with the current fleet of diesel vehicles, its use is not directly feasible, as it results in bioethanol being in gasoline engines. Whereas, the majority of rheological properties of biodiesel are optimal for being employed as biofuel in current diesel engines, the high viscosity that is exhibited constitutes the main problem.

Since the renewal of interest in vegetable oil-derived fuels, during the late 1970s, four possible solutions to the problem of high viscosity were investigated: Transesterification reaction, pyrolysis, dilution with conventional petroleum-derived diesel fuel, and micro-emulsification. The initial researches, on a laboratory scale or in a pilot plant, showed that the mixing of vegetable oil with diesel cannot exceed 10%, since the viscosity rises excessively. Micro-emulsification with short chain alcohols also presents solubility problems. Pyrolysis was considered more complex from a technical point of view. Thus, transesterification with methanol is currently the most common method and leads to methyl esters blend of vegetable oils and fats (FAME), usually called biodiesel. Biodiesel is biodegradable, nontoxic, renewable, has a high cetane number, a high flash point, in-built oxygen content that allows higher combustion, with very low sulfur, or aromatic components as well as other pollutants emissions. In addition, it perfectly fits into existing engines with no modification, being able to be used pure or in mixtures with fossil diesel, in any proportion. Consequently, biodiesel has been the subject of intense research in recent decades which continue to progress despite the level of its development throughout thousands of scientific papers [35]. However, this process presents a serious handicap related to the unavoidable production of glycerol as a byproduct of the transesterification reaction, Figure 1.

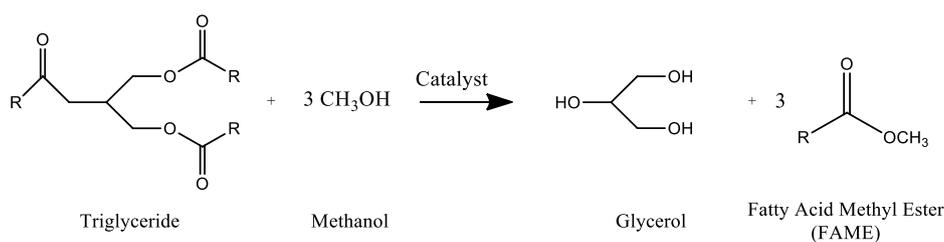


Figure 1. Transesterification reaction of triglyceride molecules with methanol by conventional base catalysis.

Thus, the high production of biodiesel, mainly in the last three decades, has produced large volumes of waste with glycerol as the major product, being 10–20% of the total volume of biodiesel produced [36,37]. This excess of glycerol has caused a decrease in its commercial value, not only by the huge amount produced but also by its low quality, since it is mixed with other products such as methanol, water, and salts [38]. Since there are currently no industrial processes capable of adsorbing this continuous increase in the production of glycerol, this problem is far from disappearing. In fact, it is expected that by 2020, the global production of crude glycerol will reach 7.66 million tons [39]. To solve this problem, extensive efforts in catalysis research are currently being directed to the development of new and economically viable ways to valorize crude glycerol mass generated in the industrial production of biodiesel [36–39].

But even in the case of being able to solve the problems associated with the management of the increasing amounts of poor-quality glycerol, the conventional transesterification process also presents other serious problems such as the low atom yield (or atom efficiency) of the process. Atom yield can be defined as the conversion efficiency of a chemical process in terms of all atoms involved and the desired products produced. As such, the atom yield is an important concept of green chemistry, since it is a different concern than chemical yield, because a high-yielding process can still result in substantial by-products, as is the case in biodiesel production. In addition to this problem, the biodiesel obtained has to be cleaned from the residual glycerol, together with the alkaline impurities, from the homogenous catalyst currently used in the industrial transesterification process. This supposes an additional cleaning process, which is usually carried out by successive washing steps with water, requiring a large consumption of water, energy, and time to obtain the elimination of glycerol in order to comply the limits established by the quality standard EN 14214 [39–42]. Furthermore, the effects of water on the quality of biodiesel are not negligible [40], therefore various types of adsorbents have been proposed to eliminate the residues that contaminate the FAME mixture that constitute biodiesel [41,42].

Therefore, due to the generation of glycerol as a secondary compound in the apparent simplicity of the process, shown in Figure 1, a subsequent very complex design to make possible the industrial production of biodiesel [43] must be taken into consideration, Figure 2.

Generally, the transesterification reaction is carried out in a discontinuous reactor under constant agitation and at 60 °C of the reaction temperature. Then, glycerol is separated by decantation, together with the excess of methanol that will be recovered by distillation. This crude biodiesel contains catalyst residues which must be neutralized and eliminated. Besides, an important amount of glycerol is also present in this primary reaction product. Glycerol cleaning is a very important and laborious step, as abovementioned. According to EN 14214, the amount of glycerol in the refined biodiesel should not exceed the 0.02%, because the reaction of this glycerol with oxygen inside the engine at high temperature, produces acrolein, that by polymerization generates deposits of carbonaceous compounds on the injector nozzles, pistons, and valves in the engines, thus reducing its efficiency and even its service life [30].

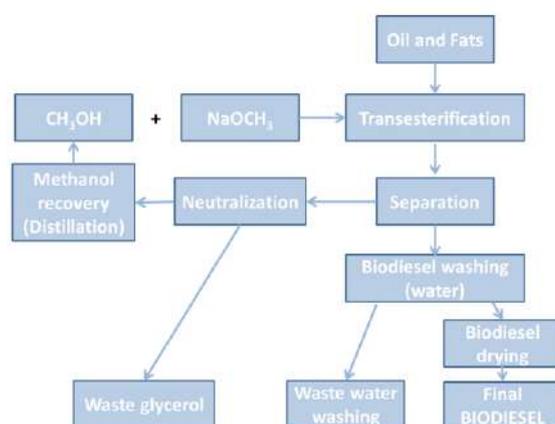


Figure 2. Standard design diagram of a conventional biodiesel plant.

Biodiesel purification is usually carried out commonly by neutralization and several washing steps with hot water to remove glycerol as well as all inorganic impurities. After washing the biodiesel, it is dried in an evaporator to remove residual water [40]. Purification of biodiesel may also be obtained by dry washing, employing organic resins, or using starch and cellulose as adsorbents of impurities [41,42].

