REVIEW

Production of Biodiesel in the Presence of Co-Solvents in Transesterification: A Review

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Consumption of fossil fuels has resulted in several economic and environmental consequences, prompting a quest for renewable energy sources rather than a reliance on fossil fuels. Biodiesel is a renewable source of energy that can be substituted for fossil fuel-based diesel fuel. Transesterification is the most economically viable way of producing biodiesel. However, the biodiesel manufacturing method based on transesterification has a disadvantage due to the immiscibility of the two key reactants, alcohol and oil, which results in a mass transfer resistance and reduces biodiesel yield. Several researchers have investigated using another solvent called a co-solvent to overcome the mass transfer barrier in the reaction medium. The purpose of this review was to examine the influence of several co-solvents on biodiesel synthesis that had been previously investigated the research.

Keywords: Biodiesel, Co-solvent, Fossil fuels, Renewable energy, Transesterification.

INTRODUCTION

Dependence on imported crude oil, along with concerns about global climate change produced by greenhouse gas emissions from fossil fuels, is having an increasingly negative influence on several countries' national security, economic and environmental policies. As the world's population increases, the demand for transportation increases, resulting in a rise in fossil fuel consumption [1-3]. Due to the limited supply and negative environmental impact of conventional fossil fuels, the critical need for better and longer-lasting alternative fuels derived from renewable sources has increased. The majority of renewable fuels offer a variety of environmental benefits over conventional fuels, including reduced greenhouse gas emissions and pollution [4]. Biofuel has recently gained substantial interest in many countries globally due to its renewable nature, low carbon impact and biodegradability [4,5]. Among biomass sources, vegetable oils and animal fats have garnered considerable attention as a potential source for producing a petroleum based diesel fuel substitute [6]. Vegetable oils have played a significant role in developing alternative fuels, despite the numerous issues connected with utilizing them directly in diesel engines, especially direct injection engines. These issues linked

with the large triglyceride molecule and its larger molecular mass can be resolved by chemically modifying vegetable oils to produce biodiesel, comparable to diesel [6]. As a result of this growing attention, the quest for alternative renewable fuels such as biodiesel has intensified. According to estimations, biodiesel/bioethanol may replace 10% of diesel fuel consumption in Europe and 5% of total fuel demand in Southeast Asia [2].

Biodiesel is a type of fuel that is clean and ecologically friendly. It may be manufactured from vegetable oils or animal fats [3]. Microemulsion, pyrolysis (thermal cracking) and transesterification are among the alterations that have been employed. Transesterification is feasible in manufacturing a more environmental friendly and cleaner fuel from vegetable oil due to the flexibility, simplicity and high yield of readily available raw materials [6,7]. Transesterification is a reversible reaction that occurs when the reactants triglycerides and methanol are mixed with the help of catalyst (Fig. 1). The forward transesterification reaction is in the first order, whereas the reverse transesterification reaction is in the second-order [8]. The reaction of triglycerides with methanol proceeds stepwise to generate the intermediates diglyceride and monoglyceride, with succeeding reactions yielding glycerol and biodiesel [9].

R_1COOCH_2
R_2COOCH $+ CH_3OH$ $\xrightleftharpoons{\text{Catalyst}}$ R_2COOCH $+ R_1COOCH_3$
R_3COOCH_2
Triglyceride → **Diglyceride** (product: $HOCH_2$ / R_2COOCH / R_3COOCH_2)

$HOCH_2$
R_2COOCH $+ CH_3OH$ $\xrightleftharpoons{\text{Catalyst}}$ $HOCH$ $+ R_2COOCH_3$
R_3COOCH_2
Diglyceride → **Monoglyceride** (product: $HOCH_2$ / $HOCH$ / R_3COOCH_2)

$HOCH_2$
$HOCH$ $+ CH_3OH$ $\xrightleftharpoons{\text{Catalyst}}$ $HOCH$ $+ R_3COOCH_3$
R_3COOCH_2
Monoglyceride → **Glycerol** (product: $HOCH_2$ / $HOCH$ / $HOCH_2$)

Overall reaction

R_1COOCH_2
R_2COOCH $+ 3CH_3OH$ $\xrightleftharpoons{\text{Catalyst}}$ $HOCH_2$ $+ R_1COOCH_3$
R_3COOCH_2 $HOCH$ R_2COOCH_3
                                     $HOCH_2$ R_3COOCH_3
Triglyceride   **Glycerol** **Fatty acid methyl ester (biodiesel)**
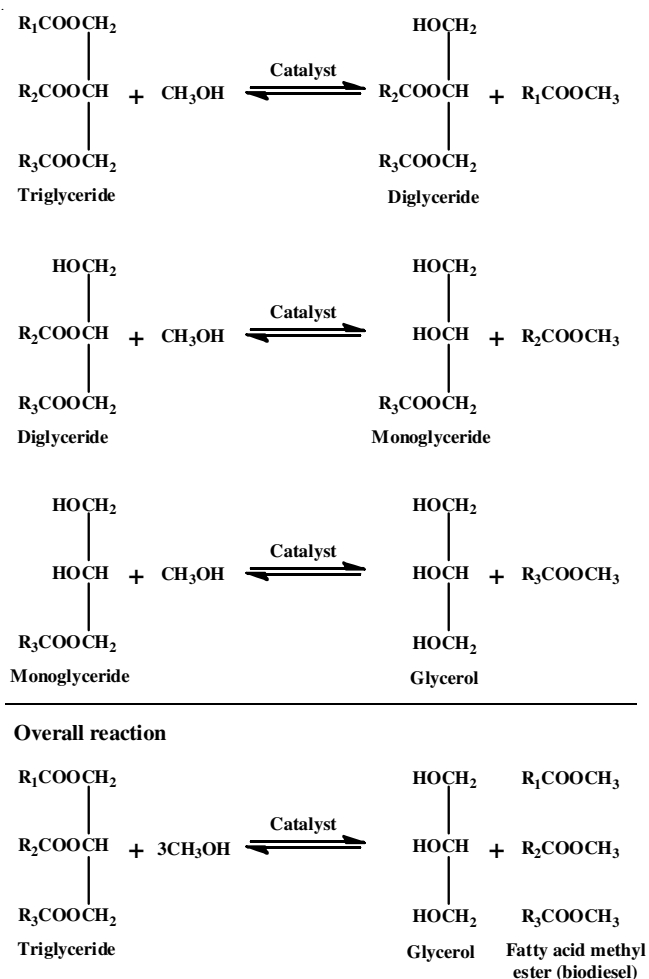
Fig. 1. Overall transesterification reaction of triglyceride [9]

The fundamental difficulty in this transesterification process is that the reactants (oils and alcohols) are not miscible due to their chemical structures. The collision rate between the glyceride and methoxide (a mixture of methanol and an alkaline catalyst–KOH or NaOH) molecules slows when the oil disperses in the methanol medium. This reduces molecular collisions and reaction rates, resulting in longer reaction times, greater operational and labour expenses, higher fixed capital expenditures and ultimately, higher product costs [10,11]. The use of a co-solvent to overcome the solubility issue has become a realistic alternative in recent years. A one-phase reaction can be induced by adding a solvent that improves the oil's solubility; this solvent is referred to as a co-solvent in this context [12]. Many researchers have lately taken an interest in solvent technology in order to improve the transesterification process.

