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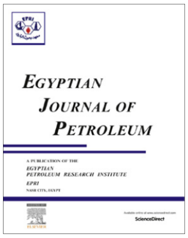

REVIEW

The effects of alcohol to oil molar ratios and the type of alcohol on biodiesel production using transesterification process

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Abstract The nature of alcohol and alcohol to oil molar ratio plays an important role on the method of biodiesel production. As a result, this paper examined different alcohols commonly used for the production of biodiesel fuel with more emphasis on methanol and ethanol. Further the different alcohol to oil molar ratios used for the production of biodiesel have been extensively discussed and reported. Also the effects of alcohol to molar ratios on biodiesel refining process and its physicochemical properties were investigated.

1. Introduction

Presently, global warming effect, fossil fuel diminishing reserves, and higher petroleum prices are the main issues driving worldwide interest on the development of alternative renewable, biodegradable and sustainable biofuels [10]. Fossil fuel combustion leads to about 98% of carbon emissions [31]. As such, renewable resources such as biofuels, wind, water, and hydrothermal energy are being widely considered as potential alternative sources of energy [74]. Biofuels such as biodiesel are considered to be a potential candidate to replace petro-diesel fuel [15]. In addition it is ranked among the fastest developing alternative to petro-diesel fuel in many developed and developing countries worldwide [74]. This is because the net level of carbon dioxide in the atmosphere is not increased by burning biofuel, and this minimizes the intensity of greenhouse effect [62]. Besides, its decreases particulate emissions, unburned hydrocarbons, and sulfur dioxide generated through its combustion process [56]. A life cycle analysis of biodiesel fuel demonstrated that overall CO_2 emission is reduced by 78% compared to petro-diesel fuel, hence eco-friendly [85]. Thus, biodiesel has the potential of lowering the net gas emissions from the transportation sector; that causes global warming and it could significantly decrease the mass and carcinogenicity of particulate matter emissions. Recently the interest in biodiesel fuel production

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has increased due to its environmental benignity [49]. For countries in which petroleum is imported, biodiesel technology is a big advantage [54].

The technologies usually employed to produce biodiesel fuel are classified into direct/blends, microemulsion, pyrolysis and transesterification reaction [26,29,32]. However, transesterification reaction is the most commercially used technology for the production of biodiesel [6,5]. Transesterification is the reaction through which triglycerides react with an alcohol in the presence of catalyst to produce biodiesel and by-product, glycerol [27,28,30,33]. This reaction is mostly affected by numerous factors among others which include: alcohol to oil molar ratio, reaction time, nature and amount of catalyst, reaction temperature, and the nature of feedstocks composition [26]. Nonetheless, alcohol to oil molar ratio is believed to be the most critical in the dynamics of biodiesel production [48].

Conventionally, biodiesel is transesterified using refined vegetable oils, catalyzed by an alkali [51]. Fig. 1 presents a schematic diagram of alkali-catalyzed transesterification for the production of biodiesel. However, edible vegetable oils contribute over 95% of global biodiesel production [48]. This process usually provides high-quality biodiesel fuel with less refining procedure. But, the prices of refined virgin oils are usually very high, hence rendering commercial biodiesel fuel production impracticable [16]. Recently, alternative feedstocks such as natural plant oils, animal fats, waste/used cooking oils, and non-edible feedstocks such as jatropha curcas, pongamia, castor and microalgal oils are used to produce biodiesel fuels, to circumvent the high prices of biodiesel fuel and improve its development [59]. Other low quality feedstocks being explored include: chicken fats, pork lard, beef tallow, and yellow grease [23]. Currently, microalgae are considered the most promising source of renewable energy. Although, these feedstocks are of low prices, the production and the refining processes of biodiesel products through such low quality feedstocks are difficult [48,24]. However several investigations have revealed the potential of biodiesel production through low-quality feedstocks. Fig. 2 shows percentage share of each renewable energy source [25]. Also, several researches have investigated the effects of alcohol to molar ratios on the production of biodiesel [63]. Therefore, this paper critically analyzed the effects of alcohols and oil to alcohol molar ratios as main variables in the production and refining of crude biodiesel products.

2. Alcohols for biodiesel production

Alcohol is one of the most important raw materials for the production of biodiesel. Alcohols are primary and secondary monohydric aliphatic alcohols comprising 1–8 carbon atoms [57]. A number of alcohols have been explored for biodiesel production, the most widely used acyl acceptors are methanol and to a slight extent, ethanol. Other alcohols utilized in producing biodiesel are the short-chain alcohols such as propanol, butanol, isopropanol, tert-butanol, branched alcohols and octanol, however these alcohols are costly [93].

Methanol and ethanol are the most often used alcohols in biodiesel production. Methanol is particularly preferred because of its physical and chemical advantages. Beside its reaction with triglycerides is quick and it can be easily dissolved in NaOH [57]. Demirbas [27] remarked that methanol, also known as "wood alcohol", is usually simpler to find compared to ethanol. Additionally triglycerides can react with varieties of alcohols. But the short-chain alcohols provide better conversions under the same reaction time [89]. Table 1 presents main production facilities of methanol and bio-methanol [27].