Therefore, the complexity of the production process, mainly associated to the production of glycerol as a secondary product, greatly increases the production costs of conventional biodiesel [36]. Thus, the high global cost is very unfavorable in comparison to that of conventional fuels. In this way, the cost of biodiesel unit price is 1.5–3.0 times higher than that of fossil diesel fuel, depending on the type of triglyceride used as feedstock [44]. In a recent study on the economic feasibility of biodiesel through its life cycle costing, it was obtained that this biofuel could be competitive with diesel fossil, if the conditions of biodiesel production were optimized enough and a low-cost material feedstock was used. Therefore, economic viability is the main weaknesses that must be considered to ensure the development of this biofuel [45]. One approach that would increase the feasibility of the process is the revalorization of the crude glycerol obtained as by-product. In fact, glycerol is currently considered as one of the main platform molecules derived from biomass and a lot of researches are focused on transforming glycerol into value-added products, such as acrolein, oxygenated fuel additives, biofuels, and polyols (e.g., 1,3-propanediol) [46–48].

In conclusion, despite the enormous interest shown worldwide by researchers, industrialists, and governments about the use of biodiesel, its economic feasibility is still one of the major drawbacks that must be taken into account in the decision to continue or not with the development of this biofuel.

3. Biodiesel-Like Biofuels Which Integrate Glycerol as a Derivative Obtained in the Same Transesterification Process

A little over a decade ago, several researchers concluded that the difficulty in managing the glycerol produced during biodiesel synthesis constitutes enough technical and economic problems to be considered as a viable option to replace fossil diesel, at the pace foreseen by the current international agreements. In this context, the production of biofuels, in the same process of obtaining FAMES, that generate glycerol derivatives instead of glycerol itself, seemed the best option to avoid the huge amounts of glycerol produced in the conventional transesterification process and also avoid the process of separation and cleaning of residual glycerol dissolved from the FAMES mixture which constitutes the raw biodiesel [28,30,49–52]. In this respect, among the alternatives described for the integration of glycerol as a biofuel, it is necessary to highlight those that prevent the generation of glycerol in the same biodiesel production process, that is, processes in which together with the corresponding FAMES mixture, some derivatives of glycerol, such as glycerol triacetate (or Glycerol), glycerol carbonate (or DMC-Biod), or monoglyceride (like Ecodiesel) are also obtained.

This process is possible by substituting the alcohols employed in the conventional process (methanol or ethanol) by esters, for instant. This methodology also exhibits an important advantage in comparison with the traditional transesterification process, an increase of the atom yield of the process (atom efficiency), since no by-products are obtained and, therefore, a significant increase of the reaction products are obtained. In the last decade, several methodologies to prepare esters from lipids using different acyl acceptors which directly afford alternative co-products are being investigated. These interesterification processes using alternative alcohol donors such as methyl or ethyl acetate and dimethyl or diethyl carbonate, instead of using methanol, are performed with the same catalysts employed in the conventional transesterification processes (acid or alkali homogeneous or heterogeneous catalysts, as well as lipases).

3.1. Biodiesel-Like Biofuels that Integrate Glycerol as Glycerol Triacetate, Obtained by Interesterification of Oils or Fats

In 2004, researchers of the Industrial Chemistry Research Institute, Varsow (Poland) patented a new type of biofuel, Gliperol [53]. Gliperol was obtained by interesterification reaction of triglycerides with methyl acetate, in the presence of a strong acid catalyst. The products of the reaction were a mixture of fatty acid methyl esters and glycerol triacetate (triacetin), Figure 3 [53–55]. Furthermore, together with triacetin, small amounts of diacetin and monoacetin are also obtained. In any case, these compounds, as well as the excess of methyl acetate, do not imply the need for their separation from the biofuel mixture, since all of them are soluble in fossil diesel. It is only necessary to clean the biofuel obtained in order to eliminate the inorganic salts which are only there if a homogeneous catalyst is employed, as consequence of the neutralization process.

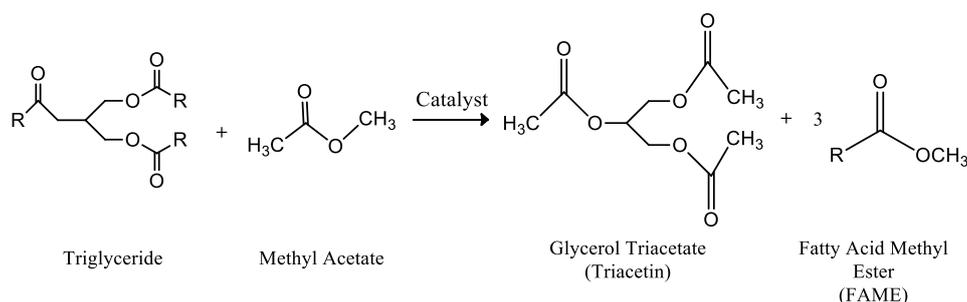


Figure 3. Interesterification reaction of a triglyceride molecule with methyl acetate obtained by a conventional catalyst, producing a mixture of fatty acid methyl esters (FAME) and glycerol triacetate (triacetin). This mixture is a biodiesel-like biofuel, patented as Gliperol[®], by the Research Institute of Industrial Chemistry Varsow (Poland) [55].

Authors studied several reaction conditions, i.e., oil/methyl acetate molar ratio in the range 1:3 to 1:9, and temperatures in the range of 40–200 °C. This biofuel exhibited similar properties as biodiesel, although the obtention process of Gliperol improves the yield, the efficiency, and the economic feasibility of the conventional biodiesel obtention process. After Gliperol was patented, a lot of subsequent studies that use homogeneous basic catalysts, such as potassium hydroxide, potassium methoxide, and polyethylene glycolate have been carried out [56–67]. These studies manifested that the reaction conditions to obtain Gliperol are similar to that for the production of Biodiesel. Likewise, this reaction has been studied over heterogeneous acid catalysts [68–79] as well as using lipases as biocatalysts, either in solvent-free systems [80–97] or in ionic liquids [98–101]. Furthermore, many other innovative technologies have also been applied, such as supercritical conditions [102–117] or ultrasonic-assisted interesterification [118–133].

Analogously to the interesterification of TG with methyl acetate, the ethyl acetate can be also considered as a good option to obtain Gliperol. Furthermore, this ethyl acetate has the advantage of its renewable character. However, to this date it has been studied less than methyl acetate [134–139].