Methanol is an excellent solvent for converting vegetable oils to their fatty acid methyl ester (FAME) equivalents. However, the reaction occurs when the parent chain carbon atom and the alkyl substituent carbon atom in the triglyceride undergo complete bond cleavage. This is the rate-determining phase of the reaction. Significant improvements in the mechanism of this nucleophilic substitution process have been demonstrated after adding another solvent to methanol to permit a co-solvent system [13]. According to Julianto & Nurlestari [14], co-solvent

is highly soluble with alcohol, fatty acids and triglycerides. The co-solvent utilized should not include any water and the more co-solvent added, the better since it will improve the solubility of oil. The selected co-solvent has a boiling point close to the methanol boiling point, which simplifies the separation process at the end of the reaction. According to Singh *et al*. [15], the addition of a co-solvent allows the reaction to be completed with a shorter contact time and a greater yield of FAME. This is due to the increase in molecule-molecule interaction. As observed by Fadhil *et al*. [16], The addition of a suitable co-solvent relieved the system's mass transfer constraints, resulting in significant reductions in reaction time and residence time and catalyst quantity and reaction temperature as well biodiesel production costs. In some cases, using a co-solvent allows biodiesel production from grain-based feedstock, waste cooking oils and animal fats; nevertheless, co-solvents must be handled cautiously because the possible risks and toxicity have been entirely excluded from the glycerol and biodiesel phases [17]. Therefore, it was suggested that the co-solvent should have a boiling point closer to of the alcohol utilized, allowing for simultaneous recycling with the excess alcohol [13,18-20]. As a result, it is exciting to study different co-solvents in their experiments have employed to increase FAME yield on transesterification. The objective of this review article is to elaborate on all co-solvents utilized in transesterification reactions and to discuss their effect on the reaction system.

Co-solvent effect of transesterification reaction on biodiesel production: Le *et al*. [21] developed and improved biodiesel production using a co-solvent method from *Vernicia montana* oil (VMO). The extraction process was performed using an ultrasound system using *n*-hexane as a solvent with a sample-to-solvent ratio of 1:1 (wt./v) for a 30 min extraction time, which extracted the VMO that consisted of $80.3 \pm 0.5\%$ α-eleostearic acid moiety (C18:3). The transesterification process was then initiated along with a co-solvent. Acetone was used as a co-solvent in this study. The amount of acetone varied from 10% to 40% (depending on the VMO mass %). The FAME yield increased from 96% to 99%, when the acetone content increased from 10% to 20%, which was the highest yield found for this study. A further increase in acetone levels in 30-40% region led to a reduction in FAME yield to 94-95%. This behaviour was explained by dissolving the reactant with acetone to slows down the reaction due to the dilution. These findings showed that solvent volumes were significant for obtaining high FAME yields. The optimum amount of acetone as a co-solvent for VMO-based biodiesel synthesis was established at 20%. Accordingly, the optimum conditions for production were methanol-to-oil molar ratio (6:1), 1 wt.% of KOH, 20 wt.% acetone as co-solvent at 40 ºC. Under these conditions, the transesterification process was completed within 30 min and $99 \pm 0.3\%$ of the conversion efficiency was obtained.

Mohammed-Dabo *et al*. [10] synthesized biodiesel from *Jatropha curcas* seed oil in the presence of a co-solvent. *J. curcas* seed oil was obtained by mechanical extraction. The FFA content of the oil was initially 14.8% and was later reduced to 0.4% by esterification. The esterification was carried out at 5 wt.% of H_2SO_4 as an acid catalyst, 20 wt.% methanol at 60 ºC

and the reaction time of 300 min with the mechanical stirrer at 700 rpm. The esterified oil was subjected to the transesterification under optimized reaction conditions that were found to be a 4:1 methanol-to-oil molar ratio, with a catalyst (NaOH) concentration of 0.5 wt.% at 40 ºC of reaction temperature for 10 min of reaction time at 200 rpm. Transesterification was carried out under established operating conditions using THF as co-solvent. At this point in the work, the volume ratio of methanol-to-co-solvent varied between 1:1, 1:2 and 1:3, while the other reaction variables remained constant. The optimal volume ratio of methanol-to-co-solvent was 1:1, resulting in a yield of 98% for this analysis. As the ratio increased, biodiesel yields decreased due to the reagent's dilution effect. Additionally, the study stated that the cost of biodiesel could be reduced by lowering the catalyst concentration and significantly lowering the energy required for stirring and reaction time, allowing for the rapid growth of biodiesel production due to using co-solvent.

Pham *et al.* [22] tested a two-step co-solvent method for the production of biodiesel from candlenut oil (CNO). Acetonitrile, a polar aprotic solvent promoting hydrolysis, was used as co-solvent. First, the esterification of CNO was carried out using acetonitrile (30 wt.%) and H_2SO_4 solvent as catalysts in order to reduce the FFA content from 7 to 0.8 wt.% in 1 h reaction time at 65 ºC. Subsequent transesterification of the crude oil was carried out using co-solvent of 20 wt.% of acetone and 1 wt.% of KOH. Ester content of 99.3% was obtained at 40 ºC in 45 min.

