



## Review

## Technological challenges for the production of biodiesel in arid lands



D. Luna<sup>a,b,\*</sup>, J. Calero<sup>a</sup>, E.D. Sancho<sup>c</sup>, C. Luna<sup>a</sup>, A. Posadillo<sup>b</sup>, F.M. Bautista<sup>a</sup>, A.A. Romero<sup>a</sup>, J. Berbel<sup>b,d</sup>, C. Verdugo<sup>e</sup>

<sup>a</sup>Departamento de Química Orgánica, Universidad de Córdoba, Campus de Rabanales, Edificio Marie Curie, E-14014 Córdoba, Spain

<sup>b</sup>Seneca Green Catalyst, S.L, Campus de Rabanales, E-14014 Córdoba, Spain

<sup>c</sup>Departamento de Microbiología, Universidad de Córdoba, Campus de Rabanales, Edificio Severo Ochoa, 14014 Córdoba, Spain

<sup>d</sup>Departamento de Economía, Sociología y Política Agrarias, Universidad de Córdoba, Campus de Rabanales, Edificio Gregor Mendel, E-14014 Córdoba, Spain

<sup>e</sup>Laboratorio de Estudios Cristalográficos, Instituto Andaluz de Ciencias de la Tierra, CSIC, Avda. Las Palmeras nº4, 18100 Armilla, Granada, Spain

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## ABSTRACT

It is currently a much debated topic the potential economic benefits of biomass use for biodiesel production in arid lands. In this respect, the main focus has been directed to determine which different plant species are highly adapted and capable to produce significant amounts of triglycerides to be used in the biodiesel industry under arid conditions. However, very few studies have addressed the technological changes that will be needed to convert triglycerides into biofuels without making a large consumption of scarce water, as it is demanded by current technology. Beside, with current conventional transesterification technology, the production of glycerine as a byproduct is also a serious problem because of the large water requirements needed for its removal from biodiesel, before it can be used in motor engines. The main methods commonly employed to reduce the viscosity of vegetable oil in order to be used in diesel engines are its high dilution with petrodiesel (<10%), the breakdown and deoxygenation of the fatty acids from triglycerides through hydrotreating, and the cleavage of the triglycerides into its fatty acid components. In the later case, the cleavage can be carried out with generating glycerine as a byproduct, or by integrating the glycerine in the biofuel using several methods recently developed. The present contribution aims to explain the current state of available technologies for the production of biofuels for diesel engines, with special emphasis on the possibilities of implementing the free or immobilized lipases for the development of new types of biofuels that integrate glycerine, and avoid waste production, that consume valuable and scarce water resources, thus achieving a feasible biofuels production in arid lands.

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## 1. Introduction

Lipid fractions of biomass have been identified as a carbon neutral substitution option for fuels from fossil sources in particular within the transports sector. Although, the diesel engine, invented by Rudolph Diesel over a century ago, first worked with peanut oil, the current combustion engines are designed to run with hydrocarbon fuels derived from petroleum. Therefore, a substitute for diesel fuel from renewable sources will need to have identical or closely similar properties to current petrofuels. The most popular existing technology to process vegetable oils or animal fats is based

on the conversion of triglycerides to fatty acids methyl esters (FAME). Other alternative processing routes are dilution of vegetable oils, emulsification, pyrolysis and hydrotreating (Vyas et al., 2010). The adequacy of each one of these alternatives for its application in the context of arid lands is discussed in this paper.

The composition of fatty acid profile of the vegetable oils it is known that depends on the different species of plants, soil conditions, moisture content of the seeds and the oil extraction method. The fatty acid composition determines its combustion properties, such as oxidation stability, cetane number and specific gravity, as well as its distillation characteristics. Vegetable oils that are rich in unsaturated fatty acids are more prone to oxidation and the formation of sludge on storage for longer period of time. The high viscosities, 10 to 20 times higher than petroleum diesel fuel, exclude the direct use of vegetable oils in fuel engines. Thus, conventional compression ignition engines that are run with vegetable oils are predisposed to suffer many problems because they are

\* Corresponding author. Departamento de Química Orgánica, Universidad de Córdoba, Campus Universitario de Rabanales, Edificio Marie Curie (C-3), Carretera Nacional IV-A, Km 396, E-14014 Córdoba, Spain. Tel.: +34 957212065; fax: +34 957212066.

E-mail address: [qo1lumad@uco.es](mailto:qo1lumad@uco.es) (D. Luna).

designed to run on petroleum diesel fuels. Some of these problems include: coking and trumpet formation on injectors, to such an extent that fuel atomization does not occur properly or is prevented as a result of plugged orifices; carbon deposits; oil ring sticking; thickening, or lubricating problems due to gelling of the lubricating oil as a result of contamination by vegetable oils (Smith et al., 2009).

The use of edible oils to produce biodiesel is not feasible in the short-term because of the increasingly big gap between demand and supply of such oils in many countries. The lack of agricultural lands to grow crops for biofuel feedstocks set limits to its expansion in productive capacity. Thus, biofuels would provide important benefits if their biomass were produced with low agricultural inputs (i.e., less water, fertilizer, pesticide and energy), or if they were produced on marginal lands (Chapagain et al., 2009; Elfeel, 2010), and required low energy input to convert feedstocks to biofuels (Hill et al., 2006). In this connection, it is claimed that plant species highly adapted to arid lands capable of assimilate CO<sub>2</sub> and to produce significant amounts of triglycerides may be good candidates for their use as feedstock in the biodiesel industry. A much debated topic is the potential economic benefits of biomass feedstock's production in arid lands with low agricultural input (de Oliveira et al., 2009; Luna et al., 2009a).

However, very low attention is currently dedicated to study the technological changes that will be needed to develop to achieve the transformation of triglycerides into biofuels without making larger expenses of energy and water, as it is demanded by the existing conventional technology, which is not easily affordable in arid lands. In this sense, the production of glycerine as a byproduct is the main drawback associated to the current conventional technology.

In this regard, it was recently introduced a standard to measure these effects by measuring the water consumption and its withdrawal, related to the production and use of transportation fuels, as the "water intensity", expressed in litre of water per kilometre travelled. Fuels more directly derived from fossil fuels are less water intensive consumers than those derived either indirectly from fossil fuels (e.g., through electricity generation) or directly from biomass. The lowest water consumptive (<0.35 L H<sub>2</sub>O/Km) and withdrawal (<2.35 L H<sub>2</sub>O/Km) rates are for light duty vehicles (LDVs) using conventional petroleum based gasoline and diesel, nonirrigated biofuels, hydrogen derived from methane or electrolysis via nonthermal renewable electricity, and electricity derived from nonthermal renewable sources (King and Webber, 2008). The conclusion is that while biofuels appear to be a mitigation solution for CO<sub>2</sub> emissions, their production may result in high water expenses. This helps to explain why today it is so difficult to replace fossil fuels by renewable ones, even if fossil fuel reserves seem to be coming to end.