Regarding the influence of triacetin on engine performance, many studies have been published to date [43,140–154]. Thus, added to biodiesel or fossil diesel, triacetin acts as an efficient anti-knock additive in direct injection (DI) diesel engines. In addition, the use of triacetin as an additive for diesel and biodiesel also reduces the emission of pollutant. Regarding the investigations carried out on the blends triacetin/biodiesel and triacetin/diesel, the combination of 10% by weight of triacetin with biodiesel is the one that shows the best results [155–170]. Finally, beneficial effects of triacetin on the cloud point and cold filter plugging point have also been revealed in several studies [171–173]. About the economic viability of the process of interesterification of triglycerides with methyl or ethyl esters of acetic acid, there are many economic studies that support their advantages in respect to conventional biodiesel processes [174–176].

Therefore, it can be concluded that the interesterification of triglycerides with methyl or ethyl acetate can be a suitable methodology to obtain conventional biodiesel (FAME or fatty acids ethyl ester (FAEE)), also including a certain amount of a well-recognized additive, the triacetin, which improves Biofuel performance, in relation to conventional biodiesel, since it reduces the emissions and greatly simplifies the biofuel synthesis process. Likewise, the process exhibits an atomic efficiency of 100% since triacetin is obtained, which is a more profitable compound compared with the glycerol obtained as a by-product in conventional biodiesel production. Furthermore, the quality of biodiesel seems to be enhanced with the presence of triacetin.

3.2. Biodiesel-Like Biofuels that Integrate the Glycerol as Glycerol Carbonate, Obtained in a Single Process of Interesterification of Oils or Fats

Analogously to methyl acetate, dimethyl carbonate (DMC) can also be used as an interesterification reagent for the obtention of glycerol esters from lipids, directly yielding alternative soluble co-products in biodiesel solutions. The reaction is quite attractive, given that DMC is considered a prototype of a green reagent since it is not harmful to both humans and the environment, in addition to being an environmentally benign molecule (non-toxic, non-corrosive, and non-flammable) and less toxic than methanol. In this regard, it should be noted that the raw materials to produce DMC, that is, methanol and carbon monoxide, are derived from synthesis gas that can be produced from the thermochemical conversion of biomass [177], although the direct synthesis of DMC from methanol and CO₂ has also been described [178]. Consequently, its utilization as a reaction medium as well as a phosgene substitute has currently been attracting much interest because of DMC's ability to act on a wide variety of reactions such as polycarbonate synthesis, polyurethane synthesis, carboxylation reagents, alkylating reagents, and polar solvents, not to mention its application as a fuel additive. In fact, DMC is also employed to obtain glycerol carbonate, considered an added-value product to revalorize the glycerol [179–191].

Therefore, a fuel produced with DMC and vegetable oils or fats as raw materials should be considered as an alternative fuel, totally derived from renewable resources. Thus, dimethyl carbonate operates as an alternative acyl acceptor. In this way, a novel biodiesel-like material (abbreviated as DMC-BioD) was developed by reaction of a vegetable oil with dimethyl carbonate, which avoids the co-production of free glycerol. According to Figure 4, the only difference between DMC-BioD and conventional biodiesel is the presence of fatty acid glycerol carbonate monoesters (FAGCs) in addition to FAMEs [192–195]. In fact, the process operates with the same basic catalysts described in the production of biodiesel, such as KOH, sodium methylate, sodium hydride, some amines, as well as different alkaline solids, operating as heterogeneous base catalysts at different experimental conditions [196–214]. Given the interest of the process, supercritical conditions [215–222] or the use of different lipases [223–239] have also been studied. DMC has been recently investigated in regards to the synthesis of fatty acid methyl esters via ionic liquids [240,241] or non-catalytic transesterification of vegetable oils with dimethyl carbonate and some amounts of silica loading operating as a dispersing agent [242].

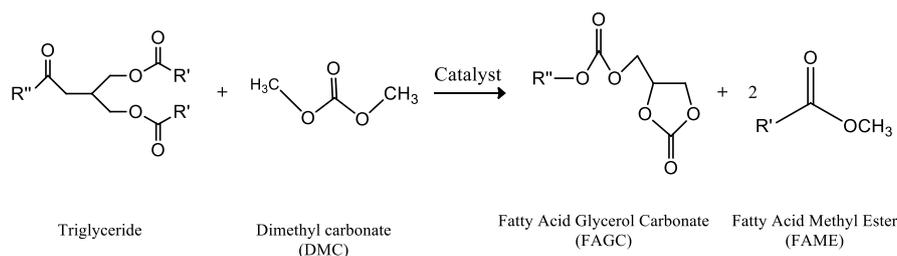


Figure 4. Alkaline catalysed transesterification reaction of the triglycerides with dimethyl carbonate (DMC), generating a mixture of two moles of FAME and one mole of glycerol carbonate fatty acid (FAGC), a biodiesel-like biofuel, patented by Polimeri Europe (Italy) as DMC-BioD [194].

This biofuel, patented with the name of DMC-BIOD [201], is obtained as aforementioned by the transesterification reaction between triglycerides and dimethyl carbonate which produces a mixture of FAMES and cyclic esters of glycerol carbonate fatty acids (FAGCs). In this mixture, a small amount of glycerol dicarbonate (GDC), and glycerol carbonate (GC) is also obtained, due to the decomposition of FAGC molecules. The short name, glycerol carbonate, is currently used for 4-hydroxymethyl-2-oxo-1,3-dioxolan, and glycerol dicarbonate for 4-(methoxycarbonyloxymethyl)-1,3-dioxolan-2-one, that also are obtained in the transesterification process [243].

In summary, the main difference between DMC-BIOD biofuel (obtained by the transesterification of triglycerides with DMC) and conventional biodiesel is the presence of some amounts of fatty acid glycerol carbonate monoesters, glycerol dicarbonate, and glycerol carbonate, in addition to the FAMES that constitute biodiesel. These glycerol derivatives are completely soluble in the biofuel, meaning that all the reaction products can be used as biofuel, without any additional separation operation, and taking advantage that the 100% of atomic efficiency is reached. It is not even necessary to separate the unreacted DMC, since it can be used as an additive for fossil diesel, due to the high oxygen content of the molecule. In fact, the DMC is attracting the interest of researchers due to the increasing importance of environmental and resource issues to the realization of a sustainable society through a green chemistry activity development [243–249].

