



# Catalyst free supercritical fluid technology for sustainable biodiesel production: A review

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## Abstract

Biodiesel, a renewable energy source has gained worldwide attention due to un-sustainability and environmental contamination caused by petroleum based fuels. Catalytic processes commonly employed for biodiesel synthesis have many limitations and disadvantages, including huge energy utilization for complex purification operations and unwanted side reactions. These inconveniences of the conventional biodiesel production methods led research towards substitute methods, with the non-catalytic supercritical transesterification emerged as one of the promising technology for commercial scale biodiesel production. Supercritical fluid technique offers a number of advantages over traditional processing technologies including elimination of catalyst necessities, feedstock flexibility, negligible impact of water and non-glyceride linked fatty acids, ease of operation and production efficacy. This article discusses the potential of supercritical fluid technology as a sustainable biodiesel production route, influence of reaction parameters on FAMES yield and process intensification protocols. Although the benefits of non-catalytic supercritical process are obvious; there are concerns about the enormous energy required to perform supercritical reaction at harsh operating conditions i.e. high temperature and pressure. Therefore, this technology faces challenges that need to be addressed before it could be a sustainable technology of future.

**Key words:** Transesterification, fatty acids, supercritical conditions, catalyst, co-solvents, fossil fuel

**Full length article** \*Corresponding Author, e-mail: [ayesha\\_mushtaq123@yahoo.com](mailto:ayesha_mushtaq123@yahoo.com)

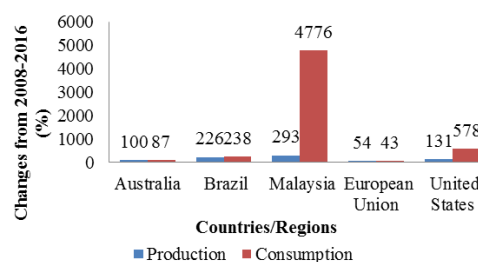
## 1. Introduction

Enhanced energy requirements in transportation, manufacturing/ production, and housing sectors have resulted in increased fuel consumption and extensive utilization of present gas and oil reserves. Escalating pollutant and greenhouse gas emissions are also because of extensive exploitation of fossil fuels [1-2]. Diminishing fuel reservoirs, growing energy demands, and environmental concerns call for an alternative green fuel. One feasible solution is the extended utilization of biodiesel as alternative fuel. Biodiesel as a clean-burning, sustainable, eco-friendly and non-hazardous transportation fuel has gained much attention in recent years. Production and utilization of biodiesel increased drastically in past eight years (2008 to 2016), as shown in (fig. 1) [3].

### 1.1. Conventional biodiesel production approaches

There are several generally accepted technologies that have been well established for the production of biodiesel. Animal fats and vegetable oils are suitable to be modified in order to decrease their viscosities to obtain the product having appropriate characteristics to be used in diesel engine. Various modification procedures are available to

obtain biodiesel of better quality including direct use and blending, microemulsions, pyrolysis, and transesterification [4-6].



**Figure1. Production and consumption of biodiesel in different regions**

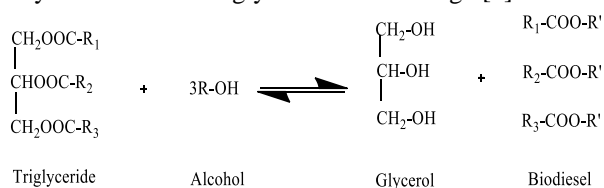
The use of vegetable oils as substitute fuels has been around since 1893, when the diesel engine inventor, Dr. Rudolph Diesel, firstly operated his compression engine using peanut oil [7]. However, direct application of vegetable oil in diesel engine has many inherent disadvantages. Vegetable oils can be diluted or directly mixed with petro-fuels to reduce viscosity so as to solve the issues associated with the use of high viscosity pure vegetable oils in diesel engine. But, direct utilization of

vegetable oils or vegetable oil blends has been generally considered impractical for both indirect and direct compression engines. Blending may improve volatility by reducing viscosity but does not affect the polyunsaturated molecular structure of vegetable oils [8]. Therefore, the use of vegetable oils in diesel engines needs considerable engine modification such as, changing of injector and piping construction materials.