2.1. Methanol

As earlier mentioned, for biodiesel production via transesterification reaction, methanol is the most common alcohol used. However, the level of water in an alcohol is crucial for its successful application in the production of biodiesel. This is because the presence of water during transesterification reaction causes hydrolysis of triglycerides to free fatty acids which leads to soap formation, and poor yield. Unfortunately, the entire short-chain alcohols are hygroscopic and could easily absorb water from the atmosphere [84,92]. On the other hand, long-chain alcohols are mostly sensitive to contamination by water [85]. Van Gerpen et al. [84] remarked that biodiesel is produced from various alcohols, and the nature of alcohol used in the production process does not make any chemical

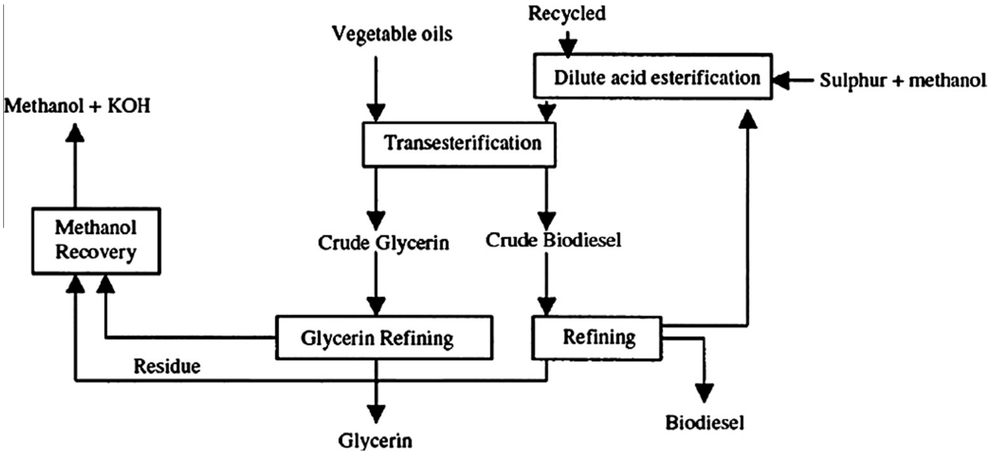

Figure 1 Schematic diagram of alkali-catalyzed transesterification for the production of biodiesel [48].

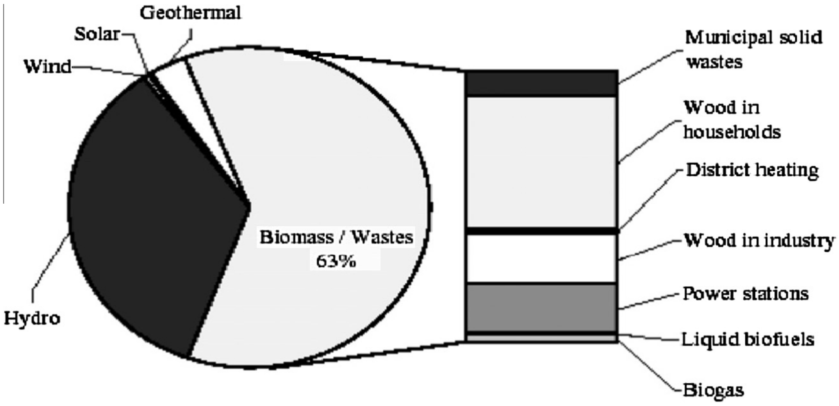

Figure 2 Percentage share of each renewable energy source in 1995 [25].

difference, as long as the finished biodiesel product meets ASTM D6751. However higher chain molecular alcohols are usually avoided during transesterification reaction, due to steric hindrance effect.

2.2. Other alcohols

For the most part, ethanol is of great interest, because it is less costly compared to methanol, and biodiesel produced from ethanol is entirely bio-based. In addition butanol could also be achieved from biological materials as a result yielding biodiesel that is also entirely bio-based. However, alcohols such as methanol, propanol, and iso-propanol are usually obtained from petrochemical materials such as methane derived from natural gas in the case of methanol. The renewability of ethanol has suggested advantages due to being carbon dioxide neutral, less toxic and environmentally based, making it the most suitable substitute to methanol [45]. However, ethanol is more expensive and less reactive than methanol [90,77]. Van Gerpen [84] remarked that removal of alcohols such as ethanol or isopropanol if used in biodiesel production is difficult, because the alcohols form an azeotrope with water. Even though, a molecular sieve can be used to remove the water.

3. Production of biodiesel via transesterification reaction

As earlier mentioned, biodiesel is usually produced via transesterification of triglycerides with alcohol in the presence of catalysts. Fig. 3 shows the structure of triglyceride [10]. Various kinds of alcohols have been used for the production of biodiesel fuels. Saka and Yohei (2009) investigated a new technique for catalyst-free biodiesel production using supercritical methyl acetate. The authors noted that comparing methanol and methyl acetate in the transesterification of triglycerides (TG), within all the temperature ranges experimented shows that the reactivity of methanol was higher. Further the overall reaction between triglycerides and alcohol to give biodiesel (fatty acid alkyl esters, FAAE) is a three sequential reaction [21]:

$$\text{Triglyceride} + \text{R}'\text{OH} \rightarrow \text{Diglyceride} + \text{FAAE} \tag{1}$$

$$\text{Diglyceride} + \text{R}'\text{OH} \rightarrow \text{Monoglyceride} + \text{FAAE} \tag{2}$$

$$\text{Monoglyceride} + \text{R}'\text{OH} \rightarrow \text{Glycerol} + \text{FAAE} \tag{3}$$

Furthermore, methanol is chosen in the production of biodiesel because it is relatively inexpensive and reactive. Besides, methanol (CH_3OH) is a simple compound and does not contain complex organic compounds or sulfur [96,13]. Van Gerpen [85] remarked that two major factors leading to the choice of methanol despite its more toxic levels are: methanol does not form azeotrope, therefore it is easily recycled and ethanol forms an azeotrope with water. Also, regarding their characteristics as fuels, biodiesel from methanol and ethanol demonstrate slight variations; for example, biodiesel fuels from methanol have slightly higher pour and cloud points and slightly lower viscosities than those obtained from ethanol [93]. However use of methanol raises environmental concern [46], since non-renewable fossil sources, such as natural gas are presently the main sources of methanol [93].

Table 1 Main production facilities of methanol and biomethanol [27].