The addition of fuel-born oxygen, in the form of DMC, (a bio-derived with a 53.3% wt. of oxygen) in a conventional pump diesel produced a notable decreased in total hydrocarbons (THCs), carbon monoxide (CO), and particulate matters (PM). These emissions were reduced by up to 50% with a 96% diesel and 4% DMC blend. A DMC and diesel blend may also have potential in the reduction of yet unregulated carcinogenic emissions such as benzene and 1,3-butadiene [250–254]. Similarly to these processes, the use of diethyl carbonate (DEC) instead of DMC has been much less investigated [221,227,234], although the available results in literature [255–266] allow us to conclude that they exhibit a behavior very similar to those obtained with DMC.

3.3. Biodiesel-Like Biofuels that Integrate Glycerol as Monoglycerides, Obtained in a Selective 1,3-Transesterification Process

Another strategy to avoid the generation of free glycerol consisted in the partial transesterification of triglycerides, generating only two equivalents molecules of FAMES, maintaining the third equivalent of fatty acids in the form of monoglyceride (MG). This procedure was initially performed over lipases, taking advantage of its 1,3-selective nature, which allows the process to be “stopped” in the second step of alcoholysis, Figure 5. Thus, several researches have been carried out using pig pancreatic lipase (PPL) in free form [267,268] and immobilized [269,270] in the selective transesterification process. In addition, to avoid the generation of glycerol, it is worth mentioning that the operating conditions of the enzymatic process are much softer and without generation of acidic or alkaline impurities, in comparison with the conventional biodiesel preparation method. Another specific feature of the enzymatic process is that it is necessary to use ethanol, instead of methanol, thus generating a mixture

of FAEEs. This biodiesel-like biofuel was patented as Ecodiesel [271], and it is soluble in both, the mixture of FAEEs and in fossil diesel.

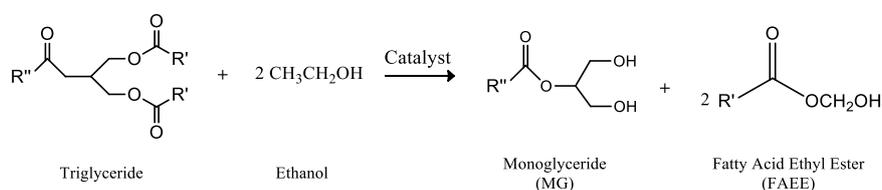


Figure 5. Biodiesel-like biofuel, patented as Ecodiesel by the University of Cordoba [271], obtained by the 1,3-Selective ethanolysis of a triglyceride molecule through the application of enzymatic catalysis, constituted by two molecules of ethyl esters of fatty acids and a monoglyceride molecule.

An important handicap of this procedure was the very early verification of the economic difficulty of carrying out this process on an industrial scale, due to the high price of PPL lipases, even with their use in immobilized form, which allows their reuse. Therefore, in the last decade, a high number of low-cost lipases, both in free as well as immobilized forms have been evaluated, demonstrating in all cases the technical efficiency of the process [272–283]. However, the economic cost of the process is still the main difficulty to guarantee the economic viability at high production level.

The high price of lipases has opened very recently new researches, to search more cost-effective process for producing Ecodiesel, such as the employ of supported KF [284] or CaO [285] as heterogeneous catalysts as well as homogeneous alkaline catalyst such as sodium methoxide [286]. Now, to obtain the same selective alcoholysis process initially achieved with enzymatic catalysis, the reaction is made by operating under kinetic control of the chemical process, i.e., using a less basic catalyst than the alkali metals employed in the biodiesel production and/or operating under softer conditions of temperature and concentration of the alcohol used as a reagent. However, in this case, methanol can also be used, which produces the FAMEs blend. In enzymatic catalysis, ethanol must be mandatory, because methanol inhibits the lipase biocatalysts ability. Thus, the weaker heterogeneous basic sites [284,285], are enough strong to perform the transesterification of primary alcohols (like those in positions one and three of glycerol) but not enough strong to get the methanolysis of secondary alcohols (like those in position two of glycerol) in general much more difficult to achieve. In the case of using homogenous alkaline metal catalysis, selectivity is achieved by operating at sufficiently low temperatures.

In this respect, very recently it has been described that the production of Ecodiesel from castor oil and also from sunflower oil, using sodium methoxide as a homogeneous catalyst, and using a mixture of methanol and ethanol in which ethanol acts as a solvent of methanol to reduce its reactivity [286]. The reaction temperature employed was 30 °C, lower than that used in the conventional biodiesel synthesis, to get the kinetic control of selective transesterification, which allows obtaining a mixture of FAMEs and MG. The behavior of these biofuels was evaluated in a conventional diesel engine, operating as an electricity generator. The emission levels produced were also evaluated based on the opacity values of the generated fumes. With the blend's diesel/Ecodiesel, a 30% of fossil diesel can be replaced, because the rheological properties of the double blends here studied, such as viscosity, pour point, and cloud point values of the different samples allow their use as biofuels in conventional diesel engines. The results obtained using a compression ignition diesel engine showed that the different biofuels studied had no differences with respect to the power generated, although in some cases a small increase in fuel consumption was obtained in respect to pure fossil diesel. However, with the biofuels used, a significant reduction is obtained, up to 40%, in the emission of pollutants, mainly with the diesel/castor oil mixture [286].

Therefore, the experimental conditions of operation to obtain a selective process that results in a high proportion of MG in the final FAME mixture, not only are much softer, but also there is no need to perform any additional purification operation, since glycerol is not produced, and the unreacted alcohol can be left as part of the mixture that constitutes the biofuel, so that the atomic efficiency of the

process is practically 100% because all reagents are integrated in the final biofuel. Furthermore, in recent researches, it has been demonstrated that MG enhance the biodiesel lubricity as well [287–295].

In this line, a recent patent proposes the use of excess glycerol, obtained in the conventional biodiesel manufacture, in the production of mixtures of monoglycerides, obtained by transesterification of triglycerides with glycerol [296,297]. The process is shown in Figure 6, where can be verified that dimethoxymethane (DMM), so-called methylal, is employed as a reagent, in addition to glycerol. This reactant is a colorless and flammable liquid with a low boiling point, low viscosity, and excellent dissolving power. It has a chloroform-like smell and a spicy taste and it is soluble in three parts of water and miscible with the most common organic solvents, salts, and other water-soluble wastes.