## 2. Biodiesel: concept and technological aspects of its production

Biodiesel typically is made by fatty acid (chains C<sub>14</sub>–C<sub>22</sub>) esters of short-chain alcohols, mainly methanol. Several methods have been reported for the production of biodiesel from vegetable or waste cooking oils and/or animal fats including direct use and blending, microemulsification, pyrolysis, and transesterification (Pinto et al., 2005). The high viscosities and low volatilities of oil and fats do not allow their direct use or in oil/petrol blends in any diesel engine type (Dorado et al., 2002), so that the main process developed to overcome this drawback nowadays is the methanolysis reaction to produce biodiesel, a biodegradable, non-toxic diesel fuel substitute that can be used in unmodified diesel engines (Fukuda et al., 2001). This biofuel has a significant added value compared to petrodiesel due to its higher lubricity, which

extends engine life and reduces maintenance costs as well as contributing to fuel economy (Kulkarni et al., 2006). The conventional methodology applied in the production of biodiesel primarily involves the use of NaOH and KOH as homogeneous catalysts. Three molecules of fatty acid methyl esters (FAME) and one molecule of glycerol are generated for every molecule of triglyceride (Ma and Hanna, 1999).

Thus, the transesterification reaction of one mole of triglyceride (TG) with three moles of alcohol produce one mole of glycerol (GLY) and three moles of fatty acid esters, but in fact it constitutes a sequence of three reversible reactions, in which the triglyceride molecule is converted, step by step, first in diglyceride (DG), then in monoglyceride (MG) and finally in glycerol (Gly). At every stage, one mole of alcohol is spent and one mole of fatty acid ester is released. The reaction scheme (Fig. 1) represents the transesterification reaction carried out with ethanol (ethanolysis process).

In the conventional method of biodiesel production, in order to shift the transesterification process to obtain the highest yield, alcohol is used in excess, with respect to the stoichiometric molar amounts. Due to this, two immiscible phases are obtained, a higher phase where the ethyl esters (or methyl), namely biodiesel, and a lower phase where the glycerine is dissolved in the excess of alcohol used. Due to this, the process is far from being environmentally friendly as the final mixture needs to be separated, neutralized and thoroughly washed, generating a great amount of wastes (e.g., salt residues, waste water). The catalyst can neither be recycled. These additional steps inevitably elevate the total overall biodiesel production costs, and reducing at the same time the quality of the glycerol obtained as by-product (Verziu et al., 2008).

Nowadays, alkaline transesterification of vegetable oils is the most attractive and widely accepted methodology for biodiesel production involving the use of homogeneous base catalysts (e.g., NaOH and KOH) under mild heating conditions (50–60 °C) (Van Gerpen, 2005). However, several reports can be recently found on the production of biodiesel involving other chemicals (Zong et al., 2007), the use of heterogeneous base catalysts (Verziu et al., 2008) or solid acids (Al-Zuhair, 2007; Melero et al., 2009) as well as enzymatic protocols as greener alternatives (Ranganathan et al.,

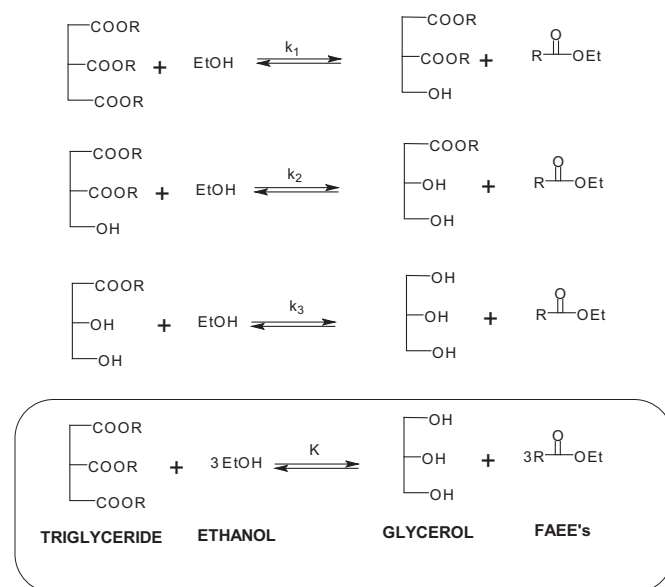


Fig. 1. Outline of the transesterification reaction of triglycerides with ethanol (ethanolysis) by base catalysis.

**Table 1**

Strengths and weaknesses of the available different methods for the production of the mixtures of methyl esters of fatty acids that constitute FAME, the conventional biodiesel.

Technology	Catalyst	Working temperature/°C	Economic charges	Improvements
Basic reaction	NaOH, KOH	60	Low	Available technology
Acid reaction	H <sub>2</sub> SO <sub>4</sub>	55–120	Low	Do not form soaps
supercritical alcohol	–	239–385	Medium	Uses no catalyst
enzymatic process	Lipases	45–55	High	Low level of wastes

2008). In all cases, the purpose of the transesterification process is to reduce oil viscosity and in this respect, the main factors affecting it include reaction temperature, alcohol/oil molar ratio, type of catalyst (and concentration) and purity of reactants (Unker et al., 2010). In any case, an excess alcohol is commonly utilized in the process to produce biodiesel in order to shift the equilibrium to the production of esters and glycerol as main by-product through a stepwise process.

From the different alternatives for biodiesel production already mentioned (Table 1), the transesterification reaction, carried out by homogeneous alkali-catalysed transesterification of vegetable oils

with methanol, using sodium hydroxide, potassium hydroxide or potassium methoxide as catalysts, is the most common technology at present due to its low cost and relative ease of implementation, when environmental costs are not considered (Marchetti et al., 2007).

### 2.1. Base catalysed transesterification process for conventional biodiesel production

The homogeneous basic transesterification reaction shows a very fast kinetic rate, but unfortunately, there are several environmental and economic problems associated with the process. A collateral saponification reaction takes place, reducing the biodiesel production efficiency. To prevent biodiesel yield loss due to the saponification reaction, oil and alcohol must be dry and the oil should have a minimum amount of free fatty acids (FFAs) (less than 1.0% wt). Biodiesel is finally recovered by repeated washing with water to remove glycerol, soap and excess of methanol.

Almost all biodiesel is currently produced using base catalysed transesterification processes, as it is the most economical one and require only moderate temperatures and pressures, with yield efficiency around 98%, (Achten et al., 2008; Chitra et al., 2005; Tiwari et al., 2007). Methods commonly used for producing biodiesel are batch and continuous processes. In general, smaller capacity plants and variable feedstock quality warrant use of batch systems (El Diwani et al., 2009, Fig. 2).

