ANIMAL FATS FOR BIODIESEL

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Abstract

This study was paying attention to several articles in major magazines to find knowledge about biodiesel as an important and renewable fuel for the solution of environmental problems. Besides, advantageously, it may replace diesel. We also looked for information regarding animal fat as a raw material that can produce biodiesel, its advantages when using this raw material, the animals that are usually used to produce biodiesel from their fat. Reactions used to produce biodiesel from animal fat, catalysts used in these reactions, and social advantages provided when producing biodiesel from animal fat are also presented.

Palabras claves: *Biodiesel; Animal Fat; Catalysts.*

Introduction

Biodiesel is currently accepted as a valid contributor to reduce fossil fuels dependency, either by its use as an extender or in total substitution of diesel fuel (Li *et al*., 2009; Días, 2012). According to the estimates of the International Energy Agency, demand reaches 90 million barrels/day by 2014, an increase of 7% on 2009 levels, with most of the increase in demand centered in China and Asia.

With a reserve to production ratio of about 53 years, there is a concern of depletion (Takuya, 2012). Due to the last reason many alternative energy resources have been continuing widening, not only by the increasing dependence on petroleum products, but also by the energy crisis and environmental issues (Guru, 2009). Since most petroleum consumption is in internal combustion engines, development of a light liquid fuel as an alternative to petroleum to be used in existing internal-combustion engines is urgent. Biodiesel is attracting attention as one of the possible alternative fuels to petroleum. Basically, biodiesel comprises fatty acid methyl esters (FAME), which are produced by the transesterification of triacylglycerols (TGs), the main component of fats and oils, with methanol. Biodiesel can be used in existing diesel engines, and as it does not contain sulfur, SO_x is not emitted. In addition, the flash point of biodiesel is high and complete combustion can be achieved, producing reduced emissions of hydrocarbons (HCs), CO, and black smoke.

Biodiesel production with postconsumer fat and oil, such as waste cooking oil, is sought-after. However, most waste cooking oil recovered from restaurants and food-service businesses contains animal fats. Biodiesel produced from animal-derived fats by a transesterification contains larger quantities of long-chain saturated FAMEs, resulting in poor low-temperature properties (Nakamori *et al*., 2005; Takuya, 2012). Another problem is that as the waste animal-derived fats contain larger quantities of free fatty acids (FFAs) than waste vegetable oil, the FFAs form soap in reactions with the catalyst and uptake of biodiesel reduces yield (Tsukii *et al*., 2008; Takuya, 2012).

It is impossible to use combust animal fats in Diesel engines directly because of its negative physical properties. These features cause poor atomization, poor vapor–air mixing, low pressure, incomplete combustion and engine deposits. Biodiesel can be used in neat form, or mixed with Diesel fuel in any amount (Guru, 2009).

1. What is animal fat?

Animal fats and oils are lipid materials derived from animals. Physically, oils are liquid at room temperature, and fats are solid. Chemically, both fats and oils are composed by triglycerides. Although many animal parts and secretions may yield oil, in commercial practice, oil is extracted primarily from rendered tissue fats obtained from livestock animals like pigs, chickens and cows. Dairy products also yield popular animal fat and oil products such as cheese, butter, and milk (Nebel and Mittelbach, 2006)

2. Characteristics of the animal fat

Flesh and animal fat have a melting temperature close to 184 °C, a boiling point of around 200 °C and an ignition point of 280 °C where it will burst into flames without spark. Certain substances such as goose fat produce a higher smoke point than other animal fats, but they are still lower than many vegetable oils such as olive or avocado. (Días, 2012)

In consumed meat products in the U.S., animal remains are found to be classified as animal fats once the particle size of bone solids is more than 3 percent, protein content is less than 14 percent and the product contains over 30 percent pure fat content (Takuya, 2012).

Animal fats are commonly consumed as part of a western diet in their semi-solid form as either milk, butter, lard, schmaltz, and dripping or more commonly as filler in factory produced meat, pet food and fast-food products. Dairy products are animal secretions which contain varying levels of water, oils, fats and animal cells from circulatory and lymphatic systems such as blood and mammary glands (Salvi, 2012).