Jomtib *et al.* [23] investigated the non-catalytic conversion of refined palm oil in the presence and absence of co-solvent such as toluene, benzene or hexane. Without using co-solvent, non-catalyzed palm oil transesterification can produce methyl esters at 300 ºC using a methanol-to-oil molar ratio of 45:1, with an 89.4% conversion after 50 min. Hexane, benzene and toluene were used as co-solvents in this study and the effect of the co-solvent-to-oil concentration (10 to 50% v/v) on the formation of methyl esters was determined. In these experiments, palm oil was transesterified at a 45:1 molar ratio of methanol-to-oil at 300 ºC for 50 min. The results indicate that when benzene and toluene (at a solvent-to-oil ratio of 10% v/v) were present, palm oil conversion increased slightly from 89.4 to 92.1% and 95.1%, respectively. However, as concentration of benzene and toluene increased (from 20 to 50% v/v in solvent-to-oil conversion), the conversion of palm oil gradually decreased. The addition of benzene and toluene may increase conversion due to the solubility of vegetable oil in these solvents and the enhanced miscibility of vegetable oil with methanol. Hexane exhibited a distinct preference for use as a co-solvent. When hexane was present, palm oil converted at a significantly lower rate. However, conversion increased as hexane volume increased, reaching 94.5% when hexane was applied at 40% (v/v). It was observed that palm oil conversion decreased precipitously to 50% (v/v) in hexane. According to the study, hexane is generally soluble in oil but less so in methanol. As a result, it acts as an antisolvent for vegetable oil in methanol, lowering the yield of biodiesel products. However, the solubility of hexane in methanol and palm oil improved significantly at higher concentrations and the oil's viscosity decreased significantly. The

lower the viscosity, the more mass exchange between the methanol and the oil, increasing product yield.

The conversion of palm oil in the presence of a co-solvent was significantly higher than that achieved in the absence of co-solvent, particularly at low methanol-to-palm oil molar ratios. Maximum conversions of 89.7% and 93.7%, respectively, were obtained in the presence of benzene and toluene as co-solvents at 25:1 methanol-to-oil molar ratio. However, the maximum conversion of 94.5% was obtained at 45:1 in the presence of hexane as co-solvent. Thus, it was concluded that using benzene or toluene as co-solvent can significantly reduce the requirement for excess methanol.

The effect of reaction temperature on palm oil conversion with various solvents was investigated. At low temperatures (250 ºC), the presence of benzene, toluene or hexane as co-solvent has little effect on the reaction but significantly increases conversion at higher temperatures (280 and 300 ºC). Julianto & Nurlestari [14] investigated the effect of acetone as co-solvent on the transesterification of waste cooking oil (WCO) in the presence of methanol. According to the study, acetone dissolves both highly polar methanol and non-polar WCO triglyceride to generate a homogeneous reaction system that speeds the transesterification reaction between methanol and triglycerides. Additionally, acetone helps in the stabilization of the methoxide ions produced when KOH is used as catalyst. These methoxide ions are a reactive intermediate in the S_N2 mechanism by which triglycerides are converted to methyl esters. The optimal ratio of acetone-to-methanol was determined in this study using a homogeneous alkaline catalyst KOH 1 wt.% at room temperature for 15 min. The WCO was used in a 1:12 molar ratio with methanol. The substance used to add acetone-to-methanol in various ratios was 1:4, 1:2 and 1:1. The addition of acetone as co-solvent more than 1:2 reduces the yield of transesterification reaction.

The lowest ratio (1:4) produced the highest FAME yield of 99.93%, followed by a 1:2 ratio that produced 99.77% and a 1:1 ratio that produced 99.87%. This indicated that the transesterification reaction was more efficient, as adding acetone as co-solvent trace increased the methyl ester produced. Excess acetone in the combination had no noticeable effect on the yield of methyl esters, although the yield of methyl esters declined with the weight of waste oil. Increased acetone content complicated the separation of methyl ester products from glycerol and residual triglycerides, as evidenced by the time required to form two organic layers containing methyl esters and glycerol. As a result, the optimal ratio was determined to be 1:4 with a 99.93% FAME yield.

Luu *et al.* [24] investigated the co-solvent-based production of biodiesel from waste cooking oil. Acetone was used as a co-solvent. While acetone has several advantages, it should be removed from the mixture using a liquid dissolved in it. The optimal conditions for transesterification to obtain FAMEs with a purity of 98% were 1 wt.% KOH catalyst, 20% acetone and a methanol-to-oil molar ratio of 5:1, at 40 ºC and a reaction time of 30 min. The volume of the co-solvent was varied between 5% and 40%. The transesterification yield was 98% when the acetone content was 20%. The results indicated that increasing

volume of the co-solvent to 30% and 40% significantly reduced the reaction effect. This was because when the concentration of acetone in the reaction mixture exceeds 20%, the concentration of the reaction mixture decreases, affecting the reaction rate. Additionally, residual acetone was dissolved in a portion of FAMEs; as a result, the yield decreased and the acetone concentration in the products was later determined to be 247 ppm.

Singh *et al*. [15] investigated the effect of co-solvent of acetone on the production of biodiesel from vegetable wastes oil utilizing dicalcium aluminate ($Ca_2Al_2O_5$) as reusable catalyst. The effect of co-solvents on reaction time was investigated in the range of 0 to 25 wt.%. The FAME conversion rate increased with time in the presence of acetone. Initially, the solubility of methanol in oil was lower due to a lower amount of acetone, resulting in a lower FAME conversion. The mixture's viscosity decreased as the number of acetone increased, as the density difference between the FAME and glycerol reduced the time required for phase separation. The highest biodiesel conversion (97.98%) was obtained with acetone (20 wt.%), a 1:6 molar ratios (oil: methanol) and 1.2 wt.% $Ca_2Al_2O_5$ at 55 ± 1 °C for 25 min. Further increased acetone concentration reduced the benefits; this could be due to diluting the optimized reactant concentration. Furthermore, the time required to separate the FAME and glycerol phases lengthen. This is since the separation of excess methanol and glycerol from the reaction mixture is proportional to their concentration. Methanol and glycerol content is higher in low acetone concentrations than in high acetone concentrations. Hence, the probability of collision between methanol and glycerol increase; they can collide faster to produce the glycerol phase differs from the reaction mixture, therefore 20 wt.% acetone was chosen for optimization.