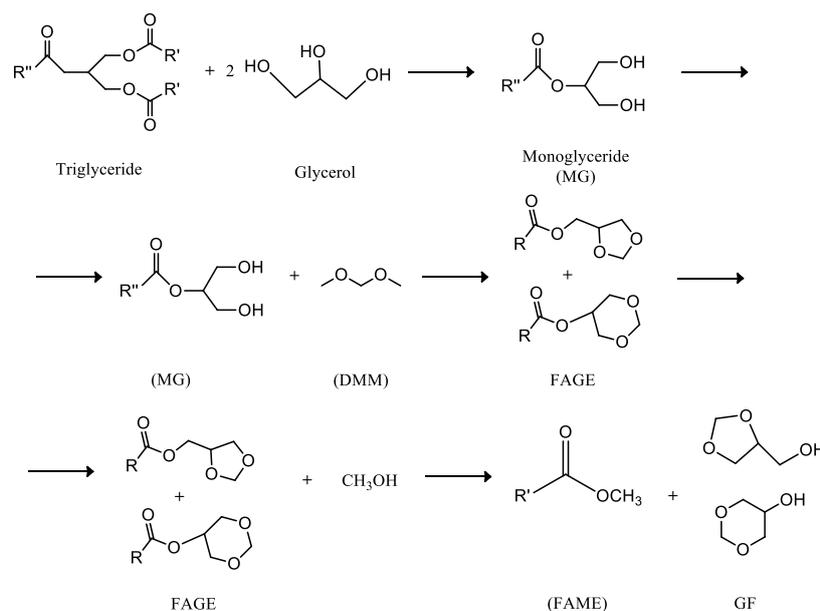


Figure 6. Glycerol-derived advanced biofuel, fatty acid formal glycerol ester (FAGE) patented by Institut Universitari de Ciència i Tecnologia, SA [296,297]. A Biodiesel-like biofuel, obtained by transesterification of triglyceride molecules with glycerol or its derivatives, to obtain a blend of monoglyceride molecules, and subsequent reaction with dimethoxymethane (DMM) to produce FAGE, a mixture of esters of formal glycerols and the formal glycerols (GF) themselves, consisting of the mixture of 5-hydroxy-1, 3-dioxane and 4-hydroxymethyl-1, 3-dioxolane.

This biofuel is proposed to be used after blending with biodiesel, petrol derived diesel, or mixtures of them. These biofuels thus obtained could allow the complete incorporation of the glycerol obtained in the current biodiesel. This new advanced biofuel, fatty acid formal glycerol ester (FAGE)—produced from crude glycerol, after blending with diesel fuel (20% FAGE content)—showed significant benefits in hydrocarbon, carbon monoxide and particle emissions, particle number, and opacity after testing in an automotive engine. Besides, it has been found that it improves the lubricity of the fuel [298–300]. In addition, the pour point and the cold filter plugging point were also improved with only a small effect on cloud point and crystallization temperature. A combination of both, acetals and cold-flow improver, is proposed as an optimal method to improve cold flow properties [173]. Thus, this innovative chemical process uses whichever oil and glycerol as reagents and yields esters of glycerol formal FAGE, which can be part of a blending component in diesel fuels. In the case of biodiesel and FAME/FAGE blends in diesel, ratios up to 20% meet all requirements set in current fuel quality standards [300]. The reaction could also be integrated in conventional biodiesel plants for a combined FAME/FAGE product [288].

4. Fossil Diesel-Like Biofuels: Green Diesel from Hydrotreated Vegetable Oils

Green diesel is a renewable fuel composed of fossil fuel-like hydrocarbons. Thus, several processes (cracking or pyrolysis, hydrodeoxygenation or hydrocracking) are currently under development for

the conversion of fats and oils to obtain fuels very similar to fossil diesel [29]. In this regard, the catalyst hydrotreatment of vegetable oils, in existing refinery processing installations, is one of the best possible solutions [301]. These procedures would be recommended for application in oils with a high content of free fatty acids, since catalysis could generate high concentrations of soaps and deactivate the catalyst. The pioneering work in this field was carried out in China in the 1930s, where the cracking of various vegetable oils was carried out, giving rise to emergency fuels, capable of replacing conventional petroleum-derived fuels during World War II [302].

Since then, and especially in the last decade, different heterogeneous catalysts have been described that by means of a hydrotreatment process are able to transform different vegetable oils into normal alkanes, with boiling points in the range of gasoline or diesel, capable of providing substitutes of fossil diesel, suitable for application in internal combustion engines, without any modification. Green fuels can be classified as naphtha, jet fuel, and diesel. In the case of green diesel, its increasing demand could reach 900 million tons by 2020 [1]. The technology to obtain green fuels from triglycerides is the same currently used in the hydrotreating of vacuum gas oil. This hydrotreating or hydrofining process involves a non-destructive hydrogenation and is used to improve the quality of petroleum distillates without significant alteration of the boiling range. However, there is an increasing interest in developing their optimal production, by obtaining the best catalysts and the most favorable operating conditions [303–354]. The hydroprocessing of triglycerides consist in the hydrogenation of the double bonds of the fatty acids and the removal of oxygen in esters bonds, Figure 7. The triglycerides are converted into hydrocarbons, mainly to n-paraffins at the temperatures between 300 and 450 °C and hydrogen pressures above 3 MPa releasing CO, CO₂, and water as by-products, throughout a complex process of several consecutive steps. The process basically first removes the oxygen, resulting in diesel-range waxy paraffins. A second reaction cracks the paraffins to smaller, highly branched molecules. Oxygen removal from triglycerides is developed through different reactions such as hydrodeoxygenation, decarboxylation, and decarbonylation that determine the final blend of hydrocarbons. Thus, there are two different reactions, hydrocracking and hydrotreating. Hydrocracking is carried out on acid sites of amorphous supports, while hydrotreating takes place on the metal active sites of the catalysts. The hydrotreating with hydrogen of most vegetable oils in the presence of metal oxide catalysts, leads to the production of a liquid blend of C15–C18 hydrocarbons, exhibiting a boiling point within the range of diesel, so that it is commonly called “green diesel”, “renewable diesel”, or “bio-hydrogenated diesel”, and therefore with the same chemical behavior that petroleum-derived diesel.