3. Fat composition.

The composition of the animals fat is:

Saturated fats: 38-43% (Palmitic acid: 25-28%; Myristic acid: 1%)

Unsaturated fats: 56-62%

Monounsaturated fats: 47-50 %(Oleic acid;44-47%) and (Palmitoleic acid;3%)

Polyunsaturated fats: 6-10 %(Linoleic acid) (CETES, 2006)

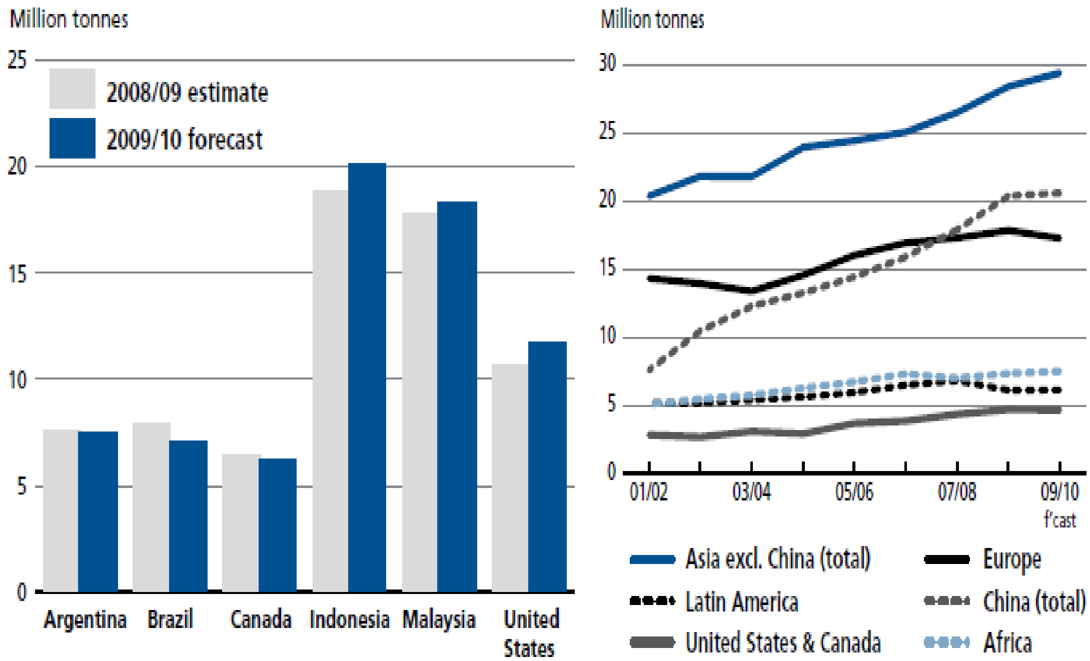
Fig.1. Animal fat as a raw material in the production of biodiesel. (CETES, 2006)

4. Different types of raw material for biodiesel production

The inedible tallow, fats, edible tallow, lard, yellow and brown grease, all these raw materials are mainly from animals like beef, pork, chicken fat and poultry, as these are most used on a large scale in the food industry and the biodiesel production, but usually at a smaller scale biodiesel is produced from animal fats such as rabbit, lamb, turkey and sea animal fats. (Al-Zuhaira *et al*., 2012)

5. Availability of raw materials in the world.

In the European Union, about one million tons of tallow is rendered each year (Mittelbach *et al*., 2000). The United States generates as an average, about 4 kg/person of yellow grease per year, and based on this statistic, Canada should produce about 120,000 ton/year of waste fats of various origins (Zhang *et al*., 2003). Brazil generates about 1,382,472 ton/year of beef tallow and 194,876 ton/year of lard from slaughter houses, which is normally used for producing meal and oil for animal feed (CETESB, 2006). According to the FAO report (2010), Asia, not including China, was the largest producer of oil and animal fat (about 30 million tons), and Indonesia was the largest exporter country followed by Malaysia, see figure. 1 a, b.