Wu *et al*. [25] designed a new transesterification process for producing biodiesel with co-solvent. In the biodiesel synthesis reaction system, bentonite was used as a water absorber to remove moisture. To improve the mutual solubility of oil and methanol, diethyl ether (DEE) was used as co-solvent. The effect of the DEE-to-methanol molar ratio on FAME yield was investigated. The presence of DEE allowed for a significant increase in FAME yield at shallow temperatures. This was attributed to the DEE's intervention, which increased mass transfer between the reactants and thus the reaction rate and conversion. The FAME yield increased as the DEE-to-methanol molar ratio increased. At a molar ratio of 0.5:1 DEE-to-methanol, the highest FAME yield (96.36 ± 0.69%) was obtained. On the other hand, an excess of DEE reduced the FAME yield because it diluted the reactants and the catalyst concentration based on total volume, leading to a decrease in the reaction rate and FAME yield. The addition of bentonite increased the FAME yield significantly. The FAME yield remained constant when the bentonite content exceeded 2 wt.%. Wu *et al*. [26] reported a significant amount of methanol was absorbed. When high doses of bentonite were used, the oil-to-methanol molar ratio decreased, limiting FAME production even further. Furthermore, soap and glycerol absorption on bentonite resulted in the loss of biodiesel during the separation process due to the formation of a gelatinous liquid. Surprisingly, the presence of DEE did

not affect the yield of FAME when the bentonite content was high. Because the addition of DEE reduced the viscosity of the reaction mixture, the absorption of glycerol in soap and bentonite inhibited the formation of the gelatinous liquid, resulting in less biodiesel loss during the phase separation process. As a result, a DEE-to-methanol molar ratio of 0.56:1, 1.07 wt.% NaOH and a methanol-to-oil molar ratio of 5.65:1 were achieved with a maximum optimum yield of 98.35 ± 0.69% under optimized reaction conditions.

Chueluecha *et al*. [27] enhanced biodiesel production in a packed microchannel by examining different co-solvents *viz*. THF, ethyl acetate and isopropanol in the presence of calcium oxide (CaO) catalyst. The highest percentage of FAME was obtained when 40% THF was added to the system in 7.1 min of settling time, whereas isopropanol (20 wt.%) was required for the highest percentage of FAME in the same residence time. The highest FAME percentage was obtained with a longer residence time (8.9 min) and a 20 wt.% ETOAc. These findings suggested that isopropanol was a more effective co-solvent for biodiesel synthesis, which provided better reaction mixture homogeneity than other co-solvents. Furthermore, the use of co-solvents (THF and ETOAc) in short residence time had a negative effect on FAME% because the mixture may take longer to homogenize due to the lower diffusion coefficients of both THF and ETOAc in both oil and methanol compared to isopropanol. It was also discovered that a residence time range of 5.3 to 7.1 min with 20 wt.% co-solvents were appropriate for studying the effect of mixing between co-solvents and reagents. The optimum conditions were established in 6.5 min, with a methanol-to-oil molar ratio of 20:1 and a co-solvent ratio of 14.5 wt.%, allowing 99% purity of methyl esters.

In addition, two sets of analyses were carried out to determine whether co-solvent should be introduced with methanol or oil. The results demonstrated that adding any co-solvent to methanol could increase the FAME% (for the same residence time) compared to pre-mixing the co-solvent and the oil. The co-solvent in the methanol phase easily penetrates the pores of the catalyst, allowing the oil and methanol to spread to the active sites of the catalyst. When the pre-mixing of THF and methanol was used instead of the pre-mixing of THF and oil, the FAME% increased from 92.5 to 95.0% for a residence time of 7.1 min. A similar effect was observed for a residence time of 5.3 min, where pre-mixing of isopropanol into methanol increased the FAME% from 92 to 95.2% compared to isopropanol pre-mixed with oil.

Parida *et al*. [28] investigated the catalyst for homogeneous alkaline transesterification using ultrasound energy and petrodiesel as co-solvent. The effects of various reactivity parameters on transesterification were investigated, including methanol-to-oil molar ratio, co-solvent ratio and catalyst concentration (NaOH) used. Within 0.5 h, an excellent yield of 92% FAMEs were obtained using an alcohol level (alcohol-to-oil molar ratio of 3:1), a 1 wt.% catalyst, an ultrasound power of 20 kHz and 30 wt.% petro-diesel. Solvent-free transesterification produced 46% of FAME under similar conditions. The use of diesel as co-solvent was further reduced co-solvent removal in the refining process, saving efficiency, economy and time as observed in

the study. The effect of petro-diesel on NaOH concentration was tested in the absence and presence of petro-diesel. The catalyst concentrations ranged between 0.25, 0.5 and 1 wt.%. The percentage yield of FAME increased significantly as the amount of NaOH in the reaction mixture increased due to the proportionate increase in the formation of methoxide ions. However, the addition of co-solvent increased the yield even more. The reaction with co-solvent yielded a maximum yield of 92% in 30 min, whereas the reaction without co-solvent yielded only 46% in 30 min at a concentration of 1 wt.% catalyst.

Four different petro-diesel concentrations, ranging from 10 to 40 wt.%, were used to investigate the transesterification rate and the effect of solvent on the product yield. The yield of FAME was discovered to increase with increasing co-solvent concentration. When the reaction time was 30 min, a co-solvent concentration of 30% facilitated a maximum yield of 92%. The maximum percentage yield of the product remained constant when the co-solvent concentration was increased to 40%. However, the yield was significantly higher in the initial reaction stage (15 min) than with a 30% solubility reaction. Under similar reaction conditions, it was discovered that only 45% of the maximum yield was obtained without the addition of co-solvent. As a result of the interaction of ultrasound energy and co-solvent, the reaction mixture becomes more homogeneous, overcoming the mass transfer limit and increasing the reaction rate, thereby increasing the product yield.

Roschat *et al.* [29] produced biodiesel using heterogeneous catalysts derived from river snail shells and co-solvent of THF. The effects of co-solvent addition on the reaction's kinetics and the FAME yield were explored. A FAME yield of 98.5 ± 1.5% was obtained under optimum conditions of 5 wt.% catalyst; methanol-to-oil molar ratio 12:1; reaction temperature 65 °C; 10% (v/v) of THF in methanol and 90 min reaction time. The addition of 10% (v/v) of THF improved % FAME yield to 95.90% at the reaction time of 90 min while the non-co-solvent system gave only 63.49% FAME yield. The k value (rate constant) obtained was 10% (v/v) THF co-solvent system 4.09×10^2 min^{-1}, which was twice as large as the non-co-solvent solution (1.84×10^2 min^{-1}). The effect of THF on reactive kinetics was observed with a decrease in activation energy (57.79 kJ/mol) and an increase in frequency factor (1.17×10^7 min^{-1}) compared to non-polar reactions (67.60 kJ/mol and 9.87×10^8 min^{-1}).

