

Review

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Supercritical fluid technology in biodiesel production

Abstract: The synthesis of biodiesel has received attention as an alternative source of energy to decrease our dependence on petroleum-based fuels. The catalyzed processes present a series of limitations and drawbacks, among them the high energy required for complex purification and undesirable side reactions. Supercritical fluid (SCF) technology is being proved an efficient approach compared to traditional methods for preparing biodiesel. This review illustrates the advances, advantages, and drawbacks involved in the use of all current biodiesel production technologies.

Keywords: biodiesel; catalyst; non-catalytic; supercritical fluid; transesterification.

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List of abbreviations

BDF, biodiesel fuel; FA, fatty acid; FFA, free fatty acid; FAAE, fatty acid alkyl ester; FAME, fatty acid methyl ester; FAEE, fatty acid ethyl ester; P_c , critical pressure; T_c , critical temperature; SCF, supercritical fluid; SCMA, supercritical methyl acetate; SCMe, supercritical methanol; sch_2O , supercritical water; SCDMC, supercritical dimethyl carbonate; UA, ultrasound-assisted

1 Introduction

The demand for energy derived from biosources is ever-increasing, due to the estimated gradual depletion of fossil fuels and related environmental issues. Biodiesel, an alternative fuel derived from vegetable oil or animal

fat, has drawn special attention in recent years due to its advantages, compared to petrodiesel, such as better lubricating properties, higher cetane rating, and cleaner combustion, as well as the property of being biodegradable [1].

According to ASTM D 6751, biodiesel is defined as the mono-alkyl esters of long-chain fatty acids (FAs) derived from a renewable lipid feedstock, i.e., edible oil (soybean, canola, corn, rapeseed, coconut, palm, sunflower seed, cottonseed, rubber seed), non-edible oil (Jatropha, Karanja...) [1–3]. Due to the similar characteristics of biodiesel and conventional diesel, it constitutes a potential alternative to diesel fuel.

Biodiesel production has been investigated by academia and industries; its biggest disadvantage is related to the expense for raw materials and synthesis, which leads to a higher cost of the final product than traditional petrodiesel. There are a number of pathways to reduce the viscosity of vegetable oil, and thus to have a product assimilable to diesel [1]. These include: blending with petrodiesel, microemulsification, pyrolysis, and transesterification. However, the most popular method used in industries and research is transesterification, which involves the reaction between a liquid oil feedstock and an alcohol (normally methanol and ethanol), with or without the presence of a catalyst.

2 Methods of biodiesel production

2.1 Direct use by blending with petrodiesel

The use of vegetable oils as alternative fuels started in 1890, when Dr. Rudolph Diesel, who invented the diesel engine, first tested peanut oil in the compression engine [1, 2].

However, the direct use of vegetable oils in diesel engines has many inherent failings [4], which can be overcome by directly mixing crude vegetable oils with diesel fuel, to solve the problems associated with the use of pure vegetable oils.

Fuel efficiency, with the use of pure vegetable oils, was found to be similar to that of diesel fuel for short-term use, and blends with 10–20% of oil in diesel fuel. However, direct use of vegetable oils and/or the use of blends of vegetable oils, has generally been considered to be not satisfactory and impractical for both direct and indirect diesel engines in the long-term.

The problems currently reported in the application of vegetable oils are the high viscosity, acid composition, free FA (FFA) content, as well as gum formation due to oxidation and polymerization during storage and combustion, carbon deposits, and lubricating oil thickening [4]. Heating and blending of vegetable oils may reduce the viscosity and improve the volatility of vegetable oils, but the molecular structure remains unchanged, hence the polyunsaturated character remains. More importantly, the use of vegetable oils in diesel engines requires significant engine modifications, including the substitution of piping and injector construction materials, otherwise engine running times are decreased, maintenance costs are increased due to higher wear, and the danger of engine failure is augmented.

2.2 Microemulsification

Formulating hybrid diesel fuels by mixing with low-molecular-alcohol is another way of reducing the viscosity of vegetable oils [1, 4]. Alcohols, such as methanol or ethanol, have limited solubility in non-polar vegetable oils; therefore, amphiphilic compounds are added to increase the solubility and dilute the oil. The formulation of hybrid diesel fuels by solubilization of vegetable oil/alcohol mixtures through the addition of amphiphiles was initially referred to as microemulsification. Microemulsions are clear, stable isotropic fluids with three components: an oil phase, an aqueous phase, and a surfactant.

2.3 Pyrolysis

Pyrolysis is the breakdown of chemical bonds in an organic substance, into smaller molecules, by means of heat, with or without the presence of a catalyst [1, 3]. The input material for this process could be a vegetable oil, animal fat, natural FAs or methyl esters of FAs. The conversion of vegetable oils and animal fats, composed mostly of triglycerides, employs thermal cracking reactions and represents a promising biodiesel production technology. This technology is especially promising in areas where the hydroprocessing industry is well established, because the

technology is very similar to that of conventional petroleum refining. The fuel properties of the liquid product of the thermally decomposed vegetable oil are similar to the ones of diesel fuel.

Many researchers have reported the pyrolysis of triglycerides to obtain products suitable for diesel engines. The research on pyrolysis of triglycerides is divided into catalytic and non-catalytic processes. Figure 1 outlines a simple diagram of the formation of hydrocarbons from the pyrolysis of triglycerides. Mechanisms for the thermal decomposition of triglycerides are complex, due to the many structures and multiplicity of possible reactions of mixed triglycerides.

The pyrolysis reactions of soybean, palm, and castor oils have been studied [4]; the adequate choice of distillation temperature ranges allowed isolation of fuels with physical and chemical properties comparable to those specified for petroleum-based fuel.

2.4 Transesterification

The most common method for biodiesel production is the transesterification of oils (triglycerides) with alcohol, which gives biodiesel (FA alkyl esters, FAAEs) as the main product and glycerin as a byproduct [1, 2, 5] (Figure 2).

The first step of the transesterification is the conversion of triglycerides to diglycerides, which is followed by

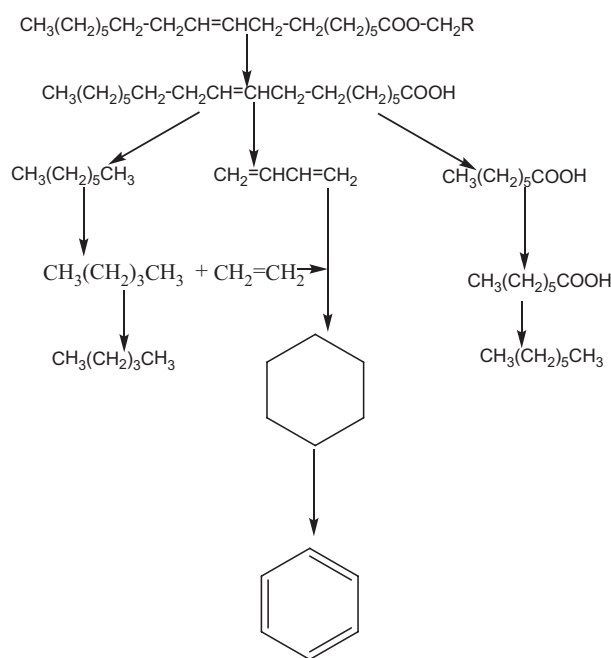


Figure 1 The formation of hydrocarbons from the pyrolysis of triglycerides.

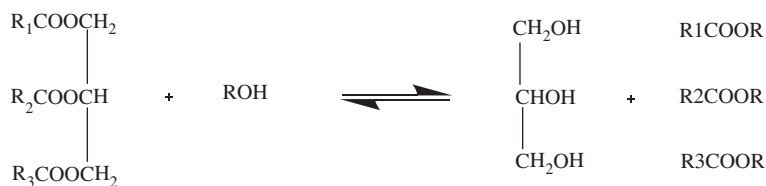


Figure 2 Transesterification reaction.

the conversion of diglycerides to monoglycerides and of monoglycerides to glycerol, yielding one methyl ester molecule from each glyceride at each step.

Transesterification, also called alcoholysis, is the use of an alcohol to form an ester and another alcohol, in a process similar to hydrolysis, except that an alcohol is used instead of water [1, 6]. The most relevant operating variables affecting the transesterification process are the reaction temperature, reaction time, reaction pressure, alcohol to oil ratio, concentration and type of catalyst, agitation, and feedstock.

Vegetable oils, such as soybeans, palm, canola, and rapeseed, are considered first generation feedstock for biodiesel production because they were the first crops to be tried for biodiesel. Most first generation biodiesel feedstock could be used alternatively to make food for humans as well.

Non-edible oils are considered as feedstock for second generation biodiesel. Energy crops, such as *Jatropha*, represent the second generation biodiesel feedstock. In addition, using technologies such as biomass to liquid, many other non-food crops could be converted to biodiesel. These feedstocks have the advantage of not affecting the human food chain by being diverted to make fuel.

Alternative sources, such as algae, are considered to be categorized into the third generation biodiesel feedstock. Algae are low-input, high-yield feedstock used to produce biofuels: algae are organisms that grow in aquatic environments and use light and carbon dioxide to create biomass. There are several reasons for the interest in the use of microalgae over other energy crops or animal fats: microalgae have higher growth rates than terrestrial crops; can be grown in non-arable or marginal lands with various qualities of water; require little maintenance; generate high concentrations of intracellular lipids; provide a means to recycle CO_2 ; and do not require diverting food resources to energy production. Microalgae with high oil productivity can reach yields that are 200 times higher than the one of the most performing traditional biodiesel crops [3], based on equivalent land occupation, being of the order of 50 tons of oil/hectare/year.

One of the major hurdles in reducing the cost of algal biodiesel, is the need to dewater the algal biomass after harvesting the algae from the growth medium. The presence of water with the harvested biomass inhibits organic solvent based extraction of lipids from algal biomass, and the transesterification itself, due to FFA formation. Methods are available to extract and/or convert algal lipids to biodiesel from wet algal biomass, but many require the use of super or subcritical fluids [7], which will be later reviewed.

2.4.1 Catalytic method

Vegetable oils can be involved in the transesterification, by heating them with an alcohol and a catalyst [4]. Catalysts used in biodiesel production are divided in two general categories: homogenous and heterogeneous types. If the catalyst remains in the same (liquid) phase as that of the reactants during transesterification, it is defined as homogeneous catalytic transesterification. By contrast, if the catalyst remains in a separate phase (i.e., solid, immiscible liquid, or gaseous) from that of the reactants, the process is called heterogeneous catalytic transesterification. In this process, the selection of a suitable catalyst is an important factor in maximizing the oil conversion yield at mild reaction conditions, and thus reducing the biodiesel production cost [4].

Commercial biodiesel is currently produced by transesterification using a homogenous catalyst solution. A factor affecting the selection of the catalyst type is the amount of FFAs present in the oil [4]. For oils having a lower amount of FFAs, a base-catalyzed reaction gives a better conversion in a relatively short time, while for higher FFAs containing oils, acid-catalyzed esterification followed by transesterification is more convenient.

Numerous studies have been performed employing various oils, different alcohols (methanol, ethanol, butanol), as well as different catalysts, including homogeneous ones, such as sodium hydroxide (NaOH) [8], potassium hydroxide (KOH) [9, 10], and sulfuric acid [11], and heterogeneous ones such as lipases, calcium oxide (CaO) [12–14] and magnesium oxide (MgO) [15].

2.4.1.1 Homogeneous catalyst

There are two kinds of homogenous catalysts, namely base and acid ones [3]. The homogenous transesterification process requires a high purity of the raw materials, and a separation of the catalyst, byproduct, and product at the end of the reaction. Both requirements contribute to the high the cost of biodiesel. The general form of a homogeneous catalytic transesterification process can be seen on a process flow diagram of Figure 3.

a. Base catalyst Biodiesel is normally produced using a homogeneous base catalyst, such as alkaline metal alkoxides and hydroxides, as well as sodium carbonate (Na_2CO_3) or potassium carbonate (K_2CO_3) [1–4]. There are some advantages in using homogeneous base catalysts: mild operation conditions, high conversion in a minimal time, high catalytic activity, and wide availability as well as being cheap catalysts.

In general, base catalytic transesterification processes are carried out at low temperatures and pressures (60–65°C and 0.14–0.42 MPa), with low catalyst concentrations (0.4–2 wt% NaOH or KOH in oil, in a transesterification with methanol) [1–3]. In addition, the typical process conditions for homogeneous base catalysis are mild, involving stoichiometric alcohol/oil molar ratio (or slightly higher), reaction at alcohol reflux temperature, atmospheric pressure or small overpressure, and low reaction times (typically 1 h).

Some drawbacks of this process are the sensitivity to the purity of the reactants, the FFAs content, as well as the amount of water in the oil sample [1, 3]. When the feedstocks contain significant amounts of FFAs

and water content, they cannot be converted into biodiesels without soap formation. FFAs react with the catalyst to produce soaps that inhibit the separation of biodiesel from glycerin, which requires more wastewater from purification. Because the presence of water leads to saponification, the base catalyst is consumed in producing soap, which reduces the catalyst efficiency. The soap causes an increase in viscosity, formation of gels, thus reducing the ester yield, and makes the separation of glycerol difficult. Therefore, side reactions such as saponification and hydrolysis must be kept to a minimum.

Several strategies were recently investigated to enhance the advantages of base-catalyzed transesterification processes, with the purpose of seeking a new way to reduce the biodiesel cost: Berchmans et al. [9] devised the reaction of a mixture of *Jatropha curcas* and waste food oil, with methanol and KOH. At a mixing speed of 900 rpm, a methanol to oil mole ratio of 6:1, and a KOH concentration of 1 wt% of oil, the total oil conversion reached 96% within <10 min.

The process intensification is another wide opportunity to increase the profitability of the process, by investigating the most suitable reactor configurations: with the same catalyst (KOH), Santacesaria et al. [10] developed a simple instrument to test the characteristics of the transesterification between soybean oil and methanol in microchannels of different sizes. With experimental conditions of a methanol to oil ratio of 6:1, KOH concentration of 2 wt%, and a temperature of 60°C, they obtained a 95% conversion with the tubular reactor filled with stainless steel ribbon wool in a very short residence time, equal to 3 min, thus highlighting

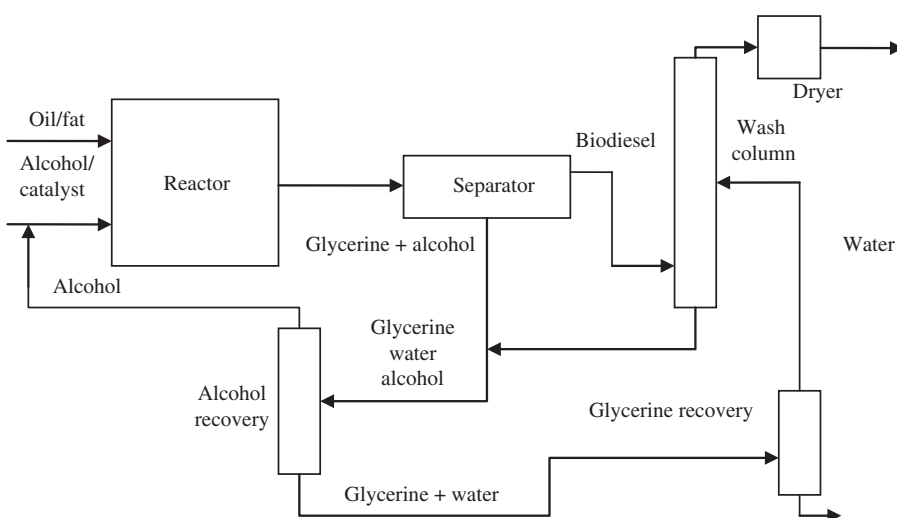


Figure 3 Homogenous catalytic transesterification process.

the importance of the involved phase mixing phenomena, and increasing the productivity per reactor volume.

Finally, other alcohols are also widely investigated in the literature, whose advantages over methanol could be their bio-derived source, like ethanol from biomasses, although the price is inevitably higher. Velickovic et al. [8] evaluated the effects of temperature, ethanol to oil molar ratio, and catalyst loading in the process of converting sunflower oil via ethanolysis with NaOH. According to the results, the maximum FA ethyl ester (FAEE) purity was 98.6% after 5 min under the optimal conditions, being a reaction temperature of 74.6°C, an ethanol to oil molar ratio of 12:1, and an amount of catalyst of 1.25 wt%.

b. Acid catalyst An alternative way of processing triglycerides for biodiesel production is to use an acid catalyst [4]. Acid catalytic transesterification of biodiesel can economically compete with base catalytic processes using virgin oil, especially when the former uses low-cost feedstock. Sulfuric acid, hydrochloric acid, and sulfonic acid are normally employed as acid catalysts. Acid-catalyzed transesterification starts by mixing the oil directly with the acidified alcohol, so that separation and transesterification occur in a single step, with the alcohol acting both as the solvent and as the esterification reagent. The use of excess alcohol reduces the time required for the homogeneous acid catalyzed reaction. Hence, Bronsted acid catalyzed transesterification requires a high catalyst concentration and a higher molar ratio to reduce the reaction time.

One advantage of homogeneous acid catalysts (over alkali ones) is their low susceptibility to the presence of FFA in the feedstock. However, homogeneous acid catalytic transesterification is especially sensitive to water concentration: as little as 0.1 wt% water in the reaction mixture is able to affect ester yields in transesterification of vegetable oil with methanol, with the reaction almost completely inhibited at 5 wt% water concentration. Other drawbacks of this process are the equipment corrosion, more waste from neutralization, difficulty to recycle, formation of secondary products, higher reaction temperature, long reaction times, relatively slow reaction rate, weak catalytic activity, and elaborate process engineering.

Wang et al. [11] studied the transesterification between methanol and waste cooking oil in the presence of sulfuric acid. A 10 h lasting reaction led to a 90% conversion of the feedstock at a temperature of 95°C, an amount of sulfuric acid equal to 4%, and a methanol to oil ratio of 16:1. The major obstacle of using acid catalyst is related to equipment, which has to withstand the acidity of the reacting medium.

2.4.1.2 Heterogeneous catalyst

In comparison with homogeneous catalysts that act in the same phase as the reaction mixture, heterogeneous catalysts act in a different phase from the reaction mixture. Hence, heterogeneous catalysts have the advantage of an easy separation and reuse. Additionally, the use of heterogeneous catalyst does not yield to soap formation. The use of heterogeneous catalytic systems for the transesterification of triglycerides implies the elimination of several steps of washing/recovery of biodiesel/catalyst, thereby bringing higher efficiency and profitability of the process as well as lowering production costs. Compared to homogeneous catalytic transesterification, the heterogeneous catalytic transesterification process can tolerate extreme reaction conditions: the temperature could go from 70°C to as high as 200°C to achieve more than 95% of yield using MgO, CaO, and TiO₂ catalysts.

Kiss et al. [16] performed a study to evaluate the cost and environmental aspects of the homogeneous and heterogeneous catalytic transesterification process in large-scale biodiesel production plants. The results revealed the advantages of the heterogeneous process in terms of higher yield of biodiesel and higher purity of glycerin, as well as lower cost of catalyst and maintenance, even though the energy consumption and associated costs are higher in the case of heterogeneous catalyst. The analysis showed that if the energy costs are below US\$85 per ton of biodiesel, the heterogeneous process can be economically viable [16]. Regarding environmental aspects, the application of the heterogeneous process would result in reduced risk associated with spillage or leakage of hazardous and flammable chemicals. Additional environmental benefits can be expected from the absence of the energy intensive and waste generating glycerin purification step.

a. Base catalyst Most of the heterogeneous solid catalysts are base oxides coated over large surface area supports. The most common solid-base catalysts are basic zeolites, alkaline earth metal oxides, and hydrotalcites. Using the solid base catalyst in the form of a fixed-bed reactor system makes the separation of catalyst from transesterified product easier. Also, the solid base catalyst is active in the transesterification at temperatures around the methanol boiling point. Similar to their homogeneous counterparts, solid base catalysts are more active than solid acid catalysts. Oxides of group II metals, particularly CaO and MgO, are cheap and readily available, which makes them desirable catalysts for industrial biodiesel production. Several studies have explored MgO as a promising candidate for transesterification from vegetable oils. Lopez et al. [17] employed

MgO calcined at 600°C, but reached only 18% conversion of the oil feedstock, due to the low surface area of the catalyst. Di Serio et al. [18] reported the highest yield of 90%, using 12:1 methanol to oil ratio, a temperature of 180°C, and a reaction time of 60 min with 5.0 wt% of the catalyst in batch conditions. Dossin et al. [15] evaluated the use of MgO in batch and continuous stirred tank reactors at industrially relevant conditions: the results indicated that MgO worked efficiently in a batch-reactor at ambient temperature, and therefore reactor heating was not required.

CaO is the most widely used alkaline metal oxide as a catalyst for biodiesel synthesis. Various studies on CaO-catalyzed transesterification have been performed with different feedstocks, such as soybean oil, palm, and coconut oil. Kouzu et al. [12] reported a high yield of FAME of 93% when converting soybean oil into biodiesel, after a 60 min reaction in the presence of CaO. However, the concentration of Ca in the final product was 3065 ppm, which exceeds the allowable range of mineral content in standard biodiesel. In a different study by the same group [13], the catalyst was collected after the reaction and analyzed with X-ray diffraction, scanning electron microscopy, and nuclear magnetic resonance: the results showed that the collected catalyst contained calcium glyceroxide, due to the reaction between CaO and glycerol. This led to the decrease in catalytic activity demonstrated by the yield of FAME, which reached 70% after 1 h. By contrast, the transformation of catalyst brings a tolerance to air-exposure, which was effective when the reaction was successfully repeated with regeneration of the collected catalyst.

One of the advantages of using CaO is the derivation from several calcium sources such as: eggshell, mollusk shell, and mud crab. CaO prepared from these sources seems to be a potential candidate for biodiesel synthesis. Boey et al. [14] utilized waste crab shell as a catalyst in the transesterification of palm oil into biodiesel. The result revealed that the main composition of the shell is calcium carbonate, which is converted into calcium oxide when heated above 700°C for 2 h. The optimal conditions were obtained with a methanol to oil mass ratio of 0.5:1, a catalyst amount of 5 wt%, and a reaction temperature of 65°C. Also, an important property of a heterogeneous catalyst is the reusability: the catalyst showed an unchanged activity after 11 reaction cycles. These good results suggested a new idea to optimize biodiesel synthesis by employing both the waste material as a catalyst and the waste feedstock, however, this method needs further research.

Cozzolino and Santacesaria [19] prepared $\text{TiO}_2/\text{SiO}_2$ with different amounts of $\text{Ti}(\text{O}^i\text{Pr})_4$, which was dissolved

in three solvents: dioxane, toluene and isopropanol. The activity of the catalyst was tested in the transesterification of soybean oil with methanol, in order to produce FAME. The obtained highest yield of FAME was around 70% in the following conditions: 0.9 g of methanol, 2.0 g of soybean oil and 0.1 g of catalyst, temperature of 180°C, 60 min. Some authors have focused on sulfated titania (TiO_2/SO_4), which is normally prepared by the sol-gel method. Almeida et al. [20] carried out the research with this catalyst on soybean and castor oil at 120°C, for 60 min and the obtained highest yields were 40% and 25%, respectively.

Zeolite has been considered a promising candidate as the catalyst for biodiesel synthesis. Zeolites have the characteristics of acidic sites and shape selectivity, due to various pore structures as well as inner electric fields. Ramos et al. [21] studied the preparation of biodiesel from sunflower oil with three types of zeolites (mordenite, beta, and X) which gave FAME yields as high as 93.5–95.1 wt% at a temperature of 60°C. Kusuma et al. [22] impregnated natural zeolite with KOH, then stirred the mixture at 60°C for 24 h; it was oven-dried at 110°C for 24 h, and finally calcined at 450°C for 4 h. The prepared KOH/zeolite was used for the transesterification, with a catalyst amount of 3%, palm oil to methanol ratio of 1:7, and a reaction temperature of 60°C. The maximum conversion was 95% for the fresh catalyst, which decreased to 86% in the second cycle. For the third cycle, the FAME yield was just only 72%. The yield reduction can be attributed to the leaching of the active species in catalyst.

b. Acid catalyst Despite their lower activity, heterogeneous solid acid catalysts have been used in many industrial processes, because they contain a variety of acid sites with different strengths of Bronsted or Lewis acidity, compared to the homogenous acid catalysts. Using solid acid catalysts has the following advantages: no sensitivity to FFA content, simultaneous esterification and transesterification, elimination of the purification step of biodiesel, easy separation of the catalyst from the reaction products, and reduction of the corrosion problem, even with the presence of acid species. Heterogeneous solid acid catalysts, such as cation-exchange resins, sulfated zirconia, and tungstated oxides, have been chosen to catalyze biodiesel transesterification due to the presence of sufficient acid site strength.

Cation-exchange resins have been reported extensively for laboratory scale biodiesel preparation, although industrial application has not yet been investigated. In a research carried out by Feng et al. [23], three cation-exchange resins (NKC-9, 001x7, and D61) were employed

to examine their activity for the synthesis of biodiesel via esterification from waste frying oils. From the results, it is reported that NKC-9 is the most active catalyst and the maximum conversion of reaction is approximately 90.0%. More importantly, it was found that the conversion of FFA remained unchanged after the first 10 runs with NKC-9. This may lead to the application of NKC-9 in industrial scale, although more extensive research is needed. The same group also investigated the conversion of FFA with NKC-9 in a fixed bed reactor [24]. The FAME yield kept over 98%, under 2.8:1 methanol to oleic acid mass ratio and temperature of 65°C.

There have been several studies on ZrO_2 as a solid acid catalyst for transesterification of different feedstocks, due to its strong surface acidity. Yee et al. [25] investigated the conversion of *Jatropha curcas* oil into biodiesel with the aid of sulfated zirconia loaded on alumina, using response surface methodology. The maximum yield of FAME of 90 wt% was achieved under the following conditions: temperature of 150°C, methanol to oil ratio of 9.88:1, and 7.61 wt% for catalyst loading after 4 h reaction.

Recently, Patel and co-workers [26] reported the esterification of oleic acid for biodiesel synthesis using sulfated zirconia as the catalyst. As can be seen from the results of this work, ZrO_2/SO_4^{2-} demonstrated a significant activity towards esterification under mild conditions, with a maximum yield of 90% of methyl oleate in the optimal conditions: reaction temperature of 60°C, amount of catalyst 0.5 g, acid to alcohol ratio of 1:40, and reaction time 12 h. Furthermore, this study also reveals the potential application of this catalyst for biodiesel production from waste cooking oil and *Jatropha* oil without any pretreatment via transesterification.

A mixed oxide of zinc and aluminum was employed in the heterogeneous process called Esterfip-H, which was developed by the French Institute of Petroleum and is designed and commercialized by Axens [27, 28]. Esterfip-H represents a major advancement in the area of biofuels, as it ensures the very high yield production of biodiesel meeting European specification EN 14214, and simultaneously directly produces glycerin of unequalled purity exceeding 98%. The key component of Esterfip-H technology is the use of a specific solid catalyst, eliminating the waste products inherent to processes using a soluble catalyst. The obvious advantage of this process, are no catalyst recovery or aqueous treatment steps, which contribute to a cleaner environment. However, the process requires extremely strict control of oil inlet composition, in terms of water content (maximum 0.1 wt%) and oil acidity (acid index below 1) [28].

2.4.1.3 Enzyme catalyst

Biocatalysts are becoming increasingly important in the discussion of biodiesel production [4]. It is even hypothesized that these catalysts will eventually have the ability to outperform inorganic catalysts. Biocatalysts are naturally occurring lipases which have been identified as having the ability to perform the transesterification reactions that are essential to biodiesel production. These lipases have been isolated from a number of bacterial and fungal species: *Pseudomonas fluorescens*, *Pseudomonas cepacia*, *Rhizomucor miehei*, *Rhizopus oryzae*, *Candida rugosa*, *Thermomyces lanuginosus*, and *Candida antarctica*. For transesterification synthesis, at least a stoichiometric amount of methanol is required for the complete conversion of triglycerides to their corresponding FAMEs. However, methanolysis is decreased significantly by adding 1/2 M equivalent methanol at the beginning of the biocatalytic transesterification. This reduction in activity caused by the polar short chain of the alcohols is the major obstacle for the enzymatic biodiesel production. In order to solve this problem, researchers use the following three options: methanol stepwise addition, acyl acceptor alterations (methyl acetate, acetate ethyl), and solvent engineering (with t-butanol, 1,4-dioxane, ionic liquid as solvents).

Glycerol is produced during the transesterification of triglycerides via biocatalysts. The presence of glycerol can then inhibit the reaction by binding to the biocatalyst instead of the triglyceride molecule. To overcome this, an acyl acceptor molecule can be used to bind the glycerol, forming a triglyceride molecule that can no longer bind to the active site of the biocatalyst. When an acyl acceptor is introduced to the reaction, the biocatalyst can exhibit a higher rate of turnover. It has also been shown that the triacetyl glycerol molecule does not diminish the properties of biodiesel when used as a fuel.

The biocatalytic transesterification process has many advantages over the inorganic-catalyzed transesterification process, such as generation of zero byproducts, no difficulty in product removal, moderate process conditions (temperature: 35–45°C), and recycling of the catalysts. Enzymatic reactions can successfully be used for the transesterification of used cooking oil, because enzymatic reactions are insensitive to FFA and water content of the feedstock. Their cost is presently a hindrance for their direct commercial use.

2.4.2 BIOX solvent process

This is an innovative process for the synthesis of biodiesel from high FFA feedstock studied and developed

by the University of Toronto in Canada [4, 29] (Figure 4). This patented process was acquired by BIOX and a commercial plant was built in Hamilton, Ontario, Canada, in 2006. Firstly, this process converts the FFAs through acid esterification, and then the triglycerides to biodiesel with a base catalyzed transesterification. By the addition of a co-solvent, the BIOX concept is a single phase, continuous process, which works at atmospheric pressures and near-ambient temperatures, and has a residence time in the two-steps of the reaction of <90 min, rather than the several hours or even days under conventional processes, reaching almost complete conversion of the feedstock. The co-solvent is then recycled and reused continuously in the process. The BIOX process handles not only grain-based feedstock, but also waste cooking greases and animal fats in order to create the competitive method for biodiesel production.

The role of the co-solvent is to form the homogeneous phase in order to reduce the need for extensive agitation, multiple batch reactor, as well as extensive reaction time, therefore, saving energy and reducing the operating cost.

2.4.3 Microwave-assisted method

Microwave irradiation is a well-established method of improving the production of biodiesel by reducing the reaction time and gaining high yields. It enhances the reaction rate and makes the separation process easier in comparison with conventional heating [30]. Lertsathapornasuk et al. [31] prepared FAEE from waste frying palm oil with a household 800 W modified microwave oven. The best conversion yield (over 97%) was obtained by applying 3.0 wt% NaOH as a catalyst, with an ethanol to oil molar ratio of 12:1 for 0.5 min. Mazzocchia et al. [32] converted the triglycerides in rapeseed oil to FAME in the

presence of montmorillonite, by using the microwave irradiation heating technique. Firstly, it was observed that the microwave technique decreased the reaction time significantly, and secondly montmorillonite was proven to be a promising catalyst for microwave-assisted production of biodiesel. It can work at a temperature of about 170°C and can lower the alcohol to oil molar ratio to 9:1.

Suppalakpanya and co-workers [33] investigated the production of ethyl ester from the esterified crude palm oil with 1.7 wt% FFA employing microwave heating. Optimum reaction parameters for the transesterification process have been identified: a molar ratio of oil to ethanol of 1:8.5, 1.5 wt% of KOH/oil, a reaction time of 5 min and a microwave power of 70 W. This research yielded 85 wt% and its ester content was 98.1 wt%; its fuel properties were within the limits prescribed by American standards for methyl ester.

A two-step transesterification process of kenaf seed oil catalyzed by KOH, was studied by Rathana et al. [34]. Biodiesel produced by this research possesses acceptable fuel properties used for diesel engines. The experimental results also indicate that a conversion level of 94% was obtained at the optimum conditions: 0.55% KOH catalyst, 4.5:1 methanol to oil molar ratio, 57.5°C and 6.5 min reaction time.

Besides the traditional base catalyst, a study on application of a solid catalyst for biodiesel production was carried out by Zhang et al. [35]. An efficient microwave-assisted transesterification technique was developed to prepare biodiesel from yellow horn (*Xanthoceras sorbifolia* Bunge) oil with a heteropolyacid catalyst, namely $Cs_{2.5}H_{0.5}PW_{12}O_{40}$. The highest yield of 96.22% was obtained with the following optimal reaction conditions: temperature of 60°C, ratio of methanol to oil of 12:1, and 1 wt% catalyst for 10 min. Koberg et al. [36] evaluated the capability of producing biodiesel from *Nannochloropsis*

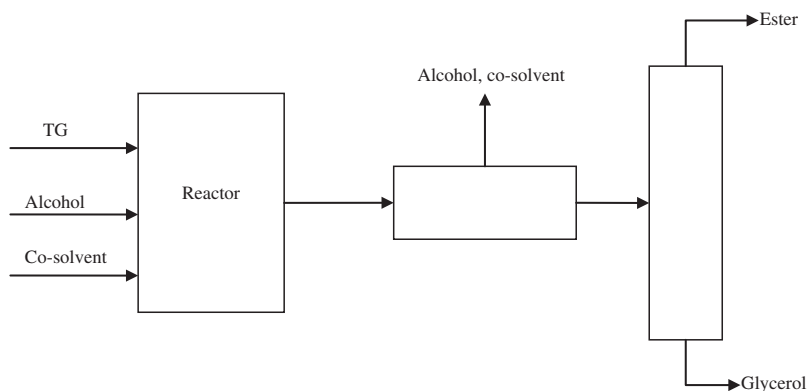


Figure 4 BIOX process.

microalgae, with the aid of SrO catalyst. It was found that a direct transesterification reaction using microwave irradiation resulted in a higher biodiesel yield of 37.1% in 5 min, while only 20.9% yield can be obtained in the same reaction time by using the ultrasound-assisted (UA) technique. This work also indicated that the use of a unique biotechnology-based environmental system utilizing flue gas from a coal burning power station for cultivating microalgae reduced the cost of algae production significantly.

Jianxun and co-workers [37] synthesized a solid base catalyst (K_2SiO_3/C) capable of microwave absorption, which was used for the transesterification of soybean oil under microwave radiation. The K_2SiO_3/C catalyst was prepared by an impregnation method that loaded K_2SiO_3 on carbon particles followed by drying at 120°C. The maximum yield of biodiesel was 96.5% after 150 min reaction time at 65°C, with a methanol to oil ratio of 30:1 and a catalyst concentration of 24 wt%.

Chen et al. [38] reported the microwave-assisted transesterification of waste cooking oil in the presence of methanol and CH_3ONa catalyst. The experimental results showed that an increase of reaction time from 1 to 3 min caused a significant increase in biodiesel yield, which decreased with a further increase to 6 min. The optimal reaction conditions are 0.75 wt% catalyst, a methanol to oil ratio of 6, a reaction time of 3 min, and a microwave power of 750 W.

Kim et al. [39] studied the microwave-assisted esterification of FFA with a heterogeneous catalyst, namely sulfated zirconia ($S-ZrO_2$), in order to demonstrate the microwave energy efficiency. In the reaction condition of 5 wt% sulfated zirconia and a ratio of oil to methanol of 20:1 at 60°C, more than 90% conversion of the esterification was achieved in 20 min by microwave heating, while the same reaction needed 130 min with conventional heating. The authors also concluded that the electric energy consumed by microwave heating was only 67% of the minimum conventional estimated heat energy due to the significant reduction in reaction time.

Recently, calcium oxide was intensively utilized in various techniques for biodiesel production including microwave-assisted process. Hsiao et al. [40] examined the effect of nanopowder CaO on the transesterification of soybean oil assisted by microwave irradiation. The reaction conditions that could reach a 96.6% of conversion, were a methanol to oil molar ratio of 7:1, 3.0 wt% catalyst, a reaction temperature of 65°C, and a reaction time of 60 min. Kamath et al. [41] investigated two-step biodiesel synthesis using microwave irradiation. Crude karanja oil, with high FFA (8.8%), was reduced to 1.1% by pretreating

the oil with methanol (33.83 w/w% methanol–oil ratio) employing H_2SO_4 as a catalyst (3.73 w/w%) and irradiating for 190 s at 180 W. The pretreated oil was used to prepared biodiesel via alkali catalyzed transesterification. The optimal parameters were a methanol to oil ratio of 33.4, a KOH concentration of 1.33 wt%, and a microwave irradiation time of 150 s at 180 W. The predicted FAME yield of 91.4% was validated experimentally.

2.4.4 UA method

Various studies implemented UA transesterification to reactions catalyzed by acid, base or enzymes, in the case of different kinds of feedstock, such as oil-bearing materials (seeds, rice, bran), waste cooking oils, fish oils, and animal fats [42]. In UA processes, batch and flow reactors with indirect or direct sonication are used. The former is performed in a reaction vessel (usually Erlenmeyer or a round-bottom flask) immersed in an ultrasonic cleaning bath and the latter is performed in a reaction vessel with an ultrasonic processing probe, known as horn, sonotrode or sonoprobe. Two sonication modes are used, either pulse (on-off cycles) or continuous.

UA transesterification is among the alternative and innovative biodiesel production processes. The use of UA transesterification has been already proved to be very effective for intensification of biodiesel production processes [42]. Despite the large potential for UA transesterification, further studies are needed to overcome considerable technical and process limitations. Several different approaches have been used in the last decade to improve the UA biodiesel production, such as the optimization of process factors using statistical methods, modeling the process kinetics, the application of *in situ* UA transesterification processes, the use of phase transfer catalysts, the use of a continuous process instead of batch ones, and the development and application of novel types of ultrasonic reactors.

One of the latest modifications is the combination between ultrasounds and microwaves, which leads to synergistic effects [43]. This approach improved process chemistry, yield, and reduction in the process time by about 15 times. Esterification processing was employed to reduce the initial acid value of the oil from 18.9 mg to 1.7 mg of KOH/g oil with the purpose of avoiding a saponification reaction during the alkaline transesterification. The molar ratio and catalyst concentrations have been optimized for the esterification and transesterification stages for microwave, ultrasound, and sequential approaches. It was observed that the optimum molar

ratio required for esterification is 1:4, 1:3, and 1:2 for the ultrasound, microwave, and sequential approach, respectively, whereas for transesterification, the optimum ratio in the same order is 1:6, 1:6, and 1:4. The reaction time for esterification and transesterification using ultrasound alone was 60 min and 20 min, respectively, and it reduced to only 15 min and 6 min, respectively, for the sequential approach. The energy required for processing and separation was reduced significantly compared with individual operation.

2.4.5 Non-catalytic process

In a catalytic reaction to produce biodiesel through transesterification, several post-reaction processes, such as purification of the esters, separation, and recovery of residual reactants and catalysts are involved [2, 4, 44]. These processes render the production of biodiesel transesterification system complicated, thus giving a reason to investigate the production of biodiesel from triglycerides via non-catalytic reactions. There are mainly two non-catalytic transesterification processes which will be discussed in detail.

The use of supercritical fluids (SCFs) is an innovative approach to be used in various industrial applications [2, 4, 44]. Numerous research works concerning biodiesel synthesis via SCFs have been investigated and the summary of all current SCF techniques will be discussed in the next part of this review.

3 SCF technology

3.1 Definition

There are some unique characteristics associated with SCFs which allow them to be applied in different industrial applications [2, 44]. One of the first applications of SCFs was the decaffeination of coffee with carbon dioxide (CO_2). More recently, SCFs have been used as benign solvents in various production stages in the microelectronics, pharmaceutical, biomedical, and biofuel industries.

In conventional biodiesel production, product separation and isolation, along with catalyst recovery, are by far the most energy intensive steps in biodiesel production and, therefore, the most economically unfavorable. SCFs are able to bring some advantages, facilitating these separation and isolation processes [2]. As a result, the use of a SCF phase as a reagent for biodiesel synthesis

seems a straightforward approach. Considering that the nature of the solvent is controlled by the pressure and temperature, the formation of a single phase between the reagents and the triglycerides can be induced. Although high pressures and temperatures are needed to reach a homogeneous phase, the transesterification reaction kinetics is favored under these harsh conditions. In aid of those conditions, the reaction can proceed in the absence of any catalyst, leading to non-catalytic biodiesel synthesis.

Furthermore, the isolation of the biodiesel from glycerol is simpler, since many discrete operations, such as catalyst neutralization and separation, are not required, leading to products of higher purity; this is also important from an economic point of view. Thus, SCF technology, even though it requires the use of high temperatures and pressures, may provide distinct advantages over conventional technologies. For instance, in the conventional alkali-catalyzed method, the final glycerol phase contains methanol, water, alkaline catalyst, and soap. Thus, the selling price value of this crude glycerol is extremely low compared with the purified glycerol commonly used in food and pharmaceutical products.

In summary, there are two main ways of biodiesel synthesis via SCFs: single-step and two-step.

3.2 Single-step SCF

The main reaction of this process is the typical transesterification with direct conversion of triglycerides into biodiesel. Although alcohols (ethanol and methanol) are popular selections for the development of non-catalytic biodiesel synthesis by transesterification reactions in SCFs, other fluids (dimethyl carbonate, methyl acetate) have also recently been taken into account.

3.2.1 SCF methanol

Supercritical methanol (SCMe), the critical parameters of which are critical temperature (T_c)=239.4°C, critical pressure (P_c)=8.1 MPa, and ρ_c =0.276 g.cm⁻³, was one of the first SCFs evaluated for the production of biodiesel. The promising results obtained with supercritical alcohols, have led to many studies on the effects of various reactions parameters on FAMES yield.

In early studies of SCMe, Saka and Kusdiana [45] and Kusdiana and Saka [46] investigated the conversion of rapeseed oil into biodiesel at 350°C and 400°C, at a pressure of 45–60 MPa, and with a fixed methanol to oil ratio

of 42:1. It was stated that, at a temperature of 350°C, after 4 min of treatment with SCF methanol, the yield of FAME was found to be higher than that of the common method with a base catalyst.

Madras et al. [47] conducted experiments (with sunflower oil employed as feedstock) over the temperature range of 200–400°C, at a constant pressure of 20 MPa. The highest FAME yield was 96% at the following optimal conditions: temperature 400°C, methanol to oil ratio 40:1, reaction time of 40 min.

The main drawback of SCF is the cost of equipment, due to the harsh operation conditions at high temperatures and high pressure. Some authors have employed a catalyst for SCMe, with the ultimate purpose of gaining milder conditions, so as to reduce the expenditure for the whole process.

Wang et al. [48] carried out the transesterification reaction of rapeseed oil with SCMe in the presence of NaOH, without soap formation. Various parameters of the reaction were studied to obtain the optimal conditions for the process. A high methyl ester yield (up to 98%) was reported at a temperature of 220°C after 13 min of reaction, at a pressure of 5.6 MPa and 0.8 wt% NaOH.

In another study, by Yin et al. [49], a small amount of KOH was added to the reaction under SCMe and the yield of FAME reached 98% in 10 min at 160°C, with a methanol to oil ratio of 24:1. This yield is obviously more efficient than that of the traditional alkali-catalyzed path which produced 6% FAME with 1% catalyst at a temperature of 260°C. In order to decrease the disadvantage of homogeneous catalyst, the same authors [50] studied the synthesis of biodiesel from soybean oil in the presence of a heterogeneous catalyst tri-potassium phosphate (K_3PO_4) in SCF methanol. The outcome obtained displayed high catalytic activity of K_3PO_4 towards the transesterification of soybean oil. The highest yield of FAME was 95.6% under the following conditions: temperature of 220°C, methanol to oil ratio of 24:1, and 1 wt% catalyst.

Tateno and Sasaki [51] reported the use of MgO for SCMe with sunflower oil and obtained the highest yield of FAME of 91% at 300°C, with a methanol to oil ratio of 39.6:1 and a catalyst concentration of 1.29 wt%. Recently, Wang and Yang [52] investigated the variables affecting the conversion of soybean oil into biodiesel in the support of nano-MgO. The reaction was completed within 10 min, at a temperature of 260°C and a methanol to oil ratio of 36:1.

Yoo et al. [53] examined the synthesis of biodiesel using SCMe with some metal oxide catalysts (included CaO, SrO, ZnO, TiO_2 , and ZrO_2). ZnO was chosen as the optimal catalyst for transesterification of rapeseed oil in

SCF methanol; the yield was around 95% at 250°C and 15 MPa after 10 min. This study was believed to be more profitable than any other process, including the alkali-catalyzed process and non-catalytic supercritical process. Shin et al. [54] combined Cs-doped heteropolyacid catalyst with SCMe to investigate an efficient and environmentally friendly method for biodiesel synthesis. This study discovered that $Cs_{2.5}PW_{12}O_{40}$ exhibited highest stability in SCF methanol and the content of obtained FAME was 92% under the optimal conditions of 260°C, 20 MPa, and a methanol to oil ratio of 40:1 after 40 min reaction in the presence of 3% catalyst.

In an attempt to decrease the dependence on agriculture-based feedstock, Shin et al. [55] carried out biodiesel preparation from waste lard, which is available at restaurants after cooking. The highest yield of FAME was reached at 89.9% under the following optimal conditions: temperature of 335°C, a methanol to oil ratio of 45:1, pressure of 20 MPa, and a time reaction of 15 min. It is concluded that waste lard can be seen as an alternative source for the synthesis of biodiesel, thus replacing the expensive refined vegetable oil, and the SCMe with this feedstock should be considered as a promising process for the biofuel industry.

The obvious advantage of using SCFs is that they are capable of tuning and controlling the solvent polarity through the adjustment of temperature and pressure. Indeed, the dielectric constant of methanol decreases from 34 to 5 upon isobaric heating from 25°C to 260°C at 20 MPa [44]. The hydrogen bond network existing in liquid methanol is broken under SC conditions, leading to a fluid in which only small oligomers exist. Reduction of the polarity and hydrogen bonding can support a much stronger direct nucleophilic attack by methanol on the carbonyl group. Furthermore, a reduced dielectric constant may even lead to a single oil/alcohol phase, increasing the reaction rate. These facts explain the differences observed when the reaction is performed either under subcritical or supercritical conditions, since the reaction kinetics is highly dependent on the homogeneity of the reaction mixture. The solubility of reactants and transesterification products (homogeneous or heterogeneous) in the alcohol under various pressure-temperature-molar fraction (P-T-x) conditions is a keystone for rapid and complete transesterification reactions.

Anitescu and Bruno [56] and Anitescu et al. [57] studied the liquid-vapor-SC phase transitions for the binary/ternary systems (soybean oil and alcohol at different oil:ethanol molar ratios), by using a view cell attached to the outlet of the reactor, which was heated from 26°C to 400°C at constant volume/density. With

two liquid phases in ambient conditions, the system showed increasing homogeneity with increasing temperature and pressure, until a single SC phase was reached. Under these conditions, the conversion of triglyceride to FAMES was very rapid compared to that observed under subcritical conditions. The reaction in continuous flow conditions yields above 98% conversion, with a single clear phase at moderate pressures (10–20 MPa), high temperatures (375–400°C), low methanol ratios (3:1–6:1), and short reaction times (<3 min). These results are in contrast with those reported by Hegel et al. [58], Pereda et al. [59], and Velez et al. [60], who observed that high conversion can be obtained, in most cases, even when operating in the two-phase region. In this case, oil transesterification could mainly occur in the light supercritical phase, where the oil and the monoglycerides and diglycerides are partially soluble and the concentration of methanol is high. Moreover, the light-phase transport properties favor a higher reaction rate. The increased methanol/oil ratio leads to a homogeneous supercritical phase by increasing the system temperature while working at moderate pressures of 10–15 MPa, since an increase in the methanol/oil ratio decreases the T_c of the system. Although a high methanol ratio favors the formation of a homogeneous supercritical phase while also driving the reaction to completion, it also increases costs and energy consumption.

An additional advantage of the use of supercritical alcohols in biodiesel synthesis, is the high tolerance towards possible feedstock contaminants, mainly FFAs and water. In supercritical alcohols, esterification of the FFAs to the corresponding FAAEs takes place simultaneously to oil transesterification, yielding higher amounts of biodiesel. Thus, low cost feedstock, usually containing high portions of FFA/oil, can be used in the process without any additional pretreatment. Regarding water content, transesterification reactions catalyzed under acid or alkaline conditions are highly sensitive to the presence of water, as hydrolysis of the corresponding esters is favored in the presence of water. In contrast, the non-catalytic supercritical process can be performed even with high water contents.

3.2.2 SCF ethanol

The selection of the alcohol is based on the consideration of cost and performance. Also, the application of ethyl ester is more beneficial than that of methyl esters if being based on environmental considerations. Ethanol can be prepared from agricultural renewable feedstock, thereby

gaining total independence from petroleum-based alcohols. Moreover, ethanol, as an extraction solvent, is preferable to methanol, because of its much higher dissolving power for oils. Therefore, ethanol is sometimes used as a suitable alcohol for the transesterification of vegetable oils. Most research into vegetable oil ethanolysis has been performed in the South America countries, especially in Brazil, which is one of the greatest producers of ethanol from biomass in the world.

The fuel qualities of alkyl esters depend on the alcohol being used for transesterification. Some authors stated that higher or branched alcohols can generate biodiesel with better fuel characteristics. Some studies reported that methyl ester and ethyl ester are similar in heat content, but ethyl ester is slightly less viscous than methyl ester. Therefore, producing ethyl esters rather than methyl esters is of great interest, due to the entirely agricultural nature of the ethanol; moreover, the extra carbon atom provided by the ethanol molecule slightly increases the heat content and the cetane number.

Madras et al. [47] reported the highest conversion of sunflower oil of SCF ethanol compared to methanol when performing experiments over the temperature of (200–400°C) at a constant pressure of 20 MPa, a methanol to oil ratio of 40:1, and a reaction time of 40 min. The reason of higher yield of FAEE can be explained by the solubility of the oil in the system. In the supercritical state, there is only single phase in the mixture of reactants. The solubility of ethanol is closer to that of oil than of methanol; therefore, the conversion is higher in ethanol compared to methanol.

An optimization study on ethanol as the SCF was carried out by Gui and Lee in 2009 [61]. The reaction was performed in a batch-type tubular reactor, with palm oil employed as feedstock for a specific duration ranging from 2 to 30 min; the temperature was screened by a proportional-integral-derivative controller. This study focused on the effects of the individual parameters during the reaction. It was reported that an FAEE yield of 83.1 wt% was achieved at a temperature of 349°C, an ethanol to oil ratio of 33, and a reaction time of 29 min. The yields, obtained at the investigated reaction conditions in this work, are lower than those of other researchers, which is crucial in terms of economic viability to commercialize this process.

In a new approach to reduce the intensity of the operating conditions, Santana et al. [62] employed a co-solvent (CO_2) along with ethanol to prepare biodiesel under a supercritical state, in a fixed-bed reactor. The highest yield of biodiesel was recorded at a temperature of 200°C, a reaction time of 4 min, a molar ratio of 1:25, and a pressure of 20 MPa. The addition of CO_2 is the main reason for

lowering of the temperature, and can lead to a reduction of the operating costs.

A research team at Oregon State University (US) [63] made a breakthrough for continuous production of biodiesel with tin-based catalysts with supercritical ethanol and methanol. The catalyst was applied to 50–250 μm stainless steel plasma powder, then tested with six different kinds of oil. With all type of oils, the conversion was >90% under the following operating parameters: temperature of 305°C, pressure of 17.3 MPa, ethanol to oil ratio of 30:1, and residence time of 8 min.

3.2.3 SCF methyl acetate

A new process using methyl acetate to prevent the production of glycerol as a byproduct has been recently studied under supercritical conditions (Figure 5). The supercritical methyl acetate (SCMA) non-catalytic method converts triglycerides into FAMES and triacetin, instead of glycerol. In addition, it is believed that there were no adverse effects on the main fuel characteristics when the molar ratio of methyl oleate to triacetin was 3:1, which corresponds to the theoretically derived molar ratio from the transesterification reaction of rapeseed oil with methyl acetate. Moreover, the addition of triacetin improved the cold flow properties and has high oxidation stability. Therefore, by defining biodiesel fuel (BDF) as a mixture of methyl oleate and triacetin, the yield of SCMA can reach 105% of BDF compared with the conventional process. However, this value is lower than the theoretical maximum recovery (125% yield), due to the breakdown of some unsaturated FFMEs at the high operating temperatures. Despite this fact, the SCMA method not only improves the quality of the BDF, but also minimizes the separation and purification steps, and therefore the energy required. Moreover, triacetin is itself a valuable compound that can be used in the cosmetic and food industry, or as an additive to petroleum-based fuel.

The first study on the application of methyl acetate as SCF for biodiesel production was proposed by Saka and Isayama [64]. The conditions were set at temperatures of 270–380°C, 20 MPa of pressure, a reaction time ranging

from 10 to 120 min, and the methyl acetate to oil ratio equal to 42:1. It is reported that the highest yield of BDF was 105% (at 350°C and 20 MPa), which is still higher than the maximum conventional recovery of BDF (100%) when measured as FAME only.

Campanelli et al. [65] employed various feedstocks for biodiesel synthesis via SCMA. The process proved to be appropriate for edible, non-edible or waste oils, regardless of the FFA content. The author carried out experiments under different conditions: the reaction temperature ranged between 300°C and 450°C and the pressure between 10 MPa and 30 MPa; the methyl acetate to oil ratio varied between 25:1 and 59:1. Complete conversion was achieved after 50 min at 345°C, 20 MPa, and with methyl acetate:oil molar ratio equal to 42:1, with the highest yield of BDF being equal to 106%.

In order to obtain a deeper understanding into the SCMA, Tan et al. [66] investigated various factors, including temperature, pressure, reaction time, and the molar ratio, which have a strong influence on the reaction performance. It is critical to thoroughly examine these effects to acknowledge the prospect of SCMA for biodiesel synthesis at the industry-scale. This study showed a 99 wt% BDF yield, achieved at 400°C, a molar ratio of 30:1, and a reaction time of 60 min. More importantly, the SCMA process demonstrated a high tolerance to impurities normally found in oils/fats, such as water and FFA. This allows utilizing inexpensive triglycerides, rather than refined oils.

Goembira et al. [67] used various supercritical carboxylate esters to convert triglycerides into FAMES and triacetin, without the presence of a catalyst. The experiments were performed with a molar ratio of carboxylate ester to oil of 42:1 at 350°C in a batch-reaction vessel. The highest product yield was obtained with SCMA, 97.7 wt% when considering a mixture of both FAMES and triacetin as BDF. Lower reactivity was shown by other carboxylate esters, which seems to be related to the length of alkyl chains in the esters, e.g., longer alkyl chains in both alcohol and acyl moieties of carboxylate esters gave lower product yields.

3.2.4 SCF dimethyl carbonate

Other authors have studied the use of supercritical dimethyl carbonate (SCDMC) instead of methanol SCDMC ($T_c=274.9^\circ\text{C}$, $P_c=4.6$ MPa). In this way, triglycerides, as well as FAs, are successfully converted to FA methyl esters (FAMES). Besides, with this methodology, another valuable compound, namely glycerol carbonate, is obtained as a secondary product, instead of the undesirable glycerol, and a weak acid, such as citramalic acid, as the main

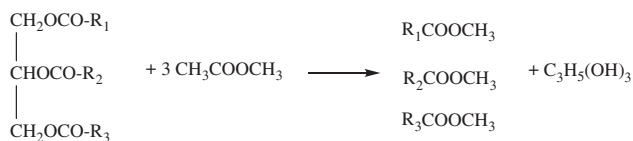


Figure 5 Transesterification between triglyceride and methyl acetate.

Table 1 Summary of operating conditions of various transesterification reactions.

No.	Method	Reactant	Catalyst/loading (wt%)	Alcohol to oil ratio	Yield (%)	T (°C)	P (MPa)	Time (min)	Reactor	Reference
1	Convention	Methanol/jatropha curcas oil	KOH/1	6/1	98	50	0.1	120	Batch-type	[8]
2	Convention	Methanol/soybean oil	KOH/2	6/1	97	60	0.1	3	CSTR	[9]
3	Convention	Ethanol/sunflower oil	NaOH/1.25	12/1	98	74.6	0.1	5	Batch-type	[7]
4	Convention	Methanol/waste cooking oil	H ₂ SO ₄ /4	20/1	90	95	0.1	600	NA	[10]
5	Convention	Methanol/waste cooking oil	Fe ₂ (SO ₄) ₃ and KOH/2	10/1	97	95	0.1	240	NA	[10]
6	Convention	Methanol	MgO	NA	18	NA	NA	NA	NA	[16]
7	Convention	Methanol/soybean oil	MgO/5	12/1	90	180	0.1	60	NA	[87]
8	Convention	Methanol/soybean oil	CaO/	NA	93	NA	NA	60	Batch-type	[11]
9	Convention	Methanol/waste cooking oil	CaO/	NA	99	NA	NA	120	Batch-type	[11]
10	Convention	Methanol/refined palm oil	CaO/5	NA	NA	65	0.1	NA	Batch-type	[13]
11	Convention	Methanol/soybean oil	TiO ₂ -SiO ₂ /0.5	NA	70	180	0.1	60	NA	[18]
12	Convention	Methanol/soybean oil	TiO ₂ /	6/1	40	120	0.5	60	NA	[19]
13	Convention	Methanol/castor oil	TiO ₂ /	6/1	25	120	0.5	60	NA	[19]
14	Convention	Methanol/sunflower oil	Zeolite X	NA	95	60	NA	NA	NA	[20]
15	Convention	Methanol/refined palm oil	Zeolite-KOH/3	7/1	95	60	0.1	120	Batch-type	[21]
16	Convention	Methanol/waste frying oil	Cation-exchange resin NKC-9	NA	90	NA	0.1	NA	Batch-type	[22]
17	Convention	Methanol/waste frying oil	Cation-exchange resin NKC-9	NA	98	65	NA	NA	CSTR	[23]
18	Convention	Methanol/jatropha curcas oil	ZrO ₂ -SO ₄ /7.6	10/1	90	150	NA	240	Batch-type	[24]
19	Convention	Methanol/jatropha curcas oil	ZrO ₂ -SO ₄ /	40/1	90	60	NA	720	NA	[25]
20	SCF	Methanol/rapeseed oil		42/1	NA	350	NA	4	NA	[30, 31]
21	SCF	Methanol/sunflower oil		40/1	96	400	20	40	Batch-type	[32]
22	SCF	Methanol/rapeseed oil	NaOH/0.8	24/1	98	220	5.6	13	Batch-type	[33]
23	SCF	Methanol/soybean oil	KOH/0.1	24/1	98	160	NA	10	Batch-type	[34]
24	SCF	Methanol/soybean oil	K ₃ PO ₄ /1	24/1	96	220	NA	30	Batch-type	[35]
25	SCF	Methanol/sunflower oil	MgO/1.3	40/1	91	300	NA	NA	Batch-type	[36]
26	SCF	Methanol/sunflower oil	MgO/3	36/1	91	300	NA	10	Batch-type	[37]
27	SCF	Methanol/rapeseed oil	ZnO/1	40/1	95	250	15	10	Batch-type	[38]
28	SCF	Methanol/waste lard		45/1	90	335	20	15	Batch-type	[40]
29	SCF	Ethanol/sunflower oil		40/1	99	400	20	40	Batch-type	[32]
30	SCF	Ethanol/palm oil		33/1	83	349	NA	29	Batch-type	[46]
31	SCF	Ethanol/sunflower oil/CO ₂	NafionSAC-13	25/1	80	200	20	4	CSTR	[47]
32	SCF	Ethanol/soybean		30/1	90	305	17.3	8	CSTR	[48]
33	SCF	Methyl acetate/rapeseed oil		42/1	105	350	20	10	NA	[49]
34	SCF	Methyl acetate/waste oil		42/1	106	345	20	50	CSTR	[50]
35	SCF	Methyl acetate/palm oil		30/1	99	400	NA	60	Batch-type	[51]
36	SCF	Dimethyl carbonate/palm oil		39/1	91	380	NA	30	Batch-type	[53]
37	SCF two-step	Methanol/rapeseed oil		NA	99	270	17	40	NA	[55]

byproduct. Glycerol carbonate has a higher commercial value than glycerol, and has a greater potential for industrial application. Hence, this methodology could have a large impact on biodiesel economics, as two high-value products are produced in a single-step reaction, leading to increased cost effectiveness, even if high temperatures and pressures are required. The FAMES produced by this method are obtained at higher yields than with SCMe, and satisfy the international standards for use as BDF. In conclusion, many works have been done to demonstrate the huge potential of SCDMC to prepare biodiesel economically.

Tan and co-workers [68] carried out the optimization study of SCDMC by using response surface methodology analysis. It was reported that the optimum conditions for SCDMC were 380°C for the reaction temperature, a dimethyl carbonate to oil ratio of 39:1, and 30 min of reaction time, which achieved a 91% yield of biodiesel.

Ilham and Saka [69] reached 97 wt% of FAME yield for the SCDMC at 300°C, 20 MPa, 20 min, and a 42:1 molar ratio of dimethyl carbonate to oil. This work also investigated the fuel properties of FAMES to ensure that they are satisfactory as biodiesels. The results demonstrated that the FAME from this method met all requirements for international biodiesel standards of Japan, Europe, and the US, except for the oxidation stability. However, this drawback can be eliminated by the addition of an antioxidant or by employing feedstocks with low levels of unsaturated FAs.

3.3 Two-step SCFs

The one-step process requires high reaction temperatures and molar ratios of alcohol to oil. Therefore, it consumes a large amount of energy, especially in the methanol recovery section. In order to decrease these harsh conditions, an alternative non-catalytic process in SCFs for the synthesis of BDF consists of a two-step process. In this process, triglycerides are firstly hydrolyzed to FFAs under subcritical water conditions, which, in a second consecutive step, are esterified to the corresponding esters with SCMe [7]. Figure 6 illustrates the process flow diagram.

The first example developed according to this concept is known as the “Saka-Dadan” process [70]. In the first step, the unique properties of H_2O in the critical state (supercritical water, scH_2O) are exploited. It is well known that the dielectric constant of water decreases from 80 at standard temperature and pressure to 31 at 225°C, pressure=10 MPa, and finally to 6 at the critical point, $T_c=374.15^\circ C$, $P_c=22.1$ MPa, due to the steady decrease in the effectiveness of the hydrogen bonds with increasing temperature.

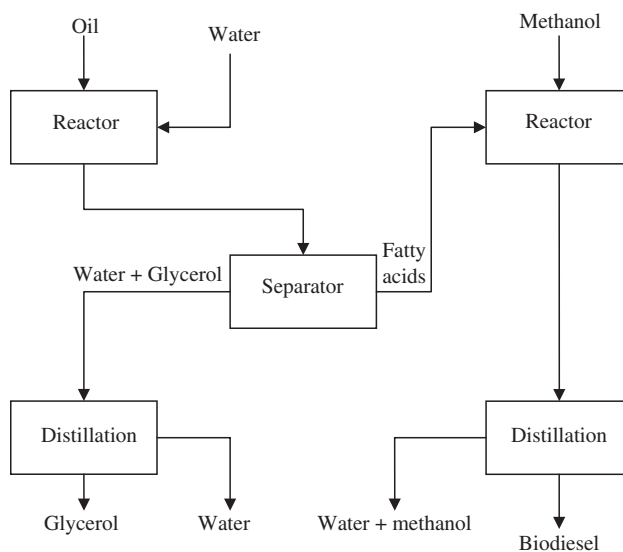
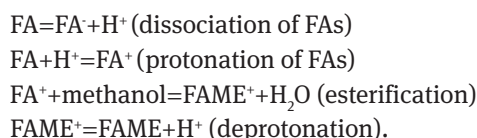


Figure 6 Diagram of process flow of two-step SCF method.

Thus, the reduction of the dielectric constant with increasing temperature promotes the miscibility between water and the oil, favoring a hydrolysis process. Furthermore, at a constant pressure of 25 MPa, the ionic product of water increases with temperature until it reaches a maximum (10–11) at 250°C. This allows acid- and base-catalyzed reactions to be performed at a high temperature, in pressurized water, and with no catalyst. Hence, scH_2O is used as both the solvent and the catalyst for the hydrolysis step at 270°C, 7 MPa, and a volumetric water/triglyceride ratio of 1:1. These conditions are milder than those reported for the original one-step process in SCMe (350°C and 20–50 MPa), thus reducing the energy consumption.

Two layers are formed after the hydrolysis, in which the upper portion contains FAs, and the main composition of the lower portion is water with glycerol. The next step is the production of FAMES under SCMe after 20 min at 270°C and 7 MPa. Due to recent findings, there is a shortage of information on reaction kinetics of esterification reactions. Saka and Minami [71] employed tubular flow reactors, made of Hastelloy C-176, to conduct the experiments, and proposed an autocatalytic reaction mechanism to model both reactions. The esterification is shown below:



The initial step involves the dissociation of FA to release a hydrogen ion. This is followed by the protonation of the carboxyl oxygen of the FAs. Then, alcohol attacks the protonated carboxyl group, and a protonated ester is formed

with the accompanied one water molecule. In the final step, a proton is liberated to produce FAME.

Another solution to apply the two-step method is to use dimethyl carbonate, named the “Saka and Ilham Process” [72]. The hydrolysis conditions are 270°C and 27 MPa, and are followed in a second step by the esterification of FAs to FAME in SCDMC at 300°C and 9 MPa. The SCDMC method is applicable to high FFAs contents, such as *Jatropha curcas* oil, with 13.6 wt% FFAs. The glycerol produced in the first step was valorized in the second step, obtaining glycerol carbonate in SCDMC (280–300°C and 9–12 MPa) without any catalyst. The non-catalytic two-step SCDMC method is a good process for producing high yields of FAMES, even from oils with high levels of unsaturated FAs, together with a value added byproduct, glycerol carbonate, under non-acidic and mild reaction conditions.

The same group has also reported a two-step process, in which the first step is transesterification of the oil to triacetin, carried out in either subcritical or supercritical acetic acid, followed by SCMe treatment [73]. A transesterification reaction occurs between acetic acid and the triglycerides under subcritical conditions, without the addition of catalysts. It was clear that FAs and triacetin could be obtained at high yields. The reaction rate in acetic acid was much higher than when either methyl acetate or methanol was used in the transesterification step. The yield of triacetin recovery from subcritical acetic acid treatment by aqueous washing was 64%. By contrast, when the oil phase from the previous treatment containing FAs was supplied to the SCMe process at 270°C and 17 MPa for 15 min, a 97 wt% yield of FAMES was obtained. The recovery rate of BDF from this process was 117 wt%, a higher value than that obtained by conventional BDF

manufacturing processes, which produce glycerol as a byproduct.

3.4 Economic viability

The biodiesel market represents a relatively young business started about 15 years ago, driven by two main factors: new environmental regulations (e.g., EU target of greenhouse gas reduction of 20% by 2020) and the dramatic increase of the price of oil.

Thus, FAME became important alternative fuels for diesel engines, due to the diminishing petroleum reserves. Nowadays, the EU biodiesel market corresponds to the world’s largest one. Biodiesel is the most important biofuel in Europe, representing, on energy basis, about 75% of total biofuel used for transport. The production volume is strongly increasing. Considering the new environmental regulations (e.g., Directive 2009/28/EC), for the near future, a continuation of the positive trend and a further increase of the biodiesel market volume can be expected.

Based on the information given in the chart biodiesel production *versus* installed plant capacities in Europe (Figure 7, taken from the European Biodiesel Board [74]), up to 2006, almost all biodiesel plants produced at full capacity, while from 2007, the difference between effective biodiesel production and installed capacities has been rising. Thus, although there was a continuous increase of production volume, many plants were closed or work was carried out at partial load. The main reason for this trend can be referred to raw material costs. The biodiesel production costs are strictly related to the feedstock price, especially vegetable oil that represents

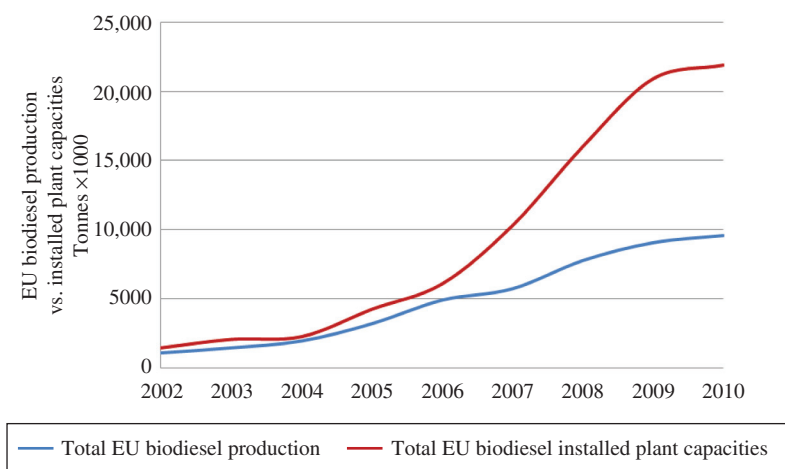


Figure 7 EU biodiesel production *versus* installed plant capacities.

typically over 70% of the total production cost [75]. The constant growth of biodiesel production resulted in a strong increase in the demand for vegetable oil, which consequently led to a sharp increase in the corresponding material price. At the current vegetable oil price, the production cost of biodiesel is quite high compared to common petroleum-based diesel. In return, many European state governments are trying to make biodiesel competitive to common petroleum-based diesel through tax advantages. However, this approach can only solve the problem in the short-term; a better long-term solution has to be found.

Thus, the competitiveness of biodiesel is nowadays hindered by the price of vegetable oils. The use of waste vegetable oil can be a solution here, because its use gives a double benefit, as it provides a cheap feedstock, and also makes use of waste.

Although SCF technology involves higher capital and running costs with respect to conventional processes [76], the possibility of exploiting low price feedstock through innovative non-catalytic supercritical processes, possibly coupled to the production of higher-added value byproducts than glycerine [77], could pave the way for a wider exploitation of biodiesel for small and medium sized enterprises.

4 Conclusions

The purpose of this article was to review the current technologies in biodiesel production, with special focus on SCF technology. Generally speaking, high viscosity appears to be at the root of many problems which occur with the direct use of vegetable oils as diesel engine fuel. The transesterification of triglycerides with an alcohol has proved to be an efficient method of choice.

Among all current transesterification methods, the reaction with homogeneous base catalysis 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. The high consumption of energy and costly separation of the homogeneous catalyst from the reaction mixture, however, have called for development of a heterogeneous catalyst. From previous research and environmental considerations, it seems that heterogeneous biocatalysts would be the method of choice.

A new technology called the BIOX process, with the use of an unrevealed catalyst, has been developed in order to overcome the problem of low solubility of methanol in oils. This process uses a co-solvent to stabilize the alcohol.

Besides the traditional methods, non-catalytic synthesis of biodiesel or supercritical alcohol was used. The advantages of SCF technology in biodiesel production compared to conventional catalytic reactions are enormous and vital in solving the issue of energy security in the future. However, there are several challenges which need to be addressed before SCF technology can play a major role as the main route for renewable and sustainable biodiesel production. Another advantage of this process is that the free FA changes completely in to esters.

A recent trend in SCF technology, is the use of a catalyst to reduce the harsh operation conditions. Some metal oxides have been studied and provide a high yield of biodiesel under milder conditions and the ability to regenerate. Hence, it is essential to concentrate on this novel approach, due to its promising results. However, additional research into the economic viability should be made, before taking into consideration an industrial biodiesel production.

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