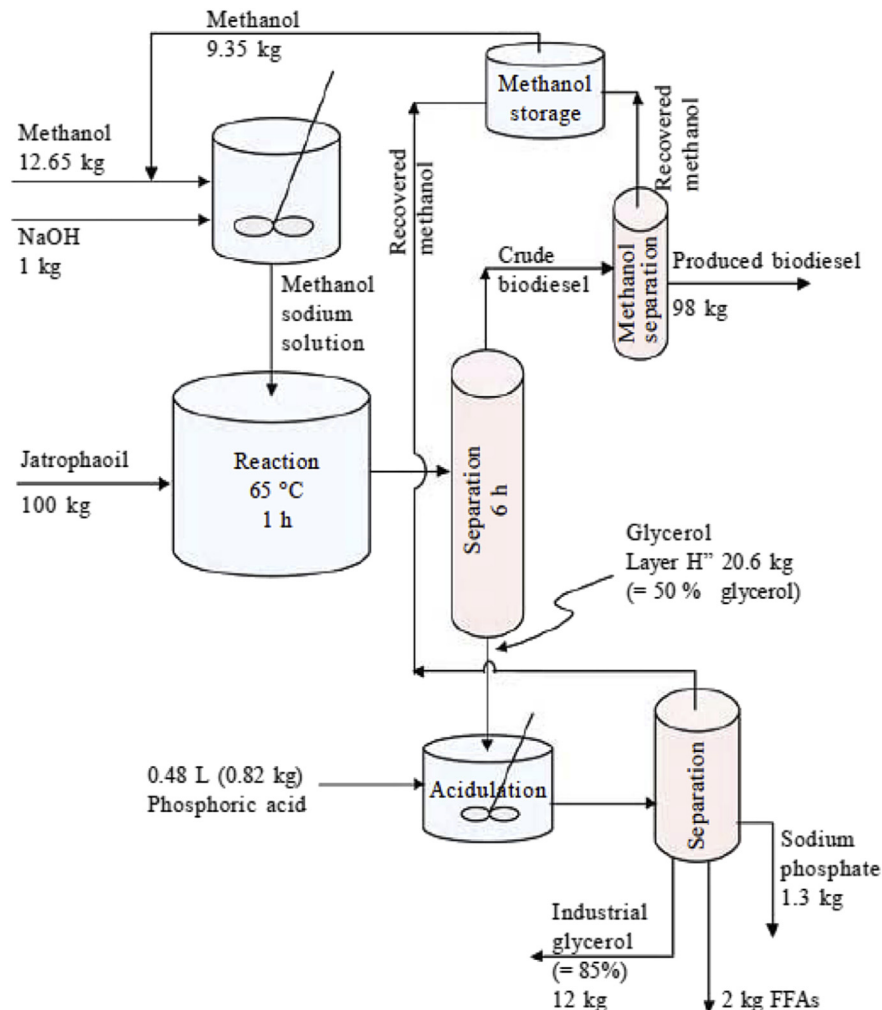


Fig. 2. Pilot scale material balance for Jatropha oil transesterification using NaOH (1%) as catalyst (El Diwani et al., 2009).

In large capacity plants, Lurgi's transesterification process is the most widely used (Lurgi, 2004a,b). Lurgi, a German company, offer biodiesel plants in sizes from 100 to 1000 tpd (tonne per day). The process involves intensive mixing of methanol with the oil in presence of a catalyst, and then separation of lighter methyl ester phase by gravity from the heavier glycerol (Fig. 3).

Oil, methanol and sodium methylate catalyst are mixed in **Reactor 1** and allowed to separate into two phases. The lighter methyl ester/oil phase is mixed with additional methanol and catalyst in **Reactor 2** followed by gravity separation. This second reactor stage maximizes the biodiesel yield and quality. The lighter phase is washed with water to remove residual glycerol or methanol dissolved in the ester phase, followed by vacuum drying to yield biodiesel. The glycerol phase from **Reactor 2** containing excess methanol and catalyst is recycled to the front end of **Reactor 1**. The glycerol phase leaving **Reactor 1** still containing excess methanol is distilled for its recovery in the Methanol Recovery Column and sent back to **Reactor 1**. The wash water from the Water Wash Column is used in the Methanol Recovery Column. Thus the entire methanol is consumed in the production of methyl ester. The heavier fraction from the Methanol Recovery Column is processed in the Glycerine Water Evaporation Column to recover crude glycerine (concentration 80–85%) as a byproduct. This can be further upgraded to pharmaceutical glycerine by distillation, bleaching, if required, and vacuum drying. Thus, the key features of Lurgi's biodiesel process are:

- A technology applicable to multiple feedstocks.
- A continuous process at atmospheric pressure and 60 °C.
- A dual Reactor System operating with a patented Glycerine Cross flow configuration for maximized conversion.
- Recovery and recycling of methanol.
- Closed loop water wash recycle to minimize waste water.
- Phase separation by gravity process (no centrifuges needed).

Although the transesterification process is quite straightforward, different kinds of oil might require modification of the input ratios of the alcohol reagent and reaction catalyst as well as variations in reaction temperature and time, in order to reach optimal biodiesel production results (Achten et al., 2008). The optimal amounts for the transesterification of conventional oils (1–3% free fatty acids) are estimated at around 20% methanol (by mass relative to oil), representing a molar ratio methanol/oil of 5.5/1, with NaOH 1.0 wt% respect to the oil, thus achieving maximum FAME performance after a reaction time of 90 min at 60 °C (Chitra et al., 2005). Optimal conversion for another oils with high free fatty acids (14%) and high acid number (28 mg KOH g/l) need a pretreatment

reaction with methanol (molar ratio methanol:oil 6.5:1) using H<sub>2</sub>SO<sub>4</sub> as catalyst (1.43%) during 88 min at 60 °C. After this pre-treatment a conversion rate larger than 99% can be achieved by transesterification with methanol (molar ratio methanol:oil 4:1) and 0.6 wt% KOH during 24 min (Tiwari et al., 2007). Thus, the quality of feed vegetable oil, particularly FFA content plays an important role to determine the most suitable process.

In summary, in this process neutralized vegetable oil and methanol are reacted in a two-stage mixer/settler arrangement in the presence of catalysts. The glycerine produced in the reaction is dissolved in the surplus methanol and can be recovered in a rectification column. Most of the glycerine and methanol are removed from the methyl ester in a counter current scrubber. Higher amounts of energy and materials will be required if pre-processing is necessary to reduce the free fatty acid content or to produce pharmaceutical quality glycerine. In cases where FFA content of the oil is above 1%, difficulties arise due to the formation of soap, which promotes emulsification during the water washing stage. If the FFA content is above 2%, the process becomes unworkable. Then, an acid pre-treatment is often needed in the homogeneous alkaline transesterification for oils having more than a 5 wt % of FFAs in order to improve the biodiesel efficiency production (Fukuda et al., 2001; Ma and Hanna, 1999; Meher et al., 2006).

On the other hand, removal of alkaline (NaOH or KOH) homogeneous catalysts after the reaction imposes an additional technical difficulty and massive amounts of waste water are produced during the separation and cleaning of products. In this respect, a little amount of glycerine as well as some residual homogeneous catalyst remains emulsified in biodiesel, so that it is necessary to carry out successive washing processes with water to obtain an adequate biodiesel (less than 0.02% glycerine). It is considered to be necessary the use of 4–7 times as much water for a given biodiesel volume, for cleaning. In order to recovery such volume of water, by distillation at low pressure, it would be necessary not only a complex infrastructure but also a high amount of energy, thus increasing economic and energy costs of the process.