Methanol	Biomethanol
Catalytic synthesis from CO and H_2	Catalytic synthesis from CO and H_2
Natural gas	Distillation of liquid from wood pyrolysis
Petroleum gas	Gaseous products from biomass gasification
Distillation of liquid from coal pyrolysis	Synthetic gas from biomass and coal

4. Effects of molar ratios on the transesterification reaction

Molar ratio of alcohol to oil is one of the most significant factors affecting the conversion efficiency, yield of biodiesel as well biodiesel production cost [57]. Also, since the stoichiometric molar ratio of alcohol to oil for the transesterification is 3:1 and the reaction is reversible, higher molar ratios are required to increase the miscibility and to enhance the contact between the alcohol molecule and the triglyceride. In practice, to shift the reaction toward completion,

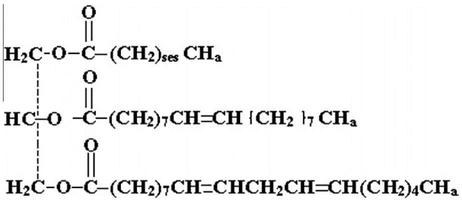

Figure 3 Shows structure of triglyceride [10].

the molar ratio should be higher than that of the stoichiometric ratio [55]. Further to break the glycerin–fatty acid linkages during transesterification of triglycerides to biodiesel, excess methanol is required [58]. Therefore, higher alcohol to oil molar ratios give rise to greater alkyl ester conversion in a shorter time [48]. Moreover, increase in the amount of alcohol to oil increases biodiesel yield and biodiesel purity. This is in line with the result reported based on neat vegetable oils [36]. On the contrary the inedible oils like pongamia and neem require more alcohol to give maximum ester yield, perhaps due to higher viscosity of inedible oil than edible oils. Nevertheless, when compared to edible oil, ester content yield was low in inedible oil but glycerol yield was more in inedible oil when compared to edible oil [36]. Balat and Balat [9] remarked that the key variables affecting transesterification are; reaction time, alcohol to oil molar ratios, reaction temperature and pressure, catalyst, water contents and free fatty acids levels in fats and oils. The authors noted that the universally accepted alcohols to glycerides molar ratios are 6:1–30:1. In addition, Behzadi and Farid [12] reported that the overall transesterification reaction is characterized by three control stages: mass transfer, kinetic and equilibrium controlled. And the slowest among these three stages is the mass transfer stage due to immiscibility of triglycerides and methanol [44]. In another study, Chew and Bhatia [20] noted that the choice of the molar ratio of alcohol to oil can significantly influence transesterification process. They reported that the process yield is increased with increase in the alcohol to oil molar ratio. Thus, methanol to oil molar ratio of 9:1 could provide the maximum yield for canola and corn oil [66]. Furthermore molar ratios between 3:1 and 15:1 were experimented in the transesterification of Cynara oil using ethanol. The yield of biodiesel was increased with an increase in the molar ratio up to a value of 12:1. Consequently molar ratios between 9:1 and 12:1 gave the best results. In addition incomplete reaction was observed for molar ratios below 6:1. And for a molar ratio of 15:1, the separation of glycerol was complicated and the apparent yield of biodiesel was reduced because a fraction of the glycerol remained in the biodiesel phase. For that reason, molar ratio 9:1 appears to be the most suitable [55].

Also, using KOH, palm oil to methanol ratio of 1:10 was selected for biodiesel production since the ratio gave the best biodiesel quality and yield; lower glycerol content as well as low residue of free fatty acid [47]. Ting et al. [83] investigated the effects of varying feedstock to methanol molar ratios (1:10–1:40) on biodiesel production. And a molar ratio of 1:15 gave conversion of 99% after 12 h of reaction at 50 °C.