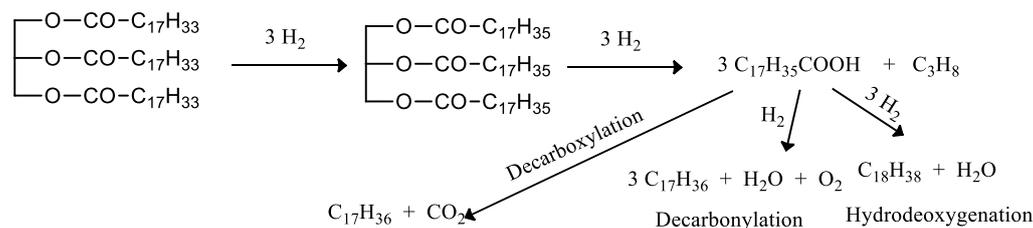


Figure 7. Set of molecular reactions occurring in the hydroprocessing of triglycerides.

This technology has been extended to the application of hydrocracking treatments to mixtures of vegetable oils with fractions of heavy petroleum crude, of equivalent molecular weights in conventional oil refineries [355–374]. Therefore, this procedure makes possible to transform triglycerides into high quality diesel fuel, with the facilities already available in conventional oil refineries, using specific catalysts. In this way, it is possible to obtain renewable liquid alkanes by treating mixtures of vegetable oils and heavy vacuum gas oil (HVO), in hydrogen streams and the same conventional catalysts currently used in the hydrocracking units, such as the bimetallic sulfides NiMo/Al₂O₃ and many other conventional ones, operating under usual conditions of 3 MPa and 300–450 °C. However, different by-products are obtained, mainly consisting of H₂, CO, CO₂, O₂, N₂, H₂S, CH₄, and C₂–C₆

hydrocarbons. In general, liquid hydrocarbons are obtained with a significantly high yield, of the order of 80% by weight. These obtained liquid hydrocarbons have a low acidity index, adequate density and viscosity, and a high cetane index. In this sense, conventional hydrodesulfurization catalysts, consisting of sulfur-supported bimetallic systems, such as NiMo/Al₂O₃, CoMo/Al₂O₃, and NiW/Al₂O₃ are currently being investigated to obtain renewable diesel in conventional oil refinery facilities. To obtain lighter hydrocarbons such as those within the boiling point range of jet fuel or gasoline, catalysts with stronger acid sites (e.g., zeolites) can be used. The zeolite supported catalysts usually contain higher acidity and therefore a more severe cracking activity than those supported on alumina. The acid sites of the catalyst increase also the isomerization degree of the molecules, thus boosting the properties of the green liquid fuels, such as a lower pour point and a higher-octane number.

In summary, the hydrotreatment units of the fossil diesel initially intended to reduce the sulfur content of the fuels to reach the fuel specifications in every countries, has taken advantage for the production of high quality diesel biofuels by treating vegetable oils or animal fats with hydrogen at varying pressures, over the same supported metal catalysts used in the desulfurization of diesel fuels of fossil origin. These high-quality diesel fuels are often referred to as renewable diesel or green diesel which contains the same components as those present in fossil diesel [375–390].

Regarding the advantages of this methodology, it must be considered that it is especially useful with oils whose content of fatty acids are high. It is also important to highlight that the application of this technology avoids the cleaning operations of the crude mixture of FAMES obtained with the conventional transesterification process, which constitute the major drawback in obtaining biodiesel, as aforementioned. However, in the synthesis of green diesel there is a decrease in the atomic performance of the process (atomic efficiency), since a significant loss of raw material is eliminated as CO₂ and H₂O. In practice, the complete loss of matter could be equivalent to glycerol obtained as a by-product in the biodiesel synthesis, with a high difference, in this case it is not required a special manage of these wastes.

When assessing this technology, it is mandatory to consider as a fundamental aspect and the main advantage, the possibility of obtention in the existing refineries [391,392]. Thus, application of the co-processing method of oils and fats of any quality, together to fossil diesel, in hydrocracking facilities, has notable advantages over the conventional methods of biodiesel production currently applied.

5. Blends of Straight Vegetable Oils (SVO) with Less Viscous and Lower Cetane (LVLC) Biofuels

Very recently, in order to reduce as much as possible the cost of manufacturing the biofuels of current diesel engines, instead of performing any chemical treatment of triglycerides, the possibility of using mixtures of vegetable oils with certain solvents of low viscosity is being studied, so that this mixture finally get a suitable value (3–5 cSt) to be used in current diesel engines [393]. Thus, it has been recently described that pine oil (viscosity 1.3 cSt) has been used in mixtures with castor oil to compensate the high viscosity of this oil (226.2 cSt).

In this way, the properties of castor oil and pine oil balance each other, achieving a suitable viscosity for blending in different proportions with fossil diesel [32]. These mixtures exhibit a low cetane number, because of the pine oil, limiting to a 30% by volume the quantity in which they can be blended for being employed in the engine properly. In this way, it has already been described that the use of various compounds, such as eucalyptus oil, orange oil, or camphor oil, which have low viscosity, but also low cetane number or LVLC fuels, for use in double mixtures with oils, or for use in triple mixtures with fossil diesel [394,395]. In this respect, there is an extensive bibliography regarding the use of low viscous vegetable oils blended with several biodiesels to get performance improvement in a diesel engine [396–402]. Furthermore, low viscous vegetable oils improved the performance of biodiesel-fueled CI engine, due to get better fuel properties. In fact, some of these compounds have demonstrated their ability to operate as biofuels either by themselves or in blends with fossil diesel [403–407].

On the other hand, fuel additives are also blended with LVLC compounds to improve their characteristics, such as better ignition, low emissions, enhance the cetane index of fuels, and solve the cold start problem. In this respect, several cetane enhancers like diethyl ether (DEE), dimethyl carbonate, and diethylene glycol dimethyl ether (DIGLYME) have been studied in blends with LVLC fuels and tested in CI engines [408–413].