Production b) Export

Fig.1. Behavior of the production and export of oil and animal fat through 2010 (FAO, 2010)

6. Reactions to produce biodiesel from animal fats.

The free fatty acids (FFA) present major problems when using a base-catalyzed transesterification process since the FFA react with the base catalyst to form soaps, which leads to loss of catalyst and ester product, and increases production processing costs. This reason makes necessary acid catalyst for transesterification of triglycerides and esterification of FFA. Strong acid catalysts are less sensitive to FFA and can conduct esterification and transesterification simultaneously. The FFA can react with alcohol to form ester (biodiesel); this reaction is very useful for handling oils of fats with high FFA, as it is shown in equation number one. (Encinar *et al*., 2011)

$$\underset{\text{FFA}}{R_1\text{–COOH}} + \underset{\text{alcohol}}{\text{ROH}} \longrightarrow \underset{\text{fatty acid ester}}{\text{R-O-CO-}R_1} + \underset{\text{water}}{H_2O} \qquad \text{ec. 1}$$

Direct use of animal fats/vegetable oils is generally considered to be unsatisfactory and high kinematic viscosities and low volatilities. Various methods have been considered to gain sufficient engine compatibility for vegetable oil and animal fat-derived high quality diesel fuels, including derivatisation (transesterification, hydrotreating, ozonation), pyrolysis/gasification, dilution, blending and microemulsification. The process of transesterification removes glycerol from the triglycerides and replaces it with an alcohol. The process decreases the viscosity but maintains the cetane number and heating value. (Salvi, 2012)

- Transesterification processes for biodiesel production from animal fats.

Ester formation constitutes one of the most important classes of reactions in value-added processing of animal fats. Typical schemes for ester formation include: (Aranda, 2008; Araujo *et al*., 2010)

ESTERIFICATION → ALCOHOLYSIS → TRANSESTERIFICATION → ACIDOLYSIS

Transesterification of animal fats is an equilibrium reaction consisting of a number of consecutive, reversible reactions in which a triglyceride is converted step wise to diglyceride(DG), monoglyceride (MG) and finally glycerol (GL), as follows: (Salvi, 2012)

Triglyceride (TG) + ROH ↔ Diglyceride (DG) + R´COOR

Diglyceride (DG) +ROH ↔ Monoglyceride (MG) + R´´COOR

Monoglyceride (MG) + ROH ↔ Glycerol (GL) +R´´´COOR

Generally speaking, there are two methods of transesterification reaction, namely with or without a catalyst. After (catalytic) transesterification of triglycerides, the products are a mixture of esters, alcohol (catalyst), tri-, di- and monoglycerides, glycerol (byproduct) and salts. Transesterification does not alter the fatty acid composition of the feedstocks. (Salvi, 2012)

Because methanol and animal fats are immiscible, it was imperative to achieve adequate mixing to produce high ester yields. Stirring the solution did not sufficiently generate an emulsion, resulting in a low conversion of TAG to methyl esters. Therefore, the solution must have the presence of catalysts due to it helps to the conversion from TAG to biodiesel. (Wyatt, *et al*.,2005)

7. Types of Catalysts

Pre-esterification conditions are used for different fats using acid and alkali catalysts as H_2SO_4, HNO_3 and HCl for acid ones, and (KOH) potassium hydroxide, (NaOH) sodium hydroxide, KOCH, $NaOCH_3$, NaO_2H_5 . In transesterification is very common the alkali catalysts as KOH**.**

On the other hand, the conventional biodiesel production, which involves the use of chemical catalyst, is carried out at relatively high temperatures closer to the boiling point of the alcohol and this produces many unwanted by-products like soap (Encinar *et al*., 2012). Separation of biodiesel from these by-products and glycerol is difficult, which renders this method costly and complicated. To overcome these drawbacks, biocatalysts (enzymes) have been proposed to replace the chemical catalysts, which have shown promising results due to their high selectivity and mild operative conditions. In addition, there is no need for feedstock purification since biocatalysts like lipase able toesterifying free fatty acids present in the feed stock along with the transesterification of triglycerides (Al-Zuhaira *et al*., 2012), other ones frequently used are Novozym 435 ® (*candida antarctica*) (Salvi, 2012), *pseudomonas cepacia*. For the enzymatic process to be feasible, lipase is preferred to be used in immobilized form, which unlike its soluble counterpart, allows easy reuse of the enzyme and control of the process.

The use of chemical solvents for biodiesel production from animal fats.

Therefore, the use of chemical solvents, that can dissolve both methanol and glycerol, results in increasing the reaction rate and yield. In addition, the use of organic solvent is essential when animal fat is to be used as a feedstock for biodiesel production. This feedstock has a high melting point which is near the denaturation temperature of lipase, and therefore must be dissolved in a solvent. However, the use of organic solvents is not recommended in food processing due to its harmful effect. In addition, product separation and solvent recovery units are inevitably required in this case.Fig.3**.** (Salvi, 2012).