4.1. Effects of molar ratios on alkali-catalyzed transesterification

For alkali-catalyzed transesterification, the optimum molar ratio of methanol to oil to produce biodiesel with more than 98w/w% yield is approximately 6:1 [10]. As a result alcohol to oil ratios greater than 6:1 does not increase yield, but could hinder glycerol separation process, as well, in transesterification reaction the molar ratio of 6:1 is employed to have enough amount of alcohol to break the fatty acid-glycerol linkages [2]. Phan and Phan [67] have transesterified waste cooking oil (WCO) using KOH catalysts to produce biodiesel fuel. The authors employed a 500 ml three-neck glass flask (reactor) connected with a reflux condenser using a thermocouple probe and tap water to condense methanol vapor. They used a stainless steel stirrer encompassing a turbine to agitate the mixture in the reactor. In addition a water bath was used to heat reactor. The reaction conditions were; temperature of 30–50 °C, methanol/oil ratios of 7:1–8:1, 0.75 wt.%, KOH catalyst, and reaction time of 80 min, with 88–90% biodiesel yield achieved. They observed that the oil conversion to biodiesel increased when the ratio was increased from 5:1 to 8:1 M ratios. The conversion increased to 64% for the ratio of 8:1 from 50% for the ratio of 5:1. A conversion difference of 24% was recorded for the molar ratios between 5:1 and 8:1 in the first 60 min. And in the last 60 min the conversion slightly decreased to 13–16%. When the methanol to WCO molar ratio increased from 8:1 to 9:1, the difference in the conversion was less than 2%. Nonetheless a reduction in the conversion was noticed when the methanol to WCO molar ratio was increased to a level above 9:1. For instance, after 80 min of reaction time, a molar ratio of 12:1 gave a conversion of 82% but when the molar ratio was 8:1 a conversion of 88% was achieved. This decrease might be due to excess of methanol which interferes with the alkyl ester and glycerol separation by increasing glycerol solubility. In consequence a portion of the diluted glycerol remaining in the alkyl ester phase caused apparent lost of ester product due to foam formation. As well, Rashid et al. [71] optimized alkali-catalyzed methanolysis for the production of biodiesel. The authors noted that the most favorable reaction conditions for the sunflower oil methanolysis were: reaction temperature of 60 °C, NaOH catalyst concentration of 1.00% (w/w) and methanol to sunflower oil molar ratio, 6:1. They obtained an optimum biodiesel yield of 97.1%. Also, Encinar et al. [37] have produced alkyl esters from vegetable oil using KOH catalyst (concentration of 1 wt. %), and the ethanol to oil molar ratio was varied between 6:1 and 15:1. The transesterification process was performed in a 1000 ml spherical reactor, provided with a mechanical stirring, sampling outlet, thermostat, and condensation systems. They found that, with a 6:1 M ratio and after 2 h, the conversion to alkyl esters was close to 45 wt.%. A further increase in the molar ratio increased the yield of alkyl esters, with a molar ratio of 12:1 producing the best biodiesel yield of 72.5%. However, 66.2% biodiesel yield was noticed, when the molar ratio was increased to 15:1 as shown in Fig. 4 [37]. This is so because higher molar ratios above 12:1 rendered glycerol separation cumbersome. In addition, the yield of alkyl esters reduced, since a portion of the glycerol remained in the alkyl esters phase. Also, a conversion of di- to monoglycerides appears to be favored using excess alcohol, and both glycerol and alkyl esters slightly recombined to monoglycerides since during the course of the reaction their concentration keeps increasing, this is in contrast with transesterification reactions carried out using low molar ratios. The authors also noted that the alkyl esters yield is lowered, when the by-product glycerol remains in solution because it helps in shifting the equilibrium back to the left. As a result, alcohol to oil molar ratio is considered to be among the most important variables affecting the yield alkyl esters. For that reason, optimization of alcohol to oil molar ratio prior to transesterification process is essential and has to be carried out for the best biodiesel yield to be achieved. Furthermore biodiesel production from soybean oil was conducted by Silva et al. [80] using ethanol/oil ratio (3:1, 6:1, 9:1, 12:1 and 15:1 M), and 0.1%, 0.5%, 0.9%, 1.3% and 1.7% w/v of NaOH, as an alkaline catalyst. The reaction conditions were; temperature of 40.0 °C, reaction time of 80 min, catalyst concentration of 1.3 wt.%, and molar ratio, of 9:1. The authors concluded that methanol can be effectively substituted with ethanol, when the ethanol is applied using optimized condition (molar ratio (9:1)). This will certainly lead to biodiesel production from sources that are completely renewable (ethanol obtained from soybean oil and sugar cane). They further affirmed that for molar ratios less than 6:1, the reaction was incomplete, and for a molar ratio of 15:1 the separation of by-product, glycerol was difficult and the apparent yield of esters was decreased. The authors also commented that for methanol, a molar ratio of 6:1 is most suitable, and for ethanol, molar ratio 9:1 is the most favorable. In contrast, Santos et al. [74] used response surface methodology (RSM) to evaluate the effects of catalyst concentration and methanol to oil ratio on soybean oil conversion to biodiesel. And observed that the overall conversion of oil to biodiesel was achieved when catalyst concentration of 0.2 w/w and alcohol to oil ratio of 9:1 were used.

Also methanol to oil molar ratio ranging from 3:1 to 9:1 was varied for karanja and jatropha oil. At a molar ratio of 6:1, the highest ester conversions from karanja were observed to be 80% and from jatropha oil to be 90–95%, respectively [66]. Similarly Meher et al. [60,61] investigated biodiesel production from Karanja oil using rate of stirring (180–600 rev. per min), temperature (37–65 °C), catalyst concentration (0.25–1.5% wt) and alcohol/oil molar ratio (6:1–24:1). They achieved biodiesel yield of 97% after 3 h of reaction time for a molar ratio of 6:1, while a similar yield was achieved in 30 min for a molar ratio of 24:1. The authors observed that a higher molar ratio of methanol to oil provided faster reaction rates while a lower methanol to oil molar ratio (6:1) requires longer reaction times to achieve equal conversion. In another study, Canoira et al. [18] transesterified Jojoba oil-wax to biodiesel and obtained a biodiesel yield of 79 wt.%. The transesterification reaction was conducted in an autoclave vigorously stirred at a speed of 600 rpm, temperature of 60 °C, with a methanol to oil molar ratio of 7.5:1, and a reaction time of 4 h. Furthermore, a statistical model predicted that at the optimized reaction conditions of a catalyst amount of 1.26%, oil-to-methanol molar ratio of 7.5:1, reaction temperature of 65 °C, and reaction time of 20 min, the highest conversion yield of lard biodiesel would be 98.6% [52].

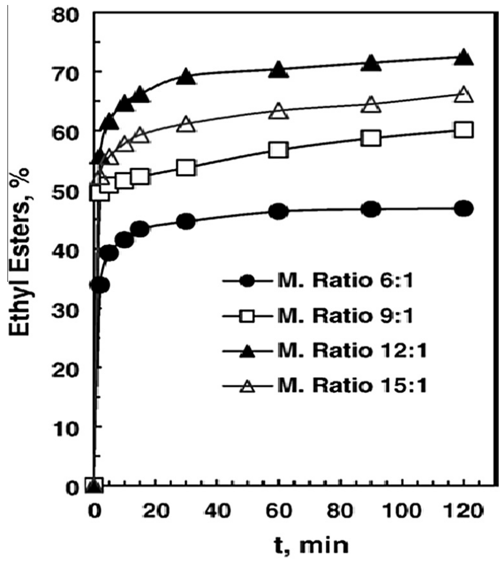

Figure 4 Esters yield vs. time. Influence of ethanol/oil molar ratio (T = 60 °C; [KOH] = 1 wt.%) [37].

4.2. Effects of molar ratios on acid-catalyzed transesterification

Because of the high cost of refined feedstocks, acid-catalyzed transesterification reactions have been explored to circumvent the problems associated with the conversion of low quality feedstocks to biodiesel. Fig. 5 shows the mechanism of acid catalyzed esterification of fatty acids [27], and Fig. 6 presents the mechanism of acid catalyzed transesterification of vegetable oils [22]. Ghadge and Raheman [40] reported that a 2-step esterification for the pretreatment process using acid catalyzed (1% v/v H_2SO_4) reaction with methanol (0.30–0.35 v/v) at a temperature of 60 °C and a reaction time of 1 h was employed to reduce high FFAs (19%) content of crude mahua oil to a value below 1%. In another study, Canakci and Gerpen [17] observed that at a temperature of 60 °C and a molar ratio of 30:1 with sulfuric acid catalyst, a biodiesel conversion of 98.4% can be obtained. The authors reported a conversion of 95.8% for fatty acid ethyl ester compared to 87.8%, 92.1%, and 92.9%, for fatty acid methyl ester, 1-bytyle fatty acid ester and 2-propyl fatty acid ester, respectively.