Another possible solution is the use of micro-emulsions to reduce the viscosity of vegetable oils. By definition, micro-emulsion is a colloidal dispersion of optically isotropic liquid microstructures having dimensions ranging from 1-150nm formed spontaneously from two non-miscible liquids and one or more amphiphilic compounds [9-10]. Micro-emulsions of vegetable oils with alcohols (butanol, hexanol, octanol) have been investigated. All micro-emulsions significantly reduced the viscosity of oil but resulted in incomplete combustion, carbon deposition, and irregular injector needle sticking in a 200 h laboratory SET (screening endurance test) [11].

Transformation of animal fats and vegetable oils mainly composed of triacylglycerols using pyrolysis or thermal cracking reactions is a promising viscosity reducing technology [12]. Thermal cracking reactions of oils from soybean, castor, and palm have been studied in the past. Appropriate selection of distillation temperature ranges allowed the separation of fuels with physicochemical properties comparable to petroleum based fuels [13]. But thermal cracking equipment is expensive with low throughputs. In addition, although the products are chemically similar to gasoline and fossil fuels, the removal of oxygen during heat treatment also removes any environmental benefits of using oxidized fuels. It produces materials of low value and sometimes more gasoline than diesel.

The most popular biodiesel production technology is transesterification of triglycerides with alcohol which produces biodiesel (main product) as well as glycerin (by-product). The basic transesterification reaction is shown in Fig 2. The initial step involves the conversion of triacylglycerol to diacylglycerol, followed by the conversion of diacylglycerol to monoacylglycerol and monoacylglycerol to glycerol producing one molecule of methyl ester from each glyceride at each stage [9].



**Figure 2. Transesterification reaction between triacylglycerol and alcohol**

Transesterification reaction catalysis can be divided roughly into two categories; chemical and enzymatic. Chemically catalyzed reactions can be performed using acid

or base, and selection of homogenous or heterogeneous phases depends upon feedstock characteristics. Base catalysis is preferred over acid catalysis as it offers enhanced reaction rates, low temperature demands, and high conversion efficiencies. Sodium hydroxide and potassium hydroxide are conventional catalysts, while, the most applied catalyst at commercial scale is sodium methoxide. The methodology involves catalyst dissolution in methanol by vigorous agitation, and mixing vegetable oil with the resultant solution to give two distinct liquid phases (glycerol and biodiesel) after several hours at 65-90 °C. However, triglycerides containing free fatty acids (>2% w/w), give poor yield with base catalysts because of soap formation. In such situations, acid catalysts such as H<sub>2</sub>SO<sub>4</sub> are used, which requires large quantities of alcohol and complete removal of free water molecules. Homogeneous catalysis generally gives better outcomes than heterogeneous catalysis. However, several complications associated with homogeneous catalysis are; high energy utilization, formation of un-wanted by-products due to presence of free fatty acids, expensive catalyst recovery, generation of huge amounts of waste water during product cleaning. On the contrary, the heterogeneous catalysts utilize less energy and can easily be separated from reaction mixture by simple filtration [6]. Enzymatic transesterification offers simple biodiesel purification protocols with following advantages; requirement of mild operating conditions, single step conversion of non-esterified and glyceride linked fatty acids, no side reactions, and production of high quality byproduct (glycerol). After completion of transesterification reaction, biodiesel is simply separated from glycerol, and neither product neutralization nor deodorization is required [14]. However, the most intriguing attribute of catalytic biodiesel production is the phase behavior of reaction system during conversion process. The starting materials, feedstock and methanol are immiscible, as well as the final products, biodiesel and glycerol. This phenomenon leads to poisoning and deactivation of immobilized enzymes due to adsorption of continuously produced by-product (glycerol) on catalyst surface. In these situations, both the reaction medium and reactor design engineering are indispensable approaches to enhance the activities of bio-catalysts. Other disadvantages of application of bio-catalysts include; high cost of biocatalysts (enzymes), requirement of extended time periods for reaction completion, and poor yield [15].