Guan *et al.* [30] investigated trilaurin transesterification in a solution containing 4 wt.% Lewis acid AlCl$_3$ dissolved in a co-solvent solution of ethanol and 5 MPa CO$_2$. Within 1 h at a low temperature of 180 °C, a more than 90% conversion rate was obtained. In this method, Lewis acid and CO$_2$ were used as co-solvent. However, CO$_2$ served as co-solvent and operated as catalyst, increasing viscosity and mass transfer. According to the mechanism, when CO$_2$ and ethanol were mixed, hydrogen bonds form between the CO$_2$ and ethanol, increasing the amount of C$_2$H$_5$O. The oxygen atom in C–O–C is attacked by AlCl$_3$, weakening the bonds to form carbonyl carbon, which C$_2$H$_5$O readily attacks to produce the transesterified product (Fig. 2). Finally, H replaces AlCl$_3$ to form glycerin and intermediates such as unmethyl esterified compounds. To convert the waste cooking oil (WCO) to biodiesel, AlCl$_3$ was used as flocculant

and catalyst. The process converted 97% free fatty acid at 120 °C in 90 min, making it one of the most efficient WCO recovery systems available.

Encinar *et al.* [17] carried out several experiments to investigate the use of various co-solvents such as acetone, diethyl ether (DEE), dibutyl ether (diBE), *tert*-butyl methyl ether (tBME), diisopropyl ether (diIPE) and tetrahydrofuran (THF) to enhance the transesterification process significantly. The biodiesel extraction with a high methyl ester content using DEE, tBME and THF had the most significant impact on this process when the methanol-to-oil molar ratio was 9:1, 0.7 wt.% KOH and 1:1 co-solvent-to-methanol molar ratio was used at 700 rpm and 30 °C reaction temperature, the maximum methyl ester content was 97-98%. The effect of changing the methanol-to-co-solvent molar ratio in the 1:0.5-1:2.0 range was investigated. In addition, to compare with these experiments, another test was performed under the same conditions but without a co-solvent. According to the results, it was found that using a small amount of co-solvent increases methyl ester yield by 6.4%. Increased methanol-to-co-solvent molar ratios up to 1:1 resulted in higher biodiesel yield, most likely due to lower methanol-to-oil solubility at low co-solvent concentrations. It was also tested in DEE, tBME and THF had the highest methyl ester yields, with more than 97 wt.%. The presence of diIPE, diBE and acetone produced the same effect as absence of co-solvent. However, after purification, the biodiesel produced with tBME, diIPE and diBE had a strong odor in the co-solvent used in each investigation. Furthermore, the study revealed that agitation speed has no significant effect on biodiesel yield. The speed varied as 500, 700, 900, 1100 rpm in the presence of DEE as a co-solvent with 1:1 with methanol because the presence of a co-solvent increased the solubility of the reagents.

Fadhil *et al.* [16] transesterified *Cyprinus carpio* fish oil (CCFO) with various co-solvents such as hexane, petroleum ether, acetone, cyclohexane and diethyl ether. When compared to other co-solvents, hexane produced the highest biodiesel (BD) yield (91.02 ± 1.06% ~ 90.11 wt.% ester content). This could be because the hexane reaction mixture is more homogeneous. Furthermore, hexane has boiling point close to methanol, allowing it to recover hexane alongside unreacted methanol as described by the study. However, the lowest biodiesel yields were observed with diethyl ether and acetone, which could be attributed to evaporation at a precipitating temperature of 60 °C, resulting in lower yields. As a result, hexane was chosen as an ideal co-solvent and was used in subsequent experiments.

The effect of the methanol-to-co-solvent volume ratio on CCFO methanolysis was investigated. The methanol volume ratio (0.5:1-3:1) from different hexane was tested at different times (15, 30, 45, 60 and 75 min), while other factors remained constant. The results showed that increasing the hexane-to-methanol volume ratio increased biodiesel yield. A methanol volume ratio of 1.5:1 hexane for 30 min of reaction produced the highest yield of biodiesel (96.88 ± 0.98% ~ 96.02 wt.%). The CCFO was also used to produce biodiesel to determine the effect of co-solvents on the methanolysis of CCFO. Compared to the non-co-solvent process, the co-solvent process produced a higher yield in a shorter time since co-solvent
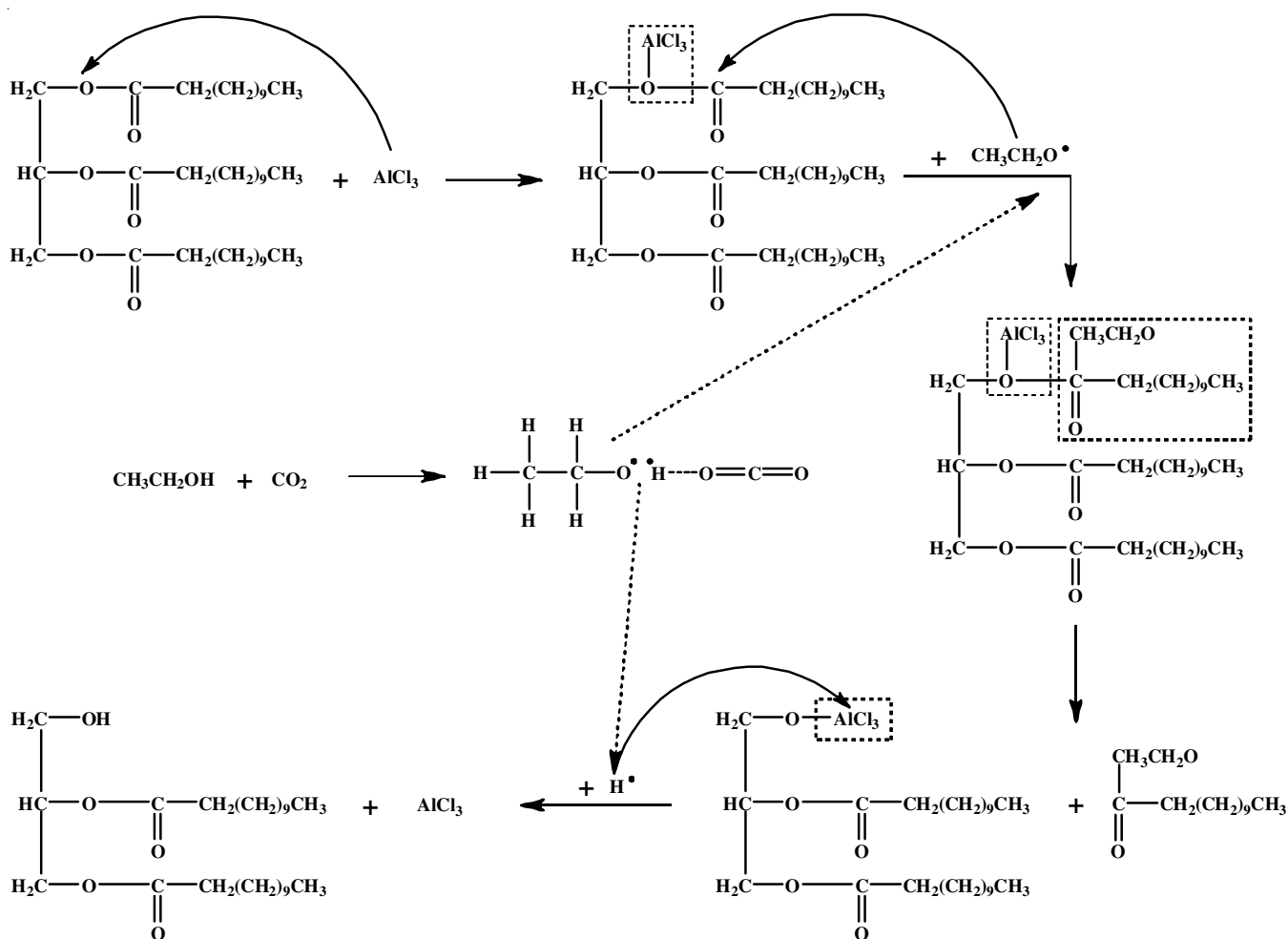
Fig. 16. Mechanism of the catalytic transesterification by AlCl$_3$ in the co-solvent of ethanol and CO$_2$ [30]