Further, Banerjee and Chakraborty [11] reported transesterification of waste frying oils via acid catalyst for biodiesel production. The optimum reaction parameters were noted to be; temperature (70 °C) and methanol/oil molar ratio (250:1). The authors observed that at a molar ratio of oil:methanol: acid of 1:74:1.9 and 1:162:4.2 at 80 °C, high biodiesel yields of 98.8%, and 98.9 were obtained respectively. In another investigation, Sahoo et al. [73] converted free fatty acids to triglycerides to reduce the acid value using a molar ratio of 6:1 and H_2SO_4 acid and achieved optimum conversion efficiency with acid value below 4 mg KOH/g. Additionally,

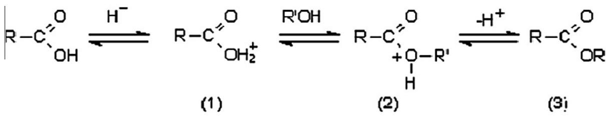

Figure 5 Mechanism of acid catalyzed esterification of fatty acids [27].

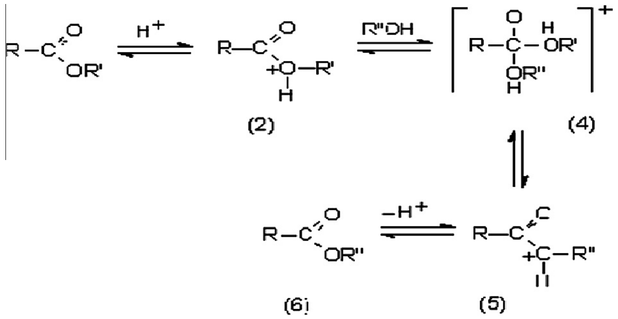

Figure 6 Mechanism of acid catalyzed transesterification of vegetable oils [22].

Soriano et al. [81] showed that the conversion of triglycerides into fatty acid methyl esters using $AlCl_3$ as catalyst was considerably affected by methanol to oil molar ratio, reaction time, temperature and the presence of THF as co-solvent. The optimum conditions with $AlCl_3$ were: 24:1 M ratio, temperature of 110 °C, and reaction time of 18 h. The authors used THF as co-solvent and achieved 98% conversion. They also noted that at higher molar ratios, the addition of THF resulted in an significant increase in the conversions of triglycerides to biodiesel. This could be attributed to the formation of a one phase system. Further using THF, the mass transfer problem normally encountered in a heterogeneous system is eliminated [81].

Moreover, Chongkhong et al. [21] have esterified palm fatty acid distillate using an 8:1 M ratio of methanol to palm fatty acid distillate with 1.8 wt.% of sulfuric acid at 60 °C and a retention time of 60 min. Further, Predojević [68] employed 2-step catalyzed transesterification to produce biodiesel from waste sunflower. The authors used alcohol to molar ratio of 6:1 and achieved a biodiesel yield of 92%. Similarly, Veljkovic et al. [86] reduced the FFA content of tobacco seed oil from 17 wt.% to less than 2 wt.% using a molar ratio of 18:1 of methanol to oil. Pisarello et al. [69] have esterified various vegetable oils (refined and unrefined vegetables) using anhydrous methanol, ethanol and ethanol 96%. The esterification process was conducted in a glass batch reactor, working with total reflux. A thermostatic water bath was used to immerse the reactor. While stirring with a magnetic stirrer, the reaction was conducted at 30, 60 and 70 °C. Furthermore oil with acidity of 18% was achieved by acidifying refined sunflower oil in the laboratory using saponification followed by neutralization. In another study Hayyan et al. [47] have esterified sludge palm oil (SPO) using acid catalyst tolune-4-sulfonic monohydrate acid (PTSA). The authors revealed that batch esterification process was performed using single factor optimization to investigate the effect of PTSA in the dosage range (0.25–10% wt/wt), stirrer speed (200–800 rpm), reaction time (30–120 min), reaction temperature (40–80 °C), and molar ratio of methanol to SPO (6:1–20:1). The esterification process was employed to pre-treat the SPO by converting the high content of FFA to FAME using an acid catalyst. The initial content of FFA of the SPO used in this study was 22.33%. The methanol to SPO molar ratio was varied from 6:1 to 20:1. The yield of treated SPO slightly increased when the molar ratio increased from 6:1 to 10:1, and at a higher molar ratio no considerable change was observed. Conversely, a minimum of 10:1 M ratio was required to reduce the FFA content of SPO from 22.33% to 2%, which was the limit of FFA for transesterification reaction in their study. With an insufficient amount of methanol in the reaction, the reaction process was slower, thus decreasing the amount of conversion. Therefore, 10:1 was considered to be the optimum ratio of methanol to SPO. Furthermore FFA content of soybean oil (20.5%) was reduced to 1.1% using a 12:1 M ratio and PTSA as acid catalyst. It was also noted that for a lower molar ratio of alcohol to acid oil the reaction takes place faster but reached a lower final conversion compared to when a higher molar ratio is applied [34].

Also biodiesel production from heterotrophic microalgal oil using concentrated sulfuric acid as catalyst was studied by Miao and Wu [58]. The biodiesel specific gravity was reduced to a final value of 0.8637 from an initial value of 0.912 in about 4 h of reaction time, at a temperature of 30 °C with 56:1 methanol to oil molar to ratio. Also, at molar ratios of 45:1 and 56:1, the biodiesel yields obtained were 68% and 63%, respectively. In another similar study, Montes D'Oca et al. [35] have transesterified microalgae *Chlorella pyrenoidosa* for the production of biodiesel. The reaction was performed using H_2SO_4 acid as catalyst (3 or 10% in relation to the mass of lipids) under constant stirring for 4 h at 60 or 100 °C. The molar ratio of alcohol/lipids was 30:1 with a relatively high biodiesel yield achieved.