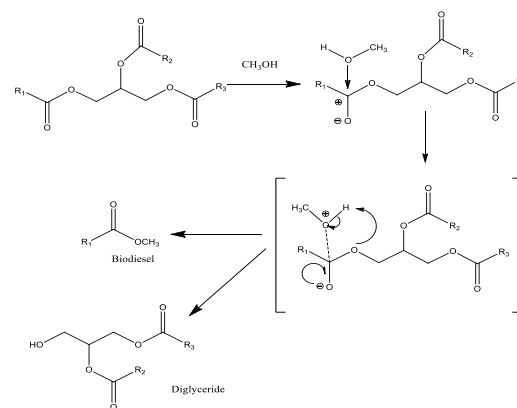
### 1.2. Supercritical technology

A comparatively new substitute to conventional production methods is synthesis of biodiesel under supercritical conditions. The idea was first given by Dadan and Saka [16]. The prime distinctive features of this technique include the absence of catalyst and development of single phase of reactants under vigorous reaction conditions. These conditions lead to a process boosting reaction rates, while permitting the real time transesterification of triacylglycerols along with FFAs

esterification, and a greater efficacy of production encompassing smaller number of steps needed for processing. Another advantage associated with this technique is its tolerance for water and FFAs, the presence of which no longer influences the product yield, which makes it pliable for a variety of feedstocks. Alcohol beyond its critical point shows a decrease in its dielectric constant while simultaneously, an increase in its density, which alters the solubility and mass transfer behavior of alcohol. As a result, triglycerides and alcohol form single phase. Reduction in polarity of alcohol combined with increase of viscosity is because of alterations in hydrogen bonding between molecules. Hence, the development of a homogeneous phase involving a non-polar triglyceride is because of its enhanced dissolution in alcohol at elevated temperature and pressure [17]. Several reports on phase behavior of triglycerides under supercritical methanolysis suggested that different dispersion patterns of biodiesel, glycerol, methanol, and triglyceride were due to their varying densities, which were dependent upon reaction conditions [18]. Below subcritical conditions, the mixture could be distinguished into two different phases. Under subcritical conditions, the phases interact more to yield products at high reaction rate and become less distinct. Around supercritical conditions, the reactants, intermediates, and products exist in single phase, reacting vigorously to give the products in short period of time.

## 2. Supercritical process

Researchers investigated the water effect on the supercritical transesterification of triacylglycerols by methanol. Reaction mechanism of processing of triglyceride to biodiesel was explained as follows: Methanol clusters first fragments into monomers under supercritical conditions, which reacts with carbon atom of triglyceride's carbonyl group and transfer methoxide moiety to form an intermediate (Fig. 3), which rearranges itself to produce the most stable compounds (biodiesel and diacylglycerol). Similarly, diacylglycerol react with another monomer of methanol to generate monoglyceride and biodiesel. Finally, the reaction between methanol molecule and monoacylglycerol results in the formation of another molecule of biodiesel and glycerol [19].



**Fig.3. Reaction mechanism of supercritical biodiesel production**

Supercritical process has been used to transform a large number of raw materials into high quality commercially available biodiesel using variety of alcohols including methanol, ethanol and 1-propanol. It is noteworthy that supercritical reactors generally used are made from stainless steel, and are usually small, several meters long and a few millimeters wide. The process can be simplified as follows: both the feedstock oil and alcohol are pumped and preheated in separate lines, and then fed into supercritical reactor after mixing near reactor inlet. The reagent mixture is then immersed in an electrically heated salt bath. Therefore, after reaching the desired pressure and temperature, the reagents reach a supercritical state, and react vigorously to produce biodiesel and glycerol or water, depending on FFA's concentration found in triglycerides. Reaction vessel is then cooled by immersion in cold water bath and the products are collected by decompression by means of a pressure regulator. After removal of glycerol and alcohol by evaporation or distillation, the resultant biodiesel can be characterized through gas chromatography or any other technique.

## 3. Impact of reaction parameters

A variety of raw materials have been utilized for the synthesis of biodiesel, with the exploitation of a wide range of alcohols in combination with co-solvents, catalysts, and subcritical pretreatment approaches. However, in each of these works, the reaction have been strongly influenced by one or more of the following parameters that determine the optimal efficiency, kinetic, as well as thermodynamic feasibility of the process to make it economical. Table 1 lists various research works that were reported using supercritical reagents for biodiesel production, with reaction conditions giving optimum yield.