enhanced mass transfer and conversion rates. As a result, the optimal volume ratio of hexane-to-methanol was determined to be 1.5:1.

Transesterification was used to establish a relationship between temperature and co-solvent. The yield of biodiesel at each temperature was observed to increase as the volume of methanol-to-hexane was increased. Additionally, it was observed that the decreasing the reaction temperature resulted in increased conversion as the hexane-to-methanol ratio increased. The yield of biodiesel increased from 76.22% at 0.5:1.0 hexane-to-methanol volume ratio to 95.03% at 2.5:1.0 hexane-to-methanol volume ratio as hexane reduced the viscosity of fish oil, increasing the oil's miscibility with alcohol. However, increasing the hexane-to-methanol ratio to greater than 2.5:1 resulted in a slight yield decrease due to the dilution effect. The highest yields of biodiesel (98.55 ± 1.02% ~ 97.24 wt.% ester content) were obtained at 50 ºC and a volume ratio of 1.5:1 of hexane-to-methanol.

Zhang *et al*. [31] investigated a direct transesterification process utilizing 75% ethanol and a co-solvent to reduce energy consumption during the lipid extraction process and increase the conversion yield of microalgae biodiesel. Experiments with petroleum ether, *n*-hexane, carbon tetrachloride, ethyl ether, *n*-butanol, chloroform and acetone were conducted to deter-

mine the optimal co-solvent for lipid extraction 75% ethanol was used. Various solvents *viz*., petroleum ether, *n*-hexane and chloroform demonstrated high efficiency using with the selected co-solvents. These effects are due to the non-polar nature of *n*-hexane and petroleum ether, which dissolve the long-chain triglycerides and combine with ethanol to form a homogeneous catalyst. It was discovered that chloroform with a high polarity helps in disrupting the cell walls and removing the lipids from microalgae cells. Because *n*-hexane is less expensive than petroleum ether and more environmentally friendly than chloroform, it was chosen as the ideal co-solvent. Up to a volume ratio of 75% *n*-hexane-to-ethanol of 1:2, 6.0 mL mixed solvent, 90 ºC reaction temperature, 2.0 mL reaction time and up to 0.6 mL catalytic volume. The direct transesterification process for microalgal biomass produced up to 90.02 ± 0.55 wt.% high conversion output.

Dianursanti *et al*. [32] used co-solvent to increase the yield of direct transesterification reaction on *Nannochloropsis* sp. for 2 h at a ratio of lipid-to-methanol of 1:200, a KOH concentration of 2% mass of biomass, a biomass mass of 1 g and a reaction temperature of 60 ºC, which the biodiesel yield was 90.9%. The addition of *n*-hexane-to-methanol at a volume ratio of 1:1 increases the yield of biodiesel by 5% when compared to a volume ratio of 1:0 or when no *n*-hexane was used. How-

ever, adding *n*-hexane 1:1.5 did not increase biodiesel yield. Excess *n*-hexane reduced lipid contact with ethanol, resulting in decreased production. Another predictable factor was that excess *n*-hexane inhibits the mass transfer between lipids and methanol and decreases transfer heat, resulting in an inefficient activation of the transesterification reaction. By incorporating co-solvent, the yield can be increased depending on the amount used. Additionally, the study reported that the addition of co-solvent helped in binding methanol to lipids.

Luu *et al.* [18] produced biodiesel using Vietnamese *Jatropha curcas* oil in two stages. The first stage was esterification, which was carried out under optimal conditions of 50 g of oleic acid, 6:1 methanol-to-FFAs molar ratio, 1% H_2SO_4, 65 ºC and 30% acetonitrile as co-solvent. Within 60 min, this step reduced the FFA concentration in the reaction mixture from 15.93 to 2.00 wt.%. In the second stage, transesterification generated 99% FAMEs in 30 min under optimal conditions, including a methanol-to-oil molar ratio of 6:1, 1% KOH, a temperature of 40 ºC and a co-solvent of 20% acetone. In the first stage, diethyl ketone, methyl ethyl ketone, acetonitrile, ethyl acetate and co-solvent measured the effect of co-solvents upon the esterification reaction with and without a co-solvent. These solvents have a high capacity to dissolve FFA to form a homogenous solution by combining methanol and sulfuric acid. They can also promote sulfuric acid dissociation as a proton catalyst ester reaction. The addition of a co-solvent with a high-boiling point increases the boiling point of the whole solution, which is beneficial for the high-temperature reaction without influencing the evaporation of methanol. According to results, acetonitrile has produced the best conversion since acetonitrile dissolves *Jatropha curcas* oil (JCO) and its FFAs, making the mixture of reactions more homogeneous and accelerating its esterification process. The impact of acetonitrile levels on FFA reduction percentage was assessed, which shows that the FFA% rapidly decreased by increasing the co-solvent concentration from 10 to 30 wt.%. Co-solvent concentrations above 40 wt.% slowed and increased the FFA level, which is attributed due to the dilution. Without using co-solvent in the first stage, the FFA content was decreased to below 2 wt.% by around 120 min, while the 30 wt.% of acetonitrile was used as co-solvent for this first stage, which only took 60 min.