The cleaning of even small amounts of glycerol from a biofuel is necessary because of its reaction with oxygen at high temperature inside the engine chamber that could produce dehydration towards acrolein that can be polymerized thus causing serious problems, including coking as well as an increase in the viscosity of the fuel. Coking can also generate deposits of different carbon compounds on the injector nozzles, pistons and valves in standard engines, thus reducing its efficiency (Mittelbach, 1996; Mittelbach and Remschmidt, 2005).

As the use of heterogeneous catalysts, which can be separated relatively easily, can eliminate these disadvantages, many

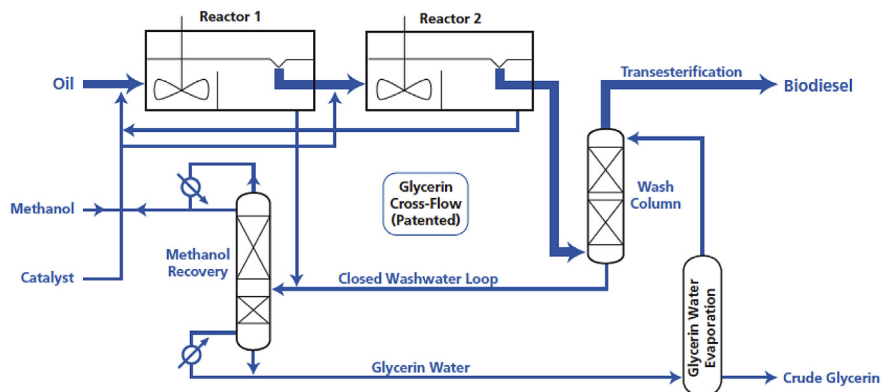


Fig. 3. Lurgi transesterification process.

researchers have studied heterogeneous alkali catalysed processes and solid base catalysts to replace the conventional process (Meher et al., 2006; Verziu et al., 2008). However, those processes require much longer reaction times (up to 24 h) and the conversion is usually lower than the one obtained with homogeneous base catalysts (Zhu et al., 2006). Consequently, the most common biodiesel manufacturing technologies suffer from problems associated with the use of homogeneous catalysts in batch or continuous processes where both reaction and separation steps can create bottlenecks leading to severe economical and environmental penalties, so that current novel reactive separation technologies are being developed for biodiesel production: reactive distillation/absorption/extraction, and membrane reactors (Kissa and Bildeab, 2012). Reactive–separation processes are based on esterification or transesterification reactions carried out in the presence of liquid or solid catalysts in integrated units such as: reactive distillation/absorption/extraction or membrane reactors that conveniently combine reaction and separation into a single unit allowing the simultaneous production and removal of products, thus improving the productivity and selectivity, reducing energy use, eliminating the need for solvents and leading to intensified, high efficiency systems with green engineering attributes.

## 2.2. Acid catalysed transesterification process

Transesterification reactions catalysed in acid medium are not as common as reactions carried out in basic medium because their reaction times are much longer. However, this reaction has the advantage of not being affected by the presence of free fatty acids, because this process consists in two reactions of esterification and transesterification simultaneously (Kulkarni et al., 2006). The catalyst used is usually  $\text{H}_2\text{SO}_4$  (sulphuric acid) and the concentration varies between 1 and 5 wt%. High concentrations of  $\text{H}_2\text{SO}_4$  can promote a higher conversion, but an excess can also promote the formation of ethers by dehydration of alcohols. Furthermore, it is needed to operate at higher temperatures to achieve high conversions in a lower time. For example, in the case of soybean oil, catalysed with 1 wt%  $\text{H}_2\text{SO}_4$ , when the operating temperature is 117 °C a full conversion can be achieved in 3 h, whereas at 77 °C the time is increased up to 20 h (Lotero et al., 2005). In summary, drawbacks of an acid homogeneous transesterification include the use of corrosive catalysts ( $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ , HCl) and slow reaction rates. Besides, high conversions only may be obtained with increasing temperatures and pressures, thus involving increased

costs (Meher et al., 2006). Solid acid catalysts also are currently under study (Jacobson et al., 2008).

## 2.3. Supercritical alcohol technology

The use of supercritical alcohol is another process that has the advantage that no catalyst is used to carry out the reaction (Kiwjaroun et al., 2009; Patil et al., 2010). Methanol is used instead, with low cost but operating under extreme conditions of temperature and high pressure. Besides a very high ratio of alcohol–oil (42:1) is used. Under supercritical conditions (350–400 °C and  $P > 80$  atm) the reaction is completed in 4 min. The costs of installation as well as energy consumption operation are very high, so that although the results of this process may be adequate and faster, the building of an industrial plant with this technology can be actually very expensive.

## 2.4. Lipase-mediated conversion of vegetable oils into biodiesel

The increasing environmental concerns have led to a growing interest in the use of enzymatic catalysis as it usually produces a cleaner biodiesel under milder conditions (Al-Zuhair, 2007), and less waste than the conventional chemical process. Many reports on biodiesel production using free lipases (Royon et al., 2007); or immobilized lipases can be found (Hsu et al., 2002; Macario et al., 2007; Ranganathan et al., 2008). The major drawback of the process is its high cost. Another limitation of the enzymatic method compared to the conventional base catalysed process deals with the alcoholysis of the 2-fatty acid esters of glycerol. Lipases have indeed a peculiar 1,3-regioselectivity which means that they selectively hydrolyse the more reactive 1 and 3 positions in the triglyceride (Bornscheuer, 1995).

In this regard, the production of biodiesel using lipases needs to take into account such specificity character (Li et al., 2008). In general, the challenging full alcoholysis of triglycerides involves long reaction times and gives conversions lower than 70% wt in fatty acid methyl or ethyl esters (Hernandez-Martin and Otero, 2008). A series of improvements in conversion levels and/or the use of methanol as alcohol to get results similar to the base catalysed transesterification reaction are currently ongoing as a consequence of legal regulations for biodiesel (EN 14214). Reasonably good results are sometimes reported due to the 1,2-acyl migration in the monoglycerides (Du et al., 2005).