4.3. Effects of molar ratios on solid-catalyzed transesterification

The formation of three phases in the early reaction time restricts the contact between reacting mixtures. For this reason, determination of the initial alcohol concentration is essential keeping a compromise between the rate of diffusion by the formation of two phases of fluid and the shifting of the reaction toward biodiesel production [38]. An investigation carried out by Zabeti et al. [94] revealed that the three phase formation between oil, solid catalyst, and alcohol which result in diffusion constraints, thus lowering the reaction rates could be circumvented using co-solvents such as *n*-hexane and ethanol, dimethyl sulfoxide (DMSO), and tetrahydrofuran (THF). These co-solvents could enhance miscibility of oil and methanol and speed up the rate of transesterification reaction. Encinar et al. [38] have transesterified 98% of rape oil using KNO_3/CaO catalyst to biodiesel fuel. The transesterification reaction was conducted in a 500 ml glass spherical reactor, provided with a sampling outlet, mechanical stirring, thermostat, and condensation systems. Alkyl esters with excellent properties were achieved using a quantity of KNO_3 of 10% impregnated in CaO, a catalyst total content of 1.0%, a methanol to oil molar ratio of 6:1, a reaction time of 3.0 h, and a reaction temperature of 65 °C. From the results obtained in Fig. 7, the experiments conducted with methanol to oil molar ratios at 9:1 and 12:1 took a lengthier time to attain a conversion near to equilibrium. Thus the final conversion values of biodiesel confirmed that the best methanol to oil molar ratio for the reaction is 6:1 [38]. In another study, Yee et al. [91] have transesterified *Jatropha curcas* L. oil catalyzed by SO_4^{2-}/ZrO_2 catalyst for the production of biodiesel. The authors found that at a reaction time of 4 h, reaction temperature of 150 °C, 7.61 wt.% for catalyst loading and methanol to oil molar ratio of 9.88 mol/mol, an optimum alkyl ester yield of 90.32 wt.% was achieved. Further, [95] investigated the optimization of the activity of CaO/Al_2O_3 catalyst for biodiesel production using response surface methodology. The authors employed fifty grams of oil into a 150 ml glass-jacketed reactor equipped with a digital magnetic stirrer and a water-cooled condenser. The transesterification process was performed using 3.5 wt.% of the catalyst, methanol to oil ratio of 12:1, and the mixture was rigorously stirred for 5 h. A water bath at a temperature of 65 °C was used to heat up the mixture and a biodiesel yield of 94% was obtained. Also, Chai et al. [19] have transesterified vegetable oil using the solid heteropolyacid $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ as a catalyst to produce high-quality biodiesel. The authors employed low catalyst concentration ($1.85 \times 10^{\times 3}$:1 weight ratio of catalyst to oil), at low temperature (338 K), low methanol-to-oil ratio (5.3:1), and a relatively short reaction time (45 min), the solid acid catalyst was found to be efficient and yielded a high yield of biodiesel (99%). Besides, the process was found to be environmentally friendly and economical. The transesterification process involving the catalyst was pronounced economical since the activity of $Cs_{2.5}PW$ was not significantly affected by the water content and the level of free fatty acid of the oil. And the catalyst was easily removed from the product mixture and reused several times. Jacobson et al. [50] investigated solid acid-catalyzed transesterification of waste cooking oil for biodiesel production. The authors optimized the reaction parameters using the most active ZS/Si catalyst identified. The optimum conditions obtained are 3 wt.% catalyst loading, temperature of 200 °C, and 1:18 oil to alcohol molar ratio, and recorded ester yield of 98 wt.%.

Further, a novel organic–inorganic hybrid membrane was developed by Shi et al. [78] as heterogeneous acid catalyst for the production of biodiesel fuel. The catalyst was prepared from sulfonated poly(vinyl alcohol) (SPVA) and zirconium sulfate ($Zr(SO_4)_2$). Acidified oil was esterified with methanol to determine the effectiveness of the hybrid membranes. The esterification results obtained revealed that the FFA conversions in acidified oil were 81.2% and 94.5% for $Zr(SO_4)_2$/PVA and $Zr(SO_4)_2$/SPVA catalytic membranes, respectively. The transesterification reaction conditions were: reaction time of 2 h, reaction temperature of 65 °C, methanol to oil molar ratio of 6:1, the weight ratio of polymer to $Zr(SO_4)_2$/SPVA was 1:1 in the catalytic membrane and the amount of catalytic membrane with respect to reactant was 4 wt.%. The $Zr(SO_4)_2$/SPVA catalytic membrane was used to esterify the acidified oil with methanol, increase in molar ratio of methanol to oil increased the conversion considerably. Additionally when the methanol to oil molar ratio was 1:1, 3:1 and 6:1, the FFA conversion was 60.2%, 80.3% and 94.5%, respectively. As well the conversion was almost kept stable, that is, 95.0% and 95.1%, respectively when the ratio was increased to 9:1, even 12:1. In another investigation, Guerreiro et al. [42] have transesterified soybean oil with methanol using solid acid catalysts (ion-exchange resins, Nafion membranes, and poly(vinyl alcohol) membranes containing sulfonic groups), at atmospheric pressure and temperature of 60 °C. The higher reaction rate (catalytic activity) was due to higher reactant concentrations in the close vicinity of the sulfonic groups. The authors noted that at the start of the reaction, methanol is likely to be hydrogen bonded to the polymer OH groups but the small size of its molecule is not enough to move away the polymer chains. Another study conducted by Boz et al. [14] employed KF loaded nano-γ-Al_2O_3 as catalyst to transesterify vegetable oil to biodiesel. During the transesterification process a biodiesel yield of 97.7 ± 2.14% was obtained using a molar ratio of methanol/oil of 15:1 and 3 wt.% catalysts.