Using different amount of acetone, the transesterification occured and increased the conversion effect with the addition of acetone, from 96 to 99%, as acetone was varied from 10 to 20 wt.%. When the co-solvent was increased from 30 to 60 wt.%, the yield of FAME was reduced from 99 to 96%.

Choi *et al.* [33] suggested alternative method for generating biodiesel from the wet wastewater sludge using xylene as co-solvent in place of hexane during the transesterification process. During transesterification, the water in the sludge was separated using xylene, which has a higher boiling point than water. Xylene raised biodiesel production to 8.12%, 2.5 times that of hexane. It was equivalent to the 9.68% biodiesel yield achieved from dry sludge. Compared to hexane, the reaction time for xylene or methanol consumption can be decreased while maintaining a similar yield. By substituting xylene for hexane as co-solvent, the conversion of fatty acids in biodiesel from FAME was nearly quadrupled. Without the need for drying, wet wastewater sludge may be used efficiently and inexpensively to the transesterification technique that utilizes xylene as co-solvent for biodiesel recovery.

Hexane and xylene had 13 and 7 FAMEs, respectively. In contrast to xylene transesterification, hexane transesterification produces biodiesel that contains contaminants other than FAMEs. As a result, the addition of xylene increased the content of FAME in crude biodiesel. In crude biodiesel, the FAMEs level of xylene transesterification was 81.9%, which was more than double hexane transesterification (45.0%) and more significant than the rate of dry sludge biodiesel. Myristic acid 13 methyl esters (C14:0) were the most prevalent FAME in the xylene transesterification, accounting for 23.85% of biodiesel. Although FAME varies depending on the transesterification procedure, conventional wastewater sludge biodiesels' main components were present. The final composition of FAME was highly reliant on the transesterification process (co-solvent type).

Alhassan *et al.* [13] converted cottonseed oil to biodiesel utilizing different methanol blends, including diethyl ether (DEE), dichlorobenzene (CBN) or acetone (ACT) as co-solvents. As a catalyst, KOH was used. The optimal volume result was reached by adding 10% (v/v) methanol-to-co-solvents for CBN and ACT. When 0.75 wt.% of KOH was employed, the optimal reaction temperature was 55 °C for 10 min. Additionally, it was found that as the proportion of methanol-to-co-solvent rose for all samples, the acid value of cottonseed oil methyl esters (COMEs) dropped due to an increase in the dissolution effect of catalyst in the co-solvent mixture. However, additional co-solvent resulted in a slight improvement in the biodiesel acid value. When employed in solution mixtures with a low volume ratio, the acid value decreased, following the expected trend. This might be because the chemical makeup of methanol was not appreciably changed at these concentrations. Consequently, adding 10 and 20% (v/v) of all co-solvents resulted in a substantial decrease in the acid value. When co-solvent was introduced to more than specific concentrations, the chemical composition of the solution began to alter. As a result, the characteristics of each solution varied. This explained why the acid value of biodiesel transesterified with methanol declined consistently, whereas the acid value of biodiesel transesterified with other co-solvent systems alternated. Therefore, this study recommended employing a minimal amount of co-solvent.

The impact of adding co-solvent to the methanol volume was also investigated. Due to the mass resistance caused by the low co-solvents miscibility in methanol and other volatile characteristics, a larger percentage of DEE was added to the total methanol (30%). In general, a modest volume of co-solvent was required to increase the yield of cottonseed oil methyl esters (COMEs). Nevertheless, a more significant proportion of co-solvent significantly decreased the percentage yield of all COMEs except DEE. The influence of reaction time (min) on the percentage yields of FAMEs demonstrated that the co-solvents exhibited respectable percentage yields (> 90%) for 45 min reaction period, with DEE co-solvent exhibiting the lowest percentage yields. Increased reaction time had no distinct influence on the yields of co-solvents. Interestingly, more than

90% yields were obtained within the first 10 min in two of the three co-solvents studied. This was due to the quickest feasible achievement of phase equilibrium.

Lam & Lee [34] focused the conversion of high-viscous microalgae lipids from *Chlorella vulgaris* to biodiesel using H_2SO_4 as catalyst with various co-solvents such as hexane, ethanol, THF, methyl acetate, ethyl acetate, chloroform. The best reaction conditions for 95% FAMEs were a 180-molar ratio of methanol-to-lipids, 35% catalyst concentration, 60 ℃ temperature and 6 h reaction time. A co-solvent was added to the reaction mixture to help reduce the requirement for methanol and catalyst concentrations. The reaction rate was significantly increased by homogenizing the reaction mixture with THF as co-solvent. The most significant result (60%) was obtained with THF followed by toluene and hexane (45% and 25%, respectively). Acetates and chloroforms did not influence FAME conversion. The increased solubility of lipid and methanol in THF resulted in more homogeneous reactant distributions. According to the study, THF and methanol have comparable boiling points (66 and 64.6 ℃). Hence, they can be recycled together, while the non-polar hexane (69 ℃) has a lower boiling point than methanol but is incompatible with methanol. Moreover, toluene's boiling point is higher than methanol's, the separation process would need more energy.