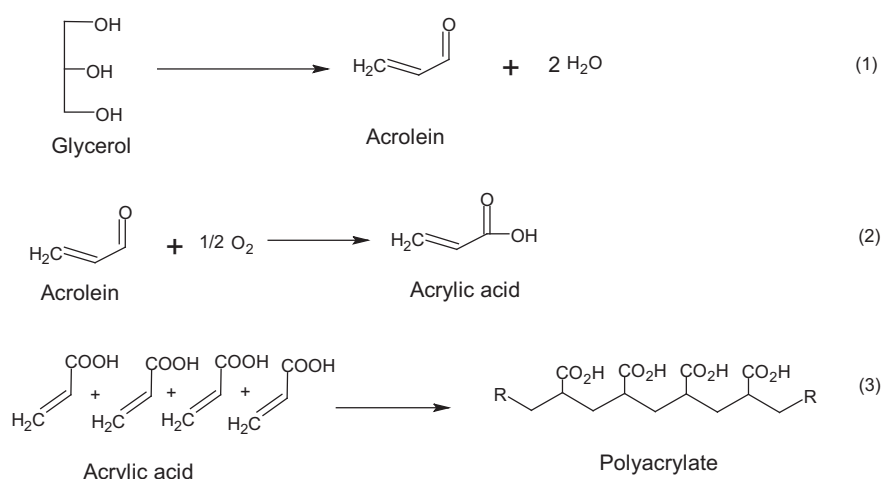
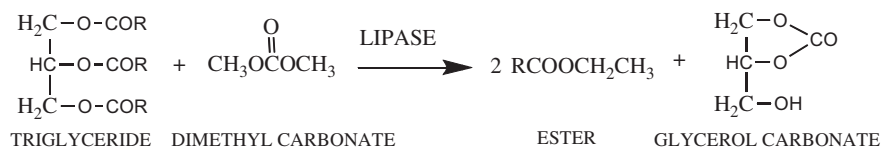


Fig. 4. Processes of Dehydration (1), Oxidation (2) and Polymerization (3), undertaken by the residual glycerol in the biodiesel, inside the engines working at higher temperatures.



**Fig. 5.** DMC-BIOD<sup>®</sup> is a patented biofuel (Notari and Rivetti, 2004) that integrates the glycerine as glycerol carbonate, in a process that can be developed by enzymatic technology (Su et al., 2007).

### 3. New biofuels that save water in its manufacture by integrating glycerine as a derivative that enhances its lubricant power

Regardless of the procedure for obtaining the so-called conventional biodiesel (EN 14214), in all cases glycerine is obtained as a byproduct (Fig. 1), representing a notable loss in the performance of the process. Production of new biodiesel that integrate the glycerine as an alternative product mixed with FAME is currently a target, given that the market is already flooded by the production of glycerine, precisely obtained as a by-product in the current manufacture of biodiesel (Behr et al., 2008; Corma et al., 2007). These biofuels not only could prevent the generation of waste but also they would get increased yields of the process, always higher than nominal 10%, by incorporating some derivative of glycerine in the reaction products.

The absence of glycerine would avoid the washing and cleaning step in the biodiesel process to comply with EU standards (up to 0.02% glycerol EN 14214), as well as an important saving water and reducing costs (Van Gerpen, 2005). Furthermore, the presence of even little amounts of glycerol in biodiesel need to be avoided because of its reaction ability with oxygen at high temperature producing dehydration towards acrolein that can be polymerized thus causing various problems, including coking (Fig. 4) that generates carbonaceous deposits on the injector nozzles, pistons and valves in engines, thus reducing its efficiency (Mittelbach, 1996; Mittelbach and Remschmidt, 2005).

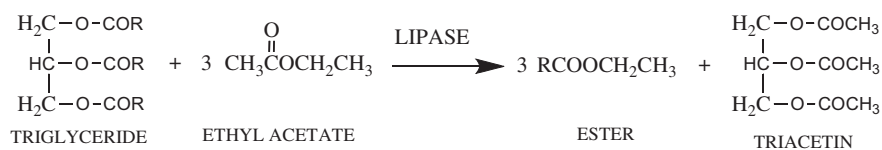
Several recent studies (Hu et al., 2005; Knothe 2006, 2008, 2009; Knothe and Steidley, 2005, 2007; Knothe et al., 2005, 2009; Lapuerta et al., 2010; Suarez et al., 2009; Wadumesthrige et al., 2009) have shown that minor components of biodiesel like free fatty acids and monoacyl glycerols (usually considered contaminants under the standard EN 14214), are essentially the main responsible for the increased lubricity of low-levels blends of biodiesel and petrodiesel. Lubricity is a very important feature of biofuels, which improves performance and preserves the life of engines. The presence of greater quantities of monoglycerides (MG) or some derivatives enhances the lubricity of biodiesel.

Accordingly, novel methodologies to prepare esters from lipids (FAME or FAEE), which generate in parallel a number of co-products from glycerine, which will be integrated in the biofuel, are currently under development (Adamczak et al., 2009). Thus, the transesterification reaction of triglycerides with dimethyl carbonate (DMC) under catalytic conditions is being studied (Fabbri et al., 2007; Kenar et al., 2005; Notari and Rivetti, 2004; Renga and

Coms, 1993; Zhang et al., 2010a), as well as under supercritical and/or non catalytic conditions (Ilham and Saka, 2009, 2010, 2011, 2012; Tan et al., 2010a) because it produces a mixture of three molecules of the FAME or FAEE and a molecule of glycerol carbonate (GC) (Fig. 5). That mixture (FAME + GC), has physical properties suitable for use as a fuel, so it has been patented as a new biofuel called the DMC-BIOD (Notari and Rivetti, 2004) that can be also accessible for enzymatic technology (Kim et al., 2007a; Min and Lee, 2011; Seong et al., 2011; Su et al., 2007; Zhang et al., 2010b). This methodology based on the production of glycerol carbonate (GC) by transesterification of oils with dimethyl carbonate is currently being studied by using several lipases, basic catalysts and/or under supercritical conditions due to the great interest in avoid the glycerin as a secondary residue in the biodiesel production.

In a similar way, transesterification reaction of triglycerides with methyl acetate (Campanelli et al., 2010; Demirbas, 2008; Du et al., 2004; Kijenski, 2007; Kijenski et al., 2004; Orçaire et al., 2006; Saka and Isayama, 2009; Tan et al., 2010b; Usai et al., 2010; Xu et al., 2003, 2005) or ethyl acetate (Kim et al., 2007b; Modi et al., 2007) produced a mixture of three molecules of FAME or FAEE and one of glycerol triacetate (triacetin). Such mixture constitute the Glycerol, another patented novel biofuel (Kijenski et al., 2004). It is composed of a mixture of three molecules of FAMES and one molecule of triacetin and it can be obtained after the transesterification of one mol of TG with three moles of methyl acetate employing lipases as catalysts (Du et al., 2004; Xu et al., 2003, 2005). When ethyl acetate is used (Modi et al., 2007; Jeong and Park, 2010) the corresponding FAEE with triacetin are obtained, following an enzymatic process (Fig. 6). When Novozyme 435 lipase was used, conversions above 90% were reported for oils such as jatropha, karanj and sunflower oil. Specific studies on the performance of biodiesel quality standards when triacetin is present in the biodiesel have proven that there would not be any restriction for amounts of up to 20 wt% according to the American Society for Testing and Materials (ASTM) D6751 guidelines (Casas et al., 2010).