Within this strategy, the use of quaternary mixtures has been described in blends with diesel fossil. Thus, straight vegetable oils, soybean biodiesel, and higher alcohols, such as propanol and pentanol were evaluated in diesel engines with the purpose of increasing fossil diesel replacement with renewable fuels [414]. Analogously, triple mixtures of vegetable oils, different alcohols, and fossil diesel have been described. Generally, ternary blends of SVO-diesel-alcohol are found to reduce smoke and could be used as potential sources of renewable energy to partially or fully replace diesel fuel [415–431]. The application of bioethanol in the triple mixtures, encounters difficulties due to its limited solubility in both, vegetable oils and fossil diesel. This has been attempted to be resolved with the addition of surfactants [432–438]. However, these triple mixtures work very well with neat castor oil because it has a high affinity for ethanol, due to the high ricinoleic acid amount in castor oil (about 90%), and hence mixes in any proportion without any phase separation. The blending of bioethanol and diesel enhances the combustion of neat castor oil as a fuel, for compression ignition engines, in spite of their high viscosity. Besides, hydroxyl group in the ricinoleic acid enhance ignitability, lubrication, and solubility characteristics of castor oil/ethanol/diesel blends. Considering the renewable nature of bioethanol, these triple mixtures achieve a high level of replacement of the fossil fuel [439–441].

On the other hand, diethyl ether, that can be produced from bioethanol, obtained by a dehydrating process from biomass, may be also considered as a biofuel. This isomer of butanol has several favorable properties for blending with diesel fuel, including very high cetane number, reasonable energy density for on-board storage, high oxygen content, low autoignition temperature, broad flammability limits, and high miscibility with vegetable oils and diesel fossil. Thus, DEE has been recently reported as a low-emission renewable fuel and high-quality combustion improver, for the utilization of several vegetable oils, as a biofuel in blends with diesel fossil [419,442–457]. Similarly, dimethyl carbonate has been used as a component of triple mixtures to reduce the viscosity of straight vegetable oils [458,459]. The strategy has even been applied for using triple mixtures using non-renewable compounds, such as gasoline, capable of reducing the viscosity of vegetable oils. The strategy has even been applied of using triple mixtures using non-renewable compounds, such as gasoline, capable of reducing the viscosity of vegetable oils. In this way, these triple blends allow the substitution of fossil diesel up to 40% with sunflower oil, and up to 25% with castor oil with a significant reduction in the emission of pollutants has also been obtained with these triple blends. [460,461].

In summary, it has been possible to verify that a suitable strategy to reduce the viscosity of vegetable oils to the values required by current CI engines can be the use of mixtures of these oils with low viscosity compounds as biofuels, although they usually present lower energy density, that is, lower octane index. However, since fossil diesel has a lower viscosity than vegetable oils, there will be an adequate percentage for each oil in the triple blends to comply with regulations of the EN 14214 standard.

6. Summary, Conclusions, Challenges, and Research Outlook

Biofuels have emerged as attractive alternative to current petroleum-based fuels, since they allow the replacement of fossil diesel in engines without any modification of the engines. In addition, they also show a favorable profile in the gases emitted in combustion, producing much less carbon monoxide, sulfur dioxide, and unburned hydrocarbons, than fossil fuel. Therefore, biofuels obtained from vegetable oils could play an essential role in replacing the current petroleum-derived fuels, since by being able to directly replace them, they can easily be integrated into the logistics systems that are currently operating in the global system of transport supply. However, in order to apply the vegetable oils in the current CI diesel engines, it is necessary a previous reduction of the viscosity of the oils.

In the current energy scenario, the complete replacement of petroleum-derived fuels with biofuels is practically impossible considering a short or medium term, from the point of view of the impossibility of producing the raw material, not only due to economic difficulties and the high prices of vegetable oils, but also because of the shortage of agricultural land suitable for it. However, energy insecurity and climate change are driving forces of enough entity to stimulate the development of biofuels throughout the world. In any case, this also implies great potential to stimulate agribusiness. Therefore, it is a priority to proceed with the gradual expansion of the currently unproductive land to devote them to the production of inedible vegetable oils in order to advance the gradual introduction of biofuels based on renewable raw materials.

Three decades ago, at the beginning of the energy transition, the most appropriate procedure to reduce the viscosity of vegetable oils was their transformation into a mixture of methyl esters of fatty acids by transesterification reaction of triglycerides. These mixtures were called biodiesel, or FAME, and they have rheological properties that allow their use as fuels in mixtures with fossil diesel in any proportion.

Throughout the following decade, and after the attempt to scale this process to industrial levels, it was found that the process exhibited a series of technical and environmental difficulties, which made this option practically unfeasible, from the technical and economical point of view. The main disadvantage of the transesterification of triglycerides was related to the production of glycerol as by-product, which implies an exhaustive process of cleaning of the biodiesel as well as the production of a huge amount of glycerol difficult to manage. Thus, several researches were initiated to get biofuels where glycerol were incorporated as a derivative in the biodiesel-like biofuel, to make this way viable for the use of vegetable oils as a raw material for obtaining biofuels applicable to current CI diesel engines.

It is also possible that the introduction of vegetable oils as completely deoxygenated renewable biofuels through their transformation into hydrocarbons, through a catalytic reaction that includes hydro processing and/or decarboxylation/decarbonylating of triglycerides to get the so-called green diesel. Finally, in the last decade the study of the mixtures of vegetable oils with different solvents of low viscosity has gained importance as a method to reduce the viscosity of vegetable oils, to the limits required for the proper functioning of current diesel CI engines. In Table 1 shows the summary of the pros and cons of current methodologies for obtaining biofuels, from different vegetable oils, applicable in current internal combustion diesel engines.

Table 1. Highlights of the main characteristics of the current available technologies to produce renewable liquid fuels from vegetable oils.

Biofuel	Biodiesel	Biodiesel-Like Biofuel	Green Diesel	LVLC Blended with Vegetable Oils
Atomic Efficiency	85%	100%	85%	100%
By-products/waste generation	Dirty glycerol (15%)	No wastes	CO, CO ₂ and H ₂ O (15%)	No wastes
Cleaning process	Complex, high water consumption	Not needed	Not needed	Not needed
Cetane Index	Slightly lower than diesel	Slightly lower than diesel	Similar to diesel	Slightly lower than diesel
Lubricity	High	High	Low	High
Industrial production	Complex	Simple	Simple	Very Simple
Environmental impact	High	Low	Low	None

Therefore, the adequate technologies are already available to carry out the process of substitution of fossil fuels, some of them with clear advantages regarding the conventional process of Biodiesel production. In fact, the technology to transform renewable triglycerides into green fuels has been developed in petroleum refineries, throughout the last five decades. However, in the last decade an increasing interest for the optimization of this procedure has been carried out, mainly focused in the search of the best catalysts and the optimal operating conditions for production of hydrogenated green fuels. In this sense, the green diesel can be obtained through the hydroprocessing of oils and fats employing the current facilities of the oil refineries, using the same catalysts and also taking advantage of the same reactors used in the hydrotreating of fossil diesel, therefore becoming a very interesting and economically viable technology. The paraffins thus obtained are high quality compounds, available for distribution immediately, using the current logistics system.