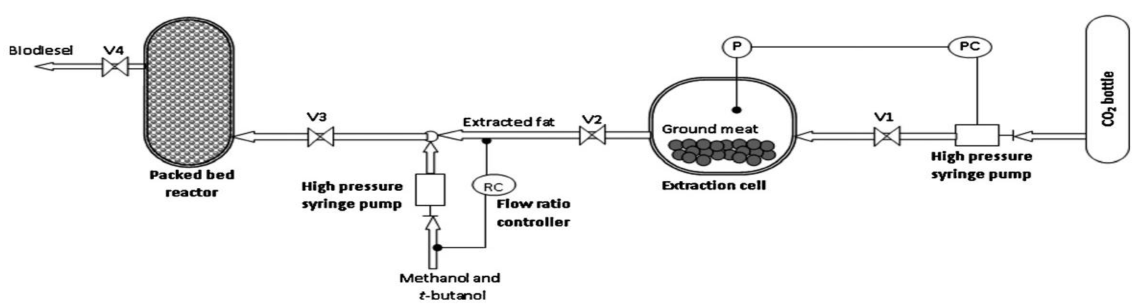


Fig.3**.** Schematic diagram of the integrated fat extraction–biodiesel production system (Salvi, 2012).

8. Aspects to consider in the production of biodiesel from animal fat.

Biodiesel is usually produced from high quality vegetable oils. These feedstocks have high cost, which currently accounts for over 85% of biodiesel production expenses. In recent years, a wide range of studies have been carried out on biodiesel production from feedstocks of low cost. Frying oils, new vegetable species and animal fats have been researched. The last kind of low cost feedstock has not been developed deeply. (Encinar et al., 2011)

8.1. Social aspect:

Animal fats are waste raw materials more abundant than frying oils. Such fats were usually used as animal feeds, but this practice strongly decreased due to the possibility of severe animal disease. The utilization of animal fats for biodiesel production is a good alternative to recycle these wastes. (Encinar et al., 2010; Mata, 2013)

8.2. Advantages of producing biodiesel from animal fat:

In comparison to biodiesel from vegetable origin, biodiesel from animal fats has the advantages: (Días, 2008; Días, 2012)

1) Higher calorific value and cetane number.

2) Waste animal fat as a cheap raw material and its low operating cost in biodiesel production make this feedstock a promising one for technological application.

3) Animal fat methyl ester blended with Diesel fuel can be used as an alternative fuel in conventional Diesel engines, generators and boilers without any major modification.

4) Low sulphur and aromatic contents

5) Magnesium and nickel based additives reduced the pour point, flash point and viscosity of biodiesel fuel, depending on the amount of additive.

6) On the other hand, the biodiesel blend (B20) cetane number is higher than that of standard Diesel fuel, and therefore, the engine runs very smoothly with biodiesel fuel. (Ataya, 2008)

7) Is a clean liquid fuel and biodegradable in aqueous solution, 95% resolve within 28 days.

8) A flash point of 150 °C which compares very favourably to diesel oil whose value is 50 °C. As its flash point is higher, handling and storage are safer than for conventional diesel fuel. It can be stored either pure or mixed.

9) It is used in the urban transport sector, miner, agricultural and marine, as well as boilers, incorporating it directly or mixed with diesel

10) Net carbon dioxide (CO_2) and sulfur dioxide (SO_2) emissions are reduced by 100%, preventing in this way global warming, acid rain, visible smoke and noxious odours.

11) Its combustion generates, depending on the stock used, an odor similar to donuts or french-fries, being nicer to people.

12) Several studies in the U.S. have shown that biodiesel reduces by 90% the risk of cancer. Positive health effects by reducing PAH and carcinogenic compounds as PADH.

13) Aromatic polycyclic hydrocarbon (PAHs) emissions are reduced. Specially the following cancer causing agents: fenantren 97% reduction, benzofluorantren 56% reduction, benzopirenos 71% reduction.

14) Soot emissions are reduced by 40 – 60 % and hydrocarbons (HC) by 10 – 50%. Carbon monoxide emissions are reduced by 10 – 50 %.

15) Lastly, aromatic compounds and aldehydes are reduced by 13%, nitrous oxide can be reduced or increased by 2-5% according to the engines wear and the fuel pump calibration.