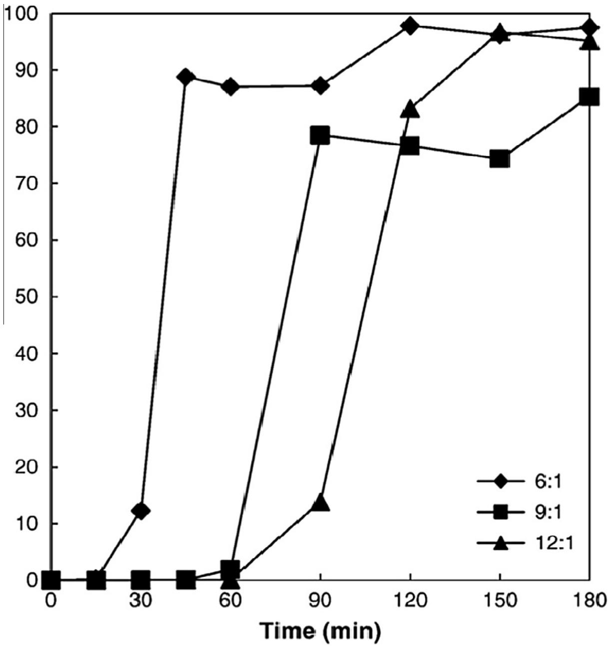

Figure 7 Influence of methanol/oil molar ratio on biodiesel yield (% impregnation: 10; catalyst/oil mass ratio: 1.0%; temperature: 65 °C; agitation rate: 900 rpm) [38].

4.4. Effects of molar ratios on enzymatic-catalyzed transesterification

Alcohol to oil molar ratios also play an important role in enzymatic-catalyzed transesterification. Pizarro and Park [70] investigated lipase-catalyzed transesterification of vegetable oil contained in waste activated bleaching earth for the production of biodiesel fuel. The authors varied oil to methanol molar ratios from 1:1 to 1:6, and the content of the oil was kept at 75% by weight of vegetable oil. An optimum conversion yield of 55% (w/w) with palm oil was achieved at the oil to methanol molar ratio of 1:4. Further, Watanabe et al. [87] experimented different molar ratios 1:2, 1:3 and 2:3 for the transesterification of vegetable oil to biodiesel using Candida antarctica lipase and achieved 95 wt.%. Antczak [3] noted that plant oils and methanol form a solution when their molar ratio is close to 1:1 at 40 °C. The author noted that adding organic solvent to the reacting mixtures increases the solubility of alcohol, guards the enzymes from deactivation and ensures one-step enzymatic transesterification. Additionally, Nie et al. [64] reported that to safeguard lipase from being denatured due to methanol toxicity; the molar ratio of methanol to oil in the reaction system should not exceed 1:1. In another study, [65] have used immobilized Pseudomonas cepacia lipase for the production of biodiesel fuel from soybean oil. The authors noted that the optimum conditions for processing 10 g of soybean oil were: 35 °C, 0.5 g water and 475 mg lipase for the reactions with methanol, 1:7.5 oil to methanol molar ratio, 35 °C, 0.3 g water and 475 mg lipase for the reactions with ethanol, 1:15.2 oil to ethanol molar ratio. Based on the optimum conditions, methyl and ethyl ester formation of 67 and 65 mol% in 1 h was obtained. As well, Ha et al. [43] reported the influence of methanol to soybean oil molar ratio on the production of biodiesel fuel in ionic liquids. The authors tested different molar ratios, and the best conversion in [Emim][TfO] was obtained at 4:1. The methanolysis in [Emim][TfO] considerably reduced when the molar ratio of methanol to soybean oil was 8:1 and greater. This scenario might be due to the deactivation of Novozym 435 caused by the high methanol concentration.

Furthermore, Tan et al. [82] noted the effects of alcohol to oil molar ratios in producing biodiesel by means of immobilized lipase. They observed that the major cause of the deactivation of lipases is the high molar ratios of ethanol to fatty acid residues. As a result of the contact of the enzyme with the immiscible polar organic phase formed. In addition, Shimada et al. [79] hypothesized that the low methanolysis (ethanolysis) commonly encountered is because of the deactivation of lipases by contact with insoluble MeOH (EtOH) which exists as drops in the oil. Table 2 summarizes the options to avoid lipase inactivation caused by methanol [82].

Table 2 Detail options to avoid lipase inactivation caused by methanol [82].

Options	Operating conditions	Yield (%)	Advantages	Disadvantage
Methanol stepwise addition	Three-step or two-step methanol addition	> 87	Higher yield is achieved without inactivation to the lipase	The operation is relative complicated in large scale production
Acyl acceptor alterations	Methyl acetate, acetate Ethyl	> 90	No inactivation effect occurs and no glycerol is produced	The reaction rate is low and the acyl acceptor cost is high
Solvent engineering	With t-butanol, 1,4-dioxane, ionic liquid as solvents	> 80	Good solvents of methanol and glycerol, so methanol inactivation and glycerol deposit are avoided	Increment of the solvent recovery cost

5. Recovery/removal of excess alcohol from crude biodiesel

The recovery of alcohol is required to minimize the waste of alcohol after the transesterification is completed. Although higher energy input for distillation is required to achieve high alcohol recovery, for processes involving recovery of methanol is considerably easier to recover than ethanol, because it does not form azeotrope. The formation of an azeotrope by ethanol with water makes its purification costly during ethanol recovery (Demirbas, 2002). Van Gerpen et al. [85] noted that to minimize environmental impacts and operating costs, recovery of residual alcohol and its recycling back into the process is essential. The authors reported that input costs for the process is saved when the unused methanol is recovered. Besides, the recovery of excess alcohol is necessary to eliminate the emissions of methanol to the surrounding. Furthermore the emission reduction is required because methanol is toxic and highly flammable.