On the other hand, we have recently developed an enzymatic protocol for a novel biofuel that integrates glycerol into their composition via 1,3-regiospecific enzymatic transesterification of sunflower oil using pig pancreatic lipase (PPL) (Caballero et al., 2009; Luna et al., 2009a, 2009b, 2012; Verdugo et al., 2010). Our results obtained using lipases in both free and immobilized form are revealing so far obtaining the 1,3 selective transesterification of TG to produce the corresponding 2-monoacyl derivatives of glycerol (MG), and two moles of FAEE, the ethyl esters of fatty acids,



**Fig. 6.** Glycerol<sup>®</sup> is a biofuel patented by the Industrial Chemistry Research Institute of Warsaw (Poland) (Kijenski et al., 2004), consisting of a mixture of three moles of FAME or FAEE and a mole of triacetin, that can be obtained by the cross transesterification of ethyl acetate and the corresponding triglycerides in an enzymatic catalysed process (Modi et al., 2007).

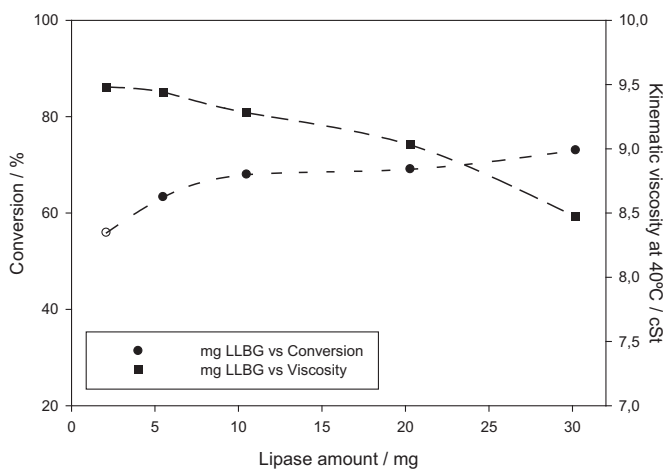


Comparatively, most studied lipases are intracellular materials obtained from bacteria or fungi, so that optimum operation conditions employed in such cases are close to neutral pH conditions.

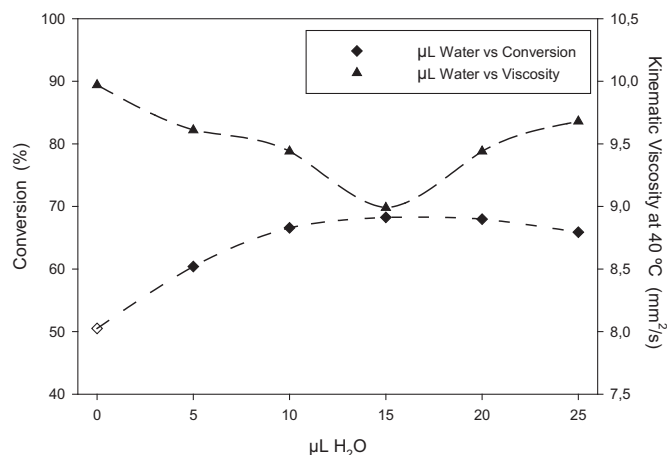
Existing limitations for the use of industrial lipases have been their high production costs, which can be overcome through the application of molecular technologies to achieve the production of enzymes purified in sufficiently high quantities. In addition to the high cost of lipases for the production of biodiesel, the real constraint of the enzyme method is its ability to produce the 2-fatty acid esters of glycerol. This is due to the 1,3-regioselective character of many lipases, which means that they selectively hydrolyse positions 1 and 3 of triglycerides (Bornscheuer, 1995; Li et al., 2008). However, we claim that it is precisely this 1,3-regioselective character that finishes the process when MG is obtained, that will allow us to get new biofuels in a very short reaction time. Thus, the research on the catalytic behaviour of the cheapest commercial lipases may be a promising route to improve the enzymatic methodology to obtain Ecodiesel.

Other very interesting results have been obtained with a purified 1,3-specific lipase from *Thermomyces lanuginosus* (Lipopan 50 BG from Novozyme), mostly used as bread emulsifier (Moayedallaie et al., 2010), evaluated as low cost 1,3 selective biocatalyst in the ethanolysis of sunflower oil for the production of biodiesel that integrates glycerine as MG (Verdugo et al., 2011). In this case, the optimization of the reaction parameters in the solvent free enzymatic transesterification process was carried out by the Response Surface Methodology (RSM), with temperature, pH, oil/ethanol ratio as well as the effect of the amount of lipase in the reaction media being researched. We found that a small amount of commercial lipase is able to get high conversion values (Fig. 8). Besides, at the optimal values obtained from RSM, the influence of water content is studied (Fig. 9).

We showed that, in order to obtain an improvement in conversion efficiency and kinematic viscosity of the transesterification of sunflower oil with ethanol in solvent free conditions, it is necessary to operate at a lower temperature (20 °C), pH near to 12, and oil/ethanol volume ratio of 12/3.5, respectively with a definite water concentration in the interval 10–15  $\mu\text{L}$  in 12 mL of oil, that is about 0.1 wt% of water in oil. Higher water amounts reduce strongly the lipase activity in the alcoholysis process. In this respect, water activity ( $a_w$ ) has been recognized as key parameter which determines the enzymatic activity (Salis et al., 2005). Physical properties of enzymes have been shown to change depending on the hydration state of the proteins, influencing the measured reaction



**Fig. 8.** Influence of lipase (from *Thermomyces lanuginosus*) amount in conversion and kinematic viscosity, of reactions carried out at oil/ethanol volume ratio 12/3.5 and pH near to 12, and 20 °C of reaction temperature.



**Fig. 9.** Influence of water content in conversion and kinematic viscosity of reactions carried out with 0.03 g of lipase (from *Thermomyces lanuginosus*), at oil/ethanol volume ratio 12/3.5 and pH near to 12, and 20 °C of reaction temperature.

rates. However, the way this phenomenon affects enzyme kinetics in detail is not known. Reaction media with  $a_w < 0.5$  has been reported to provide the highest conversions to methyl esters in the immobilized lipase-catalysed production of biodiesel from restaurant grease using *Thermomyces lanuginosus* and *Candida antarctica* lipases (Hsu et al., 2002).

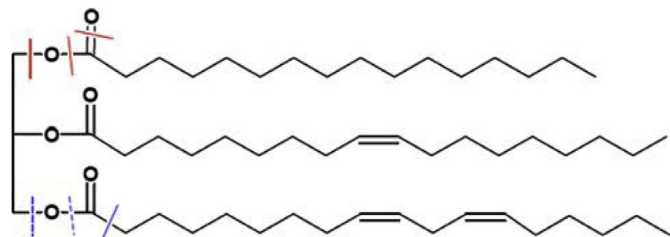
In summary, when reactions were carried out under optimum conditions, it was possible to obtain a new kind of biodiesel constituted by a mixture of monoglycerides and FAEs (1/2 nominally), that can be used in different blends with petrodiesel. This new biofuel can be obtained at very short reaction times (50 min) under soft reaction conditions, with a comparatively higher conversion than conventional biodiesel reaction (because no glycerine byproduct is generated), but also it can be used directly after its production because it is not necessary a purification step of residual glycerine minimizing wasting of scarce available water under arid conditions.