**Table 1. Impact of reaction parameters on supercritical biodiesel production**

Feedstock	Supercritical solvent	Reaction conditions				Yield (%)	References
		Temp (°C)	Pressure (MPa)	Alcohol to oil ratio	Residence Time (min)		
Canola oil	1-propanol	400	20	40:1	10	94.4	[20]
Rapeseed oil	Methanol	350	65	42:1	4	>95	[21]
Canola oil	Methanol	350	20	40:1	40	>99	[22]
Linseed oil	Methanol Ethanol	350	20	40:1	40	>99	[23]
Coconut oil	Methanol	350	19	42:1	6.67	95	[24]
Canola oil	Methanol	350	20	40:1	10	100	[22]
Jatropha oil	Methanol	320	8.4	43:1	4	100	[25]
Jatropha oil	Methanol	300	9.5	16:1	30	99.67	[26]
Sesame oil and Musturd oil	Ethanol	350	20	40:1	60	99	[27]
Rapeseed oil	Methanol	350	19	42:1	4	95	[19]
Canola oil	Ethanol	350	20	40:1	30	93.7	[28]
Rapeseed oil	Methanol	250	6	24:1	10	>97	[29]
Canola oil	tert-butyl methyl ether	400	10	40:1	12	94	[30]
Soybean oil	Methanol	320	32	40:1	25	96	[31]
Sunflower oil	Ethanol	375	10	5:1	1.56	100	[32]
Soybean oil	Ethanol	325	20	40:1	30	76	[33]
Castor oil	Methanol	266	6.8	50:1	5	96.34	[34]
Chicken fat	Methanol	400	41.1	6:1	6	88	[35]
Waste vegetable oil	Methanol	271	23.1	34:1	20.4	95.27	[36]
Waste lard	Methanol	335	20	45:1	15	89.91	[37]
Waste cooking oil	Methanol	300	10	25:1	13	90	[38]

### 3.1. Reaction temperature

A study applied continuous operation mode for a supercritical reactor system using rapeseed oil as a raw material with supercritical methanol as a reactant. An improvement in biodiesel yield was observed when temperature rose from 200 to 400°C, with an optimum yield close to 95% observed after ten minutes of reaction time. While the molar ratio of feedstock to oil was kept constant, the temperature turned out to be a more significant factor compared to the pressure, which varied from 1-20 MPa [20]. In another study, refined sunflower oil was used to produce biodiesel in a supercritical batch reactor. Methanol and ethanol were used as supercritical reagents. While the enzymatic transesterification carried out using supercritical CO<sub>2</sub>. Observations were made at constant pressure (20MPa) and constant alcohol to oil ratio (40:1). Supercritical methanol showed complete conversion of oil to fatty acid methyl esters (FAME) within ten minutes. Supercritical ethanol had same yield in lesser time, because of high solubility of oil in ethanol than methanol. By comparison, enzyme catalyzed transesterification under supercritical CO<sub>2</sub> required much longer time with low yield. Similar results were reported in supercritical methanol transesterification of rapeseed oil using batch reaction system [21]. Supercritical

methanolysis of palm kernel and coconut oil at 350 °C resulted in 96% and 95% conversion respectively, in six minutes [24]. Castor and flaxseed oil have been shown to require much higher reaction temperatures (about 350 °C) with low conversion rates, as is evident from the longer reaction time required for supercritical methanol and ethanol [23]. Almost all the data presented in (Table 1) agrees with the observation that an increase in temperature improves biodiesel yield with a wide variety of supercritical feedstock and reagent, with yield decreasing beyond 350-375 °C, as the product become susceptible to thermal degradation.

### 3.2. Alcohol-to-oil ratio

Transesterification of mustard oil and sesame oil was carried out using methanol and ethanol supercritical reagents. Under reactions performed at constant temperature (300 °C) and constant pressure (20Mpa), it was noticed that conversion rate did not enhance above the alcohol-to-oil ratio of 40:1 [27]. Similar results were reported for the supercritical transesterification of various other oils including palm oil, canola oil, linseed oil, and Jatropha oil. Some reports suggested that this is because of formation of homogeneous phase. Maintenance of homogenous phase can only be influenced by molar ratio of oil to alcohol in reaction mixture. When alcohol concentration becomes higher in reaction mixture, the homogeneity of the solution

is not further affected, thereby maintaining a constant reaction rate [31].

### 3.3. Residence time

From the results described by various researchers, the residence time appears to have a reverse relationship with supercritical reagent temperature. This can be confirmed by observing that rapeseed biodiesel yield was lower at 270°C than at 300 °C, with total conversion impossible even after 30 minutes of residence time. At a temperature of 350°C, nearly 93% transformation attained in 20 minutes, and 400 °C ensured optimum conversion in just ten minutes [20]. An inverse relationship between temperature and reaction time was observed during transesterification of castor and linseed oil using supercritical alcohol, with poor conversion at 235°C in 60 minutes, however complete conversion was reached at 350°C in less than 40 minutes [23].