In most of the researches conducted, the recovery of methanol is carried out through either vacuum or conventional distillations, evaporation or it is recovered partially in a single stage flash. Besides, falling-film evaporator is used as an alternative to distillation [88,7]. It was noted that separation and purification of alcohol at the end of the transesterification is difficult and costly [12]. Refaat [72] remarked that recovery of glycerol is rendered difficult due to excess alcohol, therefore establishing empirically ideal alcohol to oil molar ratio is essential. As well, an excess of alcohol in large amount could slow down the phase separation of glycerol and biodiesel [4]. Also, separation of glycerol from ester becomes more difficult at higher alcohol to oil molar ratios [9]. Meher et al. [60,61] observed that to ensure separation of methanol, the crude biodiesel phase is washed three times with distilled water at 50 °C in a separatory funnel, and the biodiesel phase is then dried using anhydrous Na_2SO_4. Gomes et al. [41] and Chongkhong et al. [21] reported the passing of fatty acid methyl esters phase through an evaporator to recover traces of methanol. Eevera et al. [36] employed evaporation under atmospheric condition to remove excess methanol and water in biodiesel phase. In addition a separation funnel was used to eliminate sulfuric acid, excess alcohol, and other impurities from reaction mixture [66]. Karaosmanoǧlu et al. [53] reported that the methanol in the biodiesel phase was removed using a rotary evaporator under vacuum. Also a heat exchanger was used to remove part of methanol, whereas the other part was driven off by vacuum distillation [39]. In contrast to the discussions involving acid and alkaline catalysts, the process of alcohol recovery is eliminated completely in the enzyme catalyzed route, since enzymes are inactivated at a higher alcohol concentration.

5.1. The effects of alcohol on the refining of crude biodiesel

Oils to alcohols molar ratios play a critical role in the determination of the purity and quality of alkyl esters. The higher the molar ratio the more the complexity of biodiesel separation and purification processes vice versa [8]. It was noted that the addition of higher amounts of alcohol could prolong the required separation time since biodiesel layer separation from water layer becomes more complex in the presence of a huge quantity of alcohol. This is because methanol having one hydroxyl group could act as an emulsifier, thus enhancing emulsion formation [36]. Miao and Wu (2009) noted that excess alcohol in large amounts could slow down biodiesel and glycerol separation as in the case of the values of 70:1 and 84:1 M ratios. The authors revealed that a 56:1 M ratio is the best option for the transesterification of microalgal oil.

For transesterification method involving supercritical methanol, a high molar ratio (40:1) is required [77]. However care must be taken to recover the excess alcohol after the completion of the reaction.

Furthermore, Sharma and Singh [77] noted the treatment of crude biodiesel for the removal of dissolved contaminants such as alcohol, catalysts, etc. by washing with hot distilled water. Van Gerpen [85] reported that water washing step is intended to remove any remaining methanol, soap, catalyst, free glycerol and salts from the biodiesel. Van Gerpen et al. [84] reported that warm (140 °F), softened water can be used to wash alkyl esters for the elimination of soaps and residual methanol. Saleh et al. [76] noted that methanol present in the biodiesel phase is eliminated by distillation or evaporation under vacuum or atmospheric pressure. In a different study, Saleh et al. [75] remarked the performance of membranes for glycerol separation from biodiesel, but the membrane is strongly affected by the presence of methanol. The authors noted application of decantation technique to separate alcohol phase from the organic phase (biodiesel) and the use of a rotary evaporator to eliminate the traces of methanol in the methyl ester phase.

5.2. The effects of alcohol on the quality of biodiesel fuel

The amount of glycerol, catalyst, soap, and the residual methanol, is controlled by the limits of the fuel's free glycerol, ash level, and flashpoint. Therefore meeting these limits indicates that alkyl esters can be directly applied in most modern engines without necessarily modifying it, while maintaining the engine's reliability and durability [85]. Karaosmanoǧlu et al. [53] noted that fuel must be almost free from impurities such as water, alcohol, glycerin, and catalyst. Berrios and Skelton [13] observed that the presence of methanol could lead to low flash point causing transport, storage and use problems, low values of viscosity and density, and corrosion of Zn and Al pieces. Moser [63] reported that impurities in fatty acid alkyl esters include among others mono-, di-, triglycerides, FFA, methanol, metals, soaps, water, glycerol, and catalyst. The author noted that methanol impurity in esters is indirectly measured through flash point determination following ASTM D93. Also, contamination of biodiesel with methanol may result in biodiesel failing to meet the standard specification for minimum flash point for fuels. The contamination of methanol usually occurred due to insufficient purification of esters after transesterification reaction. In addition the wear problem is believed to be caused by formic acid attack when methanol is employed (Demirbas, 2002). Saleh et al. [76] reported that the presence of high levels of methanol can accelerate the deterioration of natural rubber seals and gaskets. Also the presence of methanol could corrode engine aluminums and zinc parts as well as lower flash point of biodiesel fuels [1].

6. Conclusion and recommendation

Based on the foregoing, the following conclusions and recommendations were made:

(1) It was found that quite a number of biodiesel production facilities employ methanol due to its low cost and short-chain molar size (for the avoidance of steric hindrance effects).
(2) It was also found that methanol does not form zoetrope, hence its recovery is simple compared to ethanol.
(3) Although ethanol is more expensive than methanol but biodiesel production involving ethanol is completely bio-base, hence renewable.
(4) Most of the researchers recommend a 6:1 M ratio for methanol and a 9:1 M ratio for ethanol.
(5) Care must be taken to determine empirically ideal molar ratios to employ otherwise excess methanol will result in severe difficulty in biodiesel refining process.
(6) It was found that the presence of alcohol affects the quality of biodiesel fuel by lowering its viscosity and density values, and flash point.
(7) For solid catalysts, it was found that application of co-solvents such as *n*-hexane and ethanol, dimethyl sulfoxide (DMSO), and tetrahydrofuran (THF) could reduce diffusion problems and enhance miscibility of oil and alcohol and speed up the rate of reaction.

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