The FAME concentration grew progressively from 20% to 60% as the methanol to THF molar ratio was raised from 0.05 to 0.25. However, raising the methanol-to-THF molar ratio over 0.25 showed a negligible effect on FAME content improvement. This finding implied that a small quantity of co-solvent was necessary to dissolve the reactants (lipid and methanol) completely. Once a suitable quantity of co-solvent has been added to the reaction mixture, increasing the amount of co-solvent has a minimal influence on the reaction rate. The methanol-to-lipid molar ratio of 15, the FAME content generated with and without co-solvent was similar. The amount of methanol supplied to the reaction mixture substantially affected the rate of FAME conversion, even when a considerable amount of co-solvent was added. After 3 h, the methanol-to-lipid molar ratio was raised to 60, resulting in a 95% FAME concentration. Increasing the methanol-to-lipid molar ratio did not substantially increase FAME, indicating that the reaction was stable. In the absence of co-solvent, FAME conversion was sluggish and linearly increased with methanol-to-lipid molar ratio. It was substantially less than the reaction with co-solvent, at just 32% FAME concentration. The methanol-to-lipid molar ratio was effectively lowered from 180 to 60 by adding a co-solvent to the reaction mixture. The time to establish equilibrium was reduced from 6 to 3 h. These data suggested that co-solvents improved the methanol-lipid miscibility, hence increasing mass transfer between reactants during transesterification. The second optimization study used a methanol-to-lipid molar ratio of 60.

The effect of co-solvent on FAME conversion at various catalyst concentrations were also studied. In both reaction mixtures with and without co-solvent, the FAME content generated at a catalyst concentration of 1% was modest. After 3 h, the FAME content was only 11% and 2%. A low catalyst concentration could not achieve a fast transesterification reaction rate despite the complete homogeneity of the reaction mixture with co-solvent. The FAME content increased linearly with increasing catalyst concentration in both cases. With no co-solvent, the FAME content produced was low (32%) despite using a high catalyst concentration of 35%. Compared to co-solvent, which required a catalyst concentration of 35 wt.% to create 95% FAME, the catalyst concentration was effectively lowered to 21 wt.%. This study established the favourable influence of co-solvent on enhancing reaction solubility and decreasing catalyst quantity required to increase the reaction rate. Moreover at 25 ℃, the FAME content of reaction mixtures with and without co-solvent was only 7% and 4%, respectively. After 3 h of increasing the reaction temperature from 25 to 60 ℃, the FAME content of the reaction mixture, including co-solvent, reached 95%. Without a co-solvent, the increase was slower, with just 32% FAME was happened at 60 ℃, due to the low catalyst concentration and methanol-to-lipid molar ratio. Increasing the reaction temperature reduced the FAME concentration owing to the methanol evaporation.

Thanh *et al.* [35] pioneered the homogeneous reaction process for transesterifying vegetable oil with methanol in the presence of KOH catalyst and acetone as co-solvent. Optimal conditions were 25 wt.% acetone in oil, 1 wt.% KOH catalyst, 4.5:1 methanol-to-oil molar ratio and 25 ℃ reaction temperature. About 98% of vegetable oil was converted to FAME within 30 min in these conditions. The influence of acetone volume was studied by varying the acetone concentration from 0 to 30% based on WCO weight. Addition of acetone increased the FAME synthesis. The reaction mixture was not homogeneous if the acetone level was less than 20%, resulting in the sluggish FAME formation after 60 min of reaction with acetone concentrations of 0, 5, 10 and 15% wt.%, FAME produced 55.3, 74.3, 83.5 and 88.3%, respectively. After 40, 32 and 20 sec, the reaction mixture was homogeneous and the FAME yield was 20, 25 and 30%. The addition of acetone also speeds up the time it takes for the acetone to separate from the glycerol combination. After 60 min, glycerol separation should take 37, 30 or 50 min for acetone concentrations of 20, 25 or 30%. The incomplete reaction left many tiny droplets of methanol and glycerol in the FAME phase when the acetone concentration was less than 20% by weight. This study found that addition of acetone decreases the viscosity of the reaction mixture. It enhances the differential density between the FAME and glycerol phases, speeding up phase separation increasing the acetone content to 30 wt.% enhanced phase separation time. This behaviour is attributed to the reaction mixture concentration affecting glycerol and methanol separation. As the possibility of glycerol and methanol colliding increases, the glycerol phase develops rapidly and separates from the reaction mixture.

Guan *et al*. [36] investigated the transesterification of sunflower oil in a closed batch reactor using KOH at 25 ℃ in the presence of a variety of co-solvents *e.g.* dimethyl ether (DME), diethyl ether (DEE), *tert*-butyl methyl ether (TBME) and tetrahydrofuran (THF). The minimal DME-to-oil molar ratio was the highest of all the studied co-solvents, indicating that additional DME molecules were required to achieve the homogenous reaction mixture. The inclusion of co-solvent

enhanced the transesterification rate by roughly 78% at the methanol-to-oil molar ratio of 6 for 20 min of reaction time. At the start of the reaction time (particularly the first 20 min), oil conversion was more significant in the presence of co-solvent than in the absence of solvent. The process achieved the equilibrium at the methanol-to-oil molar ratio of 4 in the presence of DME and the oil conversion was determined to be constant. Additionally, the highest oil conversion was obtained for each solvent at the lowest co-solvent-to-methanol molar ratio. When the methanol-to-oil molar ratio was 8, the oil transformed virtually instantly into biodiesel when any co-solvent was added.

Lam & Lee [37] synthesized FAMEs *via* supercritical extraction and transesterification (SET) of *Jatropha curcas* L. seeds in a high-pressure batch reactor. Various co-solvents (1.0-5.0 mL/g liquid and 10-50 bar gas) were added to the process to analyze their impact on extraction efficiency (Ey) and FAME generation (Fy). Pentane (1.0 mL) and 50 bar CO_2 produced more substantial reactions (Ey: 102.6% and 107.0%, Fy: 100.4% and 102.3%, respectively). A solid ratio of 4.0 mg/g methanol and pentane lowered the critical conditions of reactant mixture, allowing for excellent product production at low temperatures (280 ºC). As pentane concentration increased, so did the extraction efficiency for the SET process. For heptane, the extraction efficiency increased from 1.0 to 5.0 mL/g. Addition of 1.0 mL/g pentane increased the FAME yields, whereas beyond this range of pentane decreased them. However, increasing the heptane concentration reduced the FAME generation. This was characterized as the longer reaction time, more esters are formed and the fewer polar molecules dissolved in the non-polar co-solvent are due to the solubility of ester and glyceride intermediates. Pentane lowered the methanol concentration and hence the extraction efficiency of methanol for the polar molecules, impeding their effective extraction. In the presence of toluene, the extraction efficiency increased first before decreasing rapidly to over 3 mL. However, increasing THF enhanced the extraction efficiency to