8.3. Disadvantages of animal fat to produce biodiesel

Disadvantages include being less stable to oxidation, due to the absence of natural antioxidants, and having a higher cold filter plugging point, due to greater content of saturated fatty acids. The obtained fuel might however be used 100% pure in boilers for heat generation or mixed with other raw materials, even improving some fuel characteristics (Días, 2008; Días, 2012)

9. Stages for obtaining biodiesel from animal fat.

The stages of the process of obtaining biofuel from animal fat depend on the composition of the main raw material, knowledge about the process, technology and financial resources available, among others (Nevel and Mittelbach, 2006; Mata, 2013). There are three basic steps:

1.-Extraction of fat from fatty waste materials.
2.-Pre-treatment of waste fats.
3.-Biodiesel production processes.

The procedure for extraction of animal fat from fatty materials depends on their characteristics and composition. Generally performed in three steps:

• Extraction of the oil or fat from the fatty feedstock.

• Filtration and removal of contaminants.
• Neutralization or esterification of the FFA.

The steps for extraction of fats are: (Mata, 2013)

1- Milling and grinding of raw material
2- Cooking on screw-conveyed to a batch digester, where it remains for 4-5 h to be cooked with saturated vapor at about 110°C, until it loses about 70% of its moisture content.
3- Separation of liquid fat from solids by percolation and sieving in a percolator tank heated by steam
4- Centrifugation or filtration of the fat.
5- Decantation for final separation of fat from the aqueous phase present.
6- Collection and separation of the solid material for pet food.

Another possibility for extracting lipids from fatty waste materials is by using an organic solvent, such as *n* -hexane. For example, testing nine solvents for extracting fat from meat and bone meal, obtaining about 15% fat with all solvents, but *n* -hexane was found to be the most suitable solvent to perform the extraction, because it is relatively cheap and has a low boiling point (Nevel and Mittelbach, 2006).

9.1. Pre-treatment of Waste Fats.

In the presence of free fatty acid (FFA) and moisture, saponification reactions occur during base catalysts because the fatty acids react with the catalyst to produce soaps, decreasing the methyl esters yield, or even inhibiting the transesterification reaction. The animal fats with high acidity (more than 2.5% w/w of FFA) need a pre-treatment to reduce their FFA content. This is normally done by acid-catalyzed esterification, using H2SO4 as catalyst and methanol as reagent. (Canacki, 2007)

9.2. Biodiesel Production Processes

The process through which biodiesel from animal fat is obtained is called transesterification**.** A process of chemical modification of fat where three molecules of alcohol react with one molecule of triglyceride using three alkylesters (biodiesel) and glycerine molecule, as shown in figure 4, (Akoh *et al*., 2007)

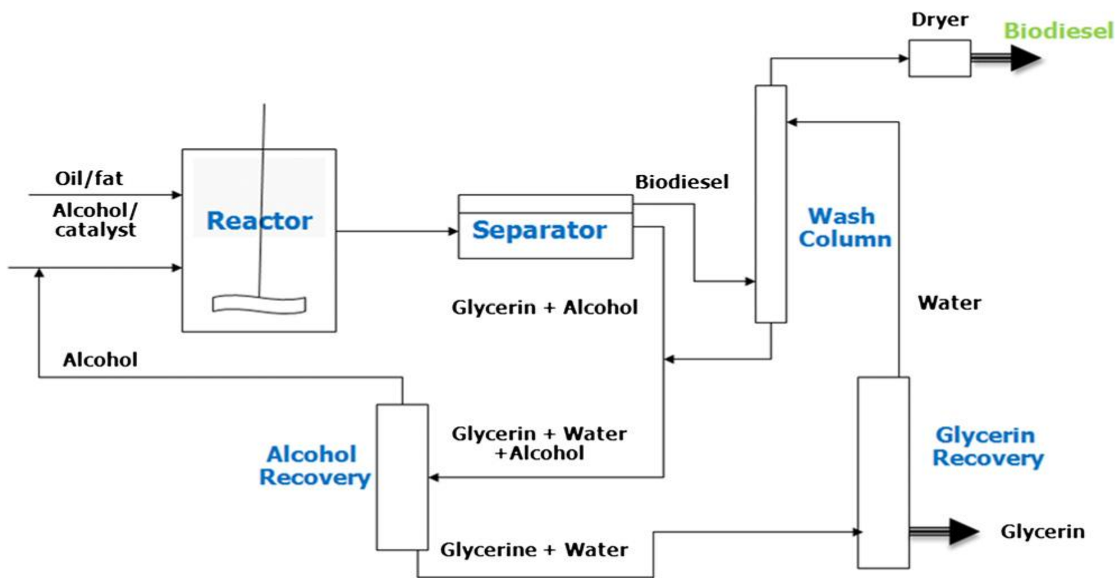


Fig. 4- Conventional process of producing biodiesel from animal fat. (Akoh *et al*., 2007)