The degree of maturity of the “Green Diesel” obtention process in conventional refineries is quite high. However, this fact should not prevent further researches in the field of biofuels, especially considering the options here discussed for the transformation of triglycerides into renewable diesel without generating glycerol as a byproduct, since a higher atomic yield among other advantages aforementioned can be reached.

In this line, in the field of biodiesel-like biofuels which are practically developed in the last decade, it is noteworthy that the atomic efficiency of 100% is always achieved without generating no wastes. Furthermore, the biofuels obtained do not require any cleaning or refining process for being employed in the current engines. This implies a considerable reduction of the economic production cost if we think at the industrial scale. In fact, the prices for their production are comparatively much lower than that of conventional biodiesel. Another interesting aspect is that all the reagents employed to treat the vegetable oils, e.g., ethanol, acetate, or ethyl carbonate are of renewable nature, because in all cases it can be obtained from bioethanol, that is obtained from different agricultural crops. It also represents an interesting opportunity to spend CO₂, generated in many industrial processes. These processes are being prioritized to contribute to the minimization of such emissions.

The main drawback regarding the production of the biodiesel-like biofuels is, perhaps, the catalytic systems used, which consist on homogeneous alkaline systems or different lipases. Undoubtedly, an interesting field is still open for the search of heterogeneous catalytic systems which overcome the drawbacks of homogeneous ones (neutralization, separation, and cleaning of the product) and also that reduce the economic price of the lipases.

In this sense, perhaps we would have to redirect the efforts made in the last decades from the subject of the catalytic processes of biodiesel production, which has been a trending topic for researchers for many years, reflected in thousands of researches but without finding effective results. This is probably because the difficulty of the process is not the chemical reaction to obtain the biofuel, but to the disadvantages of the unavoidable treatment of the reaction product. Such interesting results are obtained from the interesterification processes with different ethyl or methyl acetates or carbonates, as well as from the selective transesterification processes.

In summary, it would be of great interest to obtain heterogeneous catalysts capable of efficiently perform the interesterification processes that produce glycerol derivatives, together with the methyl or ethyl esters of fatty acids that constitute oils and fats. This would further implement the technical and economic feasibility of already very competitive processes in respect to the conventional biodiesel production. That is, heterogeneous catalysis will be one of the key factors that allow the production of biodiesel-like biofuels.

Finally, we must consider the possibilities that the most recent strategy opens the door to achieve the application of vegetable oils as biofuels in today’s diesel CI engines. The most important objective is to reduce the kinematic viscosity of oils to the appropriate levels in order to comply with the regulations. This fact can be reached by mixing the vegetable oils with low viscosity compounds of different origin. These compounds normally exhibit low values of energy density as well, so they have been called as LVLC compounds. Despite the novelty of this research field, very interesting results have been

already obtained, leading to this methodology becoming one of the best procedures to reduce as much as possible the cost of manufacturing the biofuels of current diesel engines, since it avoids the need to carry out any chemical treatment of vegetable oils.

In this respect, the viability of the process is transferred to the technical and/or the economic accessibility to the LVLC solvent. For this reason, another interesting investigation field is here open. Thus, it has been recently published that even gasoline can operate as an LVLC solvent for castor oil, achieving high fossil diesel replacement values. The incorporation of fossil diesel to these gasoline/oil mixtures produces diesel/gasoline/oil triple blends, which exhibited the suitable rheological properties to be able to operate in conventional diesel engines, allowing the substitution of fossil diesel up to 25%, with a significant reduction in the emission of pollutants.

As a general conclusion, it can be stated that any of the alternative methods proposed in the last decade are able to compete advantageously with conventional biodiesel in order to get a gradual replacement of fossil fuels by others of renewable nature, always considering the necessity of still using the fleet of existing cars, and also taking into account that no design modifications of CI diesel engines will be performed. Therefore, it is mandatory to consider that the biofuel produced, or its mixtures with fossil diesel, must be within the acceptable limits prescribed by ASTM D 6751, currently in force for conventional fossil diesel fuel. It is not consistent to demand a level as demanding as the EN 14214 standard for a biofuel, which would be finally used in a mixture with fossil diesel, with less demanding quality levels. Consequently, it would be advisable that both policy makers and researchers would direct their priorities to the development of these novel processes, instead of the initial alternative, based on the transesterification of triglycerides.

Furthermore, we must not forget that these biofuels will operate in the current engines, although the energy transition have to include vehicles that incorporate electric or hydrogen engines for urban transport. If not, it would be materially impossible to produce the necessary amounts of biofuels to supply the fleet of cars operating with diesel engines, without jeopardizing agricultural resources for feed [462,463]. However, it is not foreseeable even in the long term a scenario in which the explosion or combustion engines are not present operating with biofuels, given that for certain circumstances, electric motors or vehicles capable of using fuel cells cannot compete yet with explosion or combustion engines, especially in the field of heavy trucks, aviation, or the shipping sector [464,465].

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Abbreviations

GHG	greenhouse gas emissions
CI	compression ignition engines
SVO	straight vegetable oils
LVLC	less viscous and lower cetane fuels
FAME	fatty acids methyl esters, components of conventional biodiesel
FAEE	fatty acids ethyl esters, components of conventional biodiesel
DMC	dimethyl carbonate

FAGCs	fatty acid glycerol carbonate esters
GDC	glycerol dicarbonate
GC	glycerol carbonate
PPL	pig pancreatic lipase
MG	monoglycerides or monoacylglycerols
DG	diacylglycerols
TG	triacylglycerols or triglycerides
THC	total hydrocarbons
CO	carbon monoxide
PM	particulate matters
HAP	hazardous air pollutants emissions
DEC	diethyl carbonate
DMM	Dimethoxymethane
GF	formal glycerol
DEE	diethyl ether
DIGLYME	diethylene glycol dimethyl ether

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