#### 4. New biofuels obtained by hydroprocessing of oils and fats in the current oil refining plants. Hydrobiofuels: hydrobiodiesel, biogasoline and bioLPG

Another way to use feedstocks derived from renewable material in conventional automobile engines, avoiding the presence of glycerine, is through converting the biomaterials into hydrocarbons, similar to fossil derived fuels. It has already been known how to convert vegetable oils into paraffin's in the gasoline or diesel boiling range by a hydrotreating process (Corma et al., 2007; Donniss et al., 2009). In hydrotreating, the renewable organic material is reacted with hydrogen at elevated temperature and pressure in a catalytic reactor. This is often referred to as renewable diesel or 1½ generation biodiesel (Donniss et al., 2009).

The large advantage of hydrotreating seed oils relative to the use of FAME biodiesel (methyl and other esters of fatty acids) is the fact that the final products from the simple hydroprocessing (simple alkanes) are the same components as those present in normal fossil diesel, whereby the problematic and limiting filter plugging and cold flow properties of FAME biodiesel in the temperate part of the world are minimized. However, there is a significant loss of raw material since the oxygen present in the triglyceride is removed as  $\text{CO}_2$  and  $\text{H}_2\text{O}$  (Donniss et al., 2009). One mechanism involves a simple hydrogenation or hydrodeoxygenation (HDO) reaction (Fig. 10), which is described via an adsorbed enol intermediate and produces water, propane and three normal alkanes of the full





**Fig. 10.** Schematic representation of the two different reaction pathways in the hydrotreating process for the removal of oxygen in triglyceride molecules. Unbroken red lines indicate hydrodeoxygenation (HDO) reaction and the blue lines show decarboxylation or  $\text{CO}_2$ -elimination.

length of the fatty acid chains of the used oil n-C18 and n-C22. By this reaction, for rapeseed oil, assuming four double bonds/mole, one mole of triglyceride reacts with 16 mol of hydrogen and forms six moles of water, one mole of propane and three moles of a mixture of n-C18 and n-C22. By the other mechanism, which is usually called decarboxylation or  $\text{CO}_2$ -elimination, the triglyceride is broken down into propane, carbon dioxide and/or carbon monoxide and into an n-alkane one C-atom shorter than the total length of the fatty acid (Fig. 10). For rapeseed oil, the products of the n-alkane are n-C17 and n-C21.

Furthermore, the hydrotreating process consumes large amounts of energy, compared with the processes of transesterification. However, an important strong point of this technology is the possibility of applying existing petrochemical facilities, so that non investment would be required to be able to immediately start the production of biofuels from any renewable sources of triglycerides. Thus, an alternative technology to transform the triglycerides obtained from renewable sources is to carry out their processing in conventional oil refineries, together with the relevant portions of heavy crude oil of equivalent molecular weights. Thus, the production of high quality diesel fuel from vegetable oils has been described (Huber et al., 2007) by hydrocracking of triglycerides treated with high molecular weight hydrocarbons in conventional oil refineries.

In this way, renewable liquid alkanes can be produced by treatment of mixtures of vegetable oils and fractions of heavy oil vacuum (HVO), in flows of hydrogen and conventional catalysts, sulphured NiMo/ $\text{Al}_2\text{O}_3$ , and many others (Corma et al., 2008) under

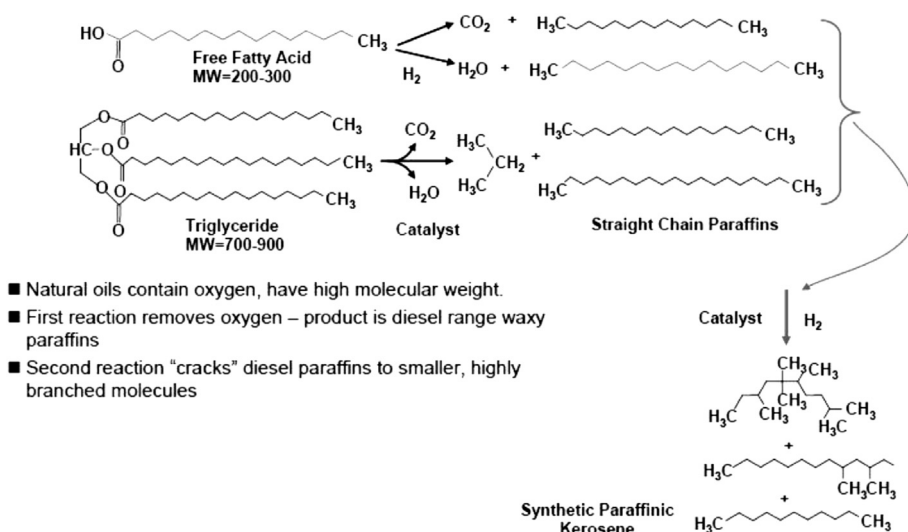
standard conditions of temperature (300–450 °C). The reaction produced involves hydrogenolysis of C–C bonds of vegetable oils, which leads to a mixture of lower molecular weight alkanes by three different routes: decarbonylation, decarboxylation and hydrodeoxygenation (Fig. 11).

In summary, the hydroprocessing route uses hydrogen to remove oxygen from the triglyceride molecules. The oxygen is easily removed via two competing reactions: decarboxylation and hydrodeoxygenation. The extent for each reaction depends on the catalyst and process conditions. The three-carbon backbone in the process to produce green diesel yields propane, which can be easily recovered and can be a valuable renewable LPG product in its own right. The oxygen contained in the feed is rejected either as carbon monoxide (CO)/carbon dioxide ( $\text{CO}_2$ ) or water ( $\text{H}_2\text{O}$ ). In addition, all olefinic bonds are saturated and produce a consistent, pure-paraffin products blend of variable composition, that in the secondary reaction, described in Fig. 11, suffer a cracking process where the initial diesel paraffin's are cracked to a smaller ones highly branched molecules that obviously will be separated in the three main components as those obtained in fossil diesel, according to their molecular weigh: propane and high ends, naphtha or jet fuel and diesel products (Fig. 12).

Taking into account their renewable nature, a variable composition of bioLPG, biogasoline and hydrobiodiesel (or H-biodiesel) is always obtained after the hydrotreating of vegetable oils. Thus, some amount of raw material is lost as  $\text{CO}_2/\text{CO}$  and water, and also a variable proportion of low molecular weigh hydrocarbons is always obtained besides to the H-biodiesel, so that the yields is necessarily lower in this biofuel that when it is applied the transesterification route. Thus, by this route a new category of renewable Hydro-biofuels are currently obtained and being commercialized as Hydrobiodiesel, biogasoline and bioLPG, all they also are sometimes named "Hydrobiofuels or biorefinery biofuels" despite of being obtained in conventional current refineries.

## 5. Concluding remarks

Regarding the introduction of renewable energies, in most cases we find today with an uncomfortable truth: currently available technologies require excessive amounts of water that makes them unsuitable for arid lands. This happens with solar power, clean coal and of course with biofuels. Therefore, in the absence of a major



**Fig. 11.** Production of high-quality biofuel from vegetable oils through removal of oxygen in triglyceride molecules by overall hydrotreatment in conventional refineries.

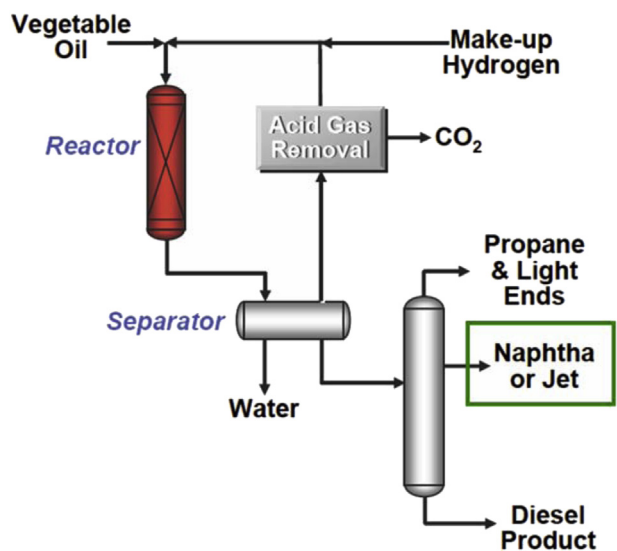


Fig. 12. Composition of the high-quality biofuels obtained from vegetable oils through the hydroprocessing routes to transportation fuels in conventional refineries.

technological advancement in these technologies a predictable scenario is one in which water availability would be a real limiting factor in the production of biofuels in arid lands, more important even than those due to production capability of crops from where raw materials are obtained (Dominguez-Faus et al., 2009).

The problem is that in the next decades fossil supplies will be increasingly lower. In this future scenario, the results of King and Webber (2008) seems to support that nonirrigated vegetable oils could offer a better integration within crude-oil refineries for fuels blending after hydrotreating in flows of hydrogen with conventional catalysts (Corma et al., 2008). As a first step, the introduction of fuels based upon feedstocks other than petroleum will be smooth and gradual, providing a production of the same commodities currently demanded but considering their renewable character are now named Hydrobiodiesel, biogasoline and bioLPG, respectively.

Several additional advantages over conventional FAME production are obtained with the H-biodiesel (or hydrobiodiesel) processing technology when it is integrated within a current crude-oil refinery setting. Hydrogen required for the reaction is actually readily available, and all olefinic bonds are saturated and produce a consistent, pure-paraffin product. In addition, all reaction products are compounds that are found in normal refinery products and do not require any special handling, so that the hydrocarbon products can all be easily blended with conventional refinery products.

However, the hydrotreating process of oils or fats, regardless of its yield in hydrocarbons, even if considering a quantitative conversion, the proportion of hydrobiodiesel always be less than that obtained from a conventional alcoholysis process, despite the lost of 10% of the raw material, which is transformed in glycerine. This is due to a cracking process obtained in the secondary reaction (Fig. 11) where the initial diesel paraffin's are broken to a smaller highly branched molecules that obviously will be separated to be used as propane and light ends, as well as like gasoline's, naphtha's or jet fuels (Fig. 12). Thus, in any case H-biodiesel paraffin's never exceed 60–70 wt% relative to vegetable oils used as raw materials.

Therefore, if biodiesel fuel is the target, it is more appropriate to use a process of alcoholysis of oils or fats. This fact could be more relevant to consider for the convenience of the alcoholysis of triglycerides compared to their hydrotreating process, than other aspects such as the lowest energy cost of the process, since the reactions of hydro-treatment is carried out at 350–400 °C, under hydrogen flow on catalysts, usually highly priced. Indeed, the

current trend is to increase the consumption of diesel fuel at the expense of gasoline, as happens in the EU where the number of diesel engines is currently far exceeding those of gasoline.

Moreover, the logistical problems associated with the transport of oils and fats, for its treatment in conventional large scale refineries, can also be decisive in selecting the processing in a specific plant for the transesterification process. In water-scarce regions a water saving process that integrates the glycerine into the biofuel will be required to use, because these technologies hardly need water to operate.

Every one of these available technologies for the production of biofuels applicable in diesel engines, are currently being the subject of legal regulation in many developed countries, in order to encourage the gradual replacement of oil as the sole source of fuel for automobiles, as the recent legal regulation made in UE (Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009, on the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC) or in Spain (Order published in the BOE 16487/ITC/2877/2008, 9 October by the Ministry of Industry, Tourism and Trade) to "encourage the use of biofuels and other renewable fuels for transport purposes", as is recognized in the preamble of that Order.

On the other hand, the synthesis of new biofuels that integrate the glycerine consist in the reaction of the oil, used as raw material, with any of the specific reagents considered (diethyl carbonate, ethyl acetate or ethanol, respectively) in a stirred tank with specific catalyst (which actually may be a lipase) or supercritical conditions. In the first case, the reactions are carried out at moderate temperatures, never above 60 °C, it is not necessary the recovery of any reactive and washing operation of the biofuel is not required. Therefore, after the reaction (even in the case where quantitative conversion is not achieved), the product obtained (along with the remains of reagents and raw materials that has not been processed), is ready for use as biofuel. With any of these processes LDV values will be exclusively due to the process of obtaining the corresponding reagent (dimethyl carbonate, methyl acetate and ethanol, respectively), but not by the biofuel synthesis process taking into account that this process does not include any operation of cooling or biofuel washing.

Among the three alternative technologies currently available for the synthesis of new biofuels that integrate the glycerine, that which is based on the selective production of monoglycerides is technologically the simplest and less demanding in water and energy because ethanol, the reagent used in this case, is clearly much less expensive and easier to obtain than diethyl carbonate or methyl acetate, which are the reagents used by the other alternative technologies.

The currently available experimental results (Verdugo et al., 2011) show that by using pig pancreatic lipase (PPL) or another lipases available on an industrial scale with low prices, as Lipopan BG, from Novozymes®, can let obtain new useful biofuels in diesel engines, like the Ecodiesel-100®, consisting in mixtures 2/1 of FAEE/MG, with a low energy spending and without consuming any water. This technology that integrates glycerine as monoglyceride, can also be applied to a very small production scale and with a minimal investment, compared with current oil refineries, so that it could be installed in areas close to where crops are produced (the biofuel plant is become actually in an additional treatment after the oil extraction of crops), so that it become clearly more competitive than the hydrotreating technology for biofuel production in arid and semi-desert areas of low productivity and geographically dispersed, where logistical problems are particularly limiting.

The development and maturation of these new technologies, that produce biofuels for engines that not generate unwieldy

glycerine and water waste which in turn requires its total elimination from the biodiesel process, increasing costs and waste of water and energy, it is expected to boost the use of biofuels in arid lands, and thus create a scenario for creating opportunities for small and medium enterprises for producing biofuels in very diverse geographical areas, including semi-arid and arid lands. These processes will make possible the cultivation of plants suitable for its “in situ” transformation into biofuels, so that agriculture can play an increasingly important role in the production of new crops in arid lands capable of supplying biofuels for industrial and energy sectors that now are completely dependent on petroleum.

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