9.3. Processes to carry out the transesterification.

In the literature the following processes are reported: (Mata, 2013)

• Acid- base catalyzed transesterification.

• Non-catalytic supercritical process using methanol or ethanol for the transesterification reaction.

• Heterogeneous or Biological catalyzed process (inorganic chemical, enzymes, and living organisms) to avoid the need for the removal and recycling of the catalyst.

• Transesterification with co-solvents to enhance the solubility of reactants, by diminishing the mixture polarity and increasing the reaction rate.

• Transesterification "In situ".

• Microwave-assisted transesterification.

• Catalytic cracking.

• Ultrasonic reactors and cavitation reactors.

One of the methods explained as an example is the following one:

Acid- base catalyzed transesterification.

Alkali-catalyzed transesterification of triglycerides with low molecular weight alcohols is more efficient, less corrosive process and the reaction is faster than the acid-catalyzed transesterification. Besides the Alkali-catalyzed transesterification requires lower amount of catalyst to carry out the reaction. To alkaline catalysts (NaOH, KOH, $NaOCH_3$, etc.) has several drawbacks, in particular, very sensitive to the lipidic feedstocks, and this ones, a pre-treatment to enhance the esterification purity, mainly operating in batch mode and needing large reaction times to obtain a complete conversion of oil and has complex biodiesel purification steps after the reaction. The transesterification reaction includes three reversible steps in series, where triglycerides are converted into diglycerides, then diglycerides are converted into monoglycerides, and these ones are converted into fatty acid alkyl monoester (biodiesel) and glycerol (by-product). Alcohols used in this reaction are ethanol, methanol, or butanol in order to obtain respectively, methyl, ethyl, or butyl esters. Commonly, an alcohol - oil molar ratio is 6:1, at a reaction temperature of about 60°C if methanol is used, or 70°C for ethanol. The amount of catalyst used in the mixture is in the range of 0.5–1.0% (w/w) (Freedman et a., 1984; Kusdiana, 2001;).

9.4. Biodiesel production from waste animal fats using pyrolysis method

This method was developed at laboratory scale, using electromagnetic induction rotating stirrer type autoclave. At a temperature around 360-390°C triglycerides are decomposed, and fatty acids are generated by cleavage of the ester bond. Short chain hydrocarbons and short-chain fatty acids were generated by cleavage of the unsaturated bonds in the hydrocarbon chain. When the retention time was extended with a reaction temperature of 420 °C, light-oil hydrocarbons were generated by decarboxylation of the fatty acids. By adding palladium supported by activated carbon (Pd/C) as a catalyst, decarboxylation was promoted, and hydrocarbons comparable to light oil were selectively obtained in high yield at 85 wt.%. The biodiesel obtained by pyrolysis showed and improvement of about −5 °C in the pseudo-cold filter plugging point (Salvi, 2012; Takuya, 2012).

10. Conclusions

Residues can be used as animal fat feedstock for the production of biodiesel using immobilized lipase. Also, the transesterfication of triglycerides by methanol, ethanol, propanol, and butanol has proved that it is currently the method of choice. On the other hand the selection of a transesterification process depends on the amount of free fatty acid and water content of the feedstock. Among all current transesterification methods, the homogeneous base catalyst is still a common and commercial method. The main reason is due to the fact that it is kinetically much faster than heterogeneously catalyzed transesterification and is economically viable. From the review of aforementioned research and environmental consideration, it seems to be that the heterogeneous and biocatalysts will be the method of choice in the future. In non-catalytic methods, where supercritical alcohol is used, it is demonstrated that the reaction rate for esterification is higher than for transesterification. Another advantage of this process is that the free fatty acid changes completely into esters. In terms of potential environmental impacts, biodiesel fuels from animal fats are considered a good alternative to both conventional diesel and first generation biodiesel.

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