### 3.4. Water and free fatty acids

In a study, fried soybean oil was trans-esterified to biodiesel using supercritical methanol and ethanol. The ideal conditions for optimum transformation were: reaction temperature (300°C), pressure (20 MPa), flow rate of methanol (1ml/min), and (40:1) molar ratio. An optimum yield of 81.7% was achieved in the existence of water compared with the yield of 72.7% in an anhydrous system, under similar reaction conditions [39]. Another study also recommended that water has a positive impact on reaction conditions, as it helps in the hydrolysis of triacylglycerols, which results in the formation of free fatty acids. Formation of free fatty acids improves the reaction rate because free fatty acids can be esterified to biodiesel, thereby increasing yield [40].

## 4. Methods of process intensification

### 4.1. Use of co-solvent

Supercritical conditions need proper care which results in huge loss of energy. Therefore, the use of co-solvents has to be recommended for the reduction of severity of supercritical situations. Upon addition of co-solvents, the obstacles observed in triglycerides solubility in methanol are significantly decreased. The direct outcome of this facilitation is the synthesis of biodiesel in mild and easier to maintain conditions. Some commonly available co-solvents include; THF (tetrahydrofuran), n-heptane, propane, ethane, n-butane, and CO<sub>2</sub>. In a recent study, propane addition to methanol with a molar ratio of 0.1 reduced reaction temperature significantly from 350-280°C, with complete transformation to biodiesel [41]. In another work, addition of CO<sub>2</sub> as co-solvent resulted in an enhancement of biodiesel yield by increasing methanolysis of feedstock (rapeseed) oil [42]. Conversely, co-solvent amount >0.1 CO<sub>2</sub>/methanol decreased the process efficiency and product yield.

### 4.2. Use of catalyst

Though the supercritical method is effective in catalyst absence, the procedure is very expensive and energy

consuming because high pressure and temperature resistant reactors required to be established. Hence, it has been suggested that the use of appropriate catalysts under supercritical conditions could lead to an enhancement in biodiesel production. In a study, sunflower oil was supercritically transesterified to biodiesel using CaO (3%wt.) catalyst. Optimum yield was recorded in a very short residence time of 6min, at a temperature of 525K with alcohol to oil molar ratio of 41:1 [32]. Another study aimed to investigate the effect of adding metal oxide catalysts such as ZrO<sub>2</sub>, CaO, TiO<sub>2</sub>, SrO, and ZnO to supercritical methanol transesterification of biodiesel. The maximum yield of 95% was obtained by adding ZrO<sub>2</sub> (1% wt.) in a residence time of 10 minutes, at a reaction temperature of 250°C, when methanol to oil molar ratio was 40:1 [43].

## 5. Challenges to SCF technology

### 5.1. Energy consumption

One of the limitations of supercritical fluid technology is the requirement of high energy to achieve supercritical conditions. The high pressure and temperature requirements during supercritical transesterification, depending upon the solvents employed, utilize a lot of energy which is not sustainable for long time. For instance, in supercritical methanol transesterification, the pressure and temperature should be above 8.1 MPa and 239°C, to reach supercritical methanol state, which make it an energy intensive technology. However, it is widely accepted that traditional production technologies require average temperature (<1500°C) and atmospheric pressure for maximum production of biodiesel [44]. There are also concerns that energy consumed in the process is greater than energy supplied by the supercritically transesterified biodiesel. The introduction of an integrated cooling and heating system can improve the supercritical fluid transesterification process in terms of energy utilization.

### 5.2. High cost

In addition to energy consumption, huge process costs are one of the main obstacles to commercializing supercritical fluid technology. For instance, the use of supercritical fluid technology for biodiesel production requires a large amount of solvent to push the reversible reaction to produce more biodiesel. Furthermore, the huge cost of reagents and additional processes required for the separation of un-reacted solvent increase the total cost of supercritical fluid reactions. In addition, the structural material for most supercritical reactors is usually manufactured with additional strength and durability to maintain extreme conditions. Therefore, the costs involved in maintenance and operation of supercritical technology are generally higher than traditional biodiesel production technologies. Consequently, the huge cost associated with materials, operation and maintenance limits the commercialization projects for supercritical based biodiesel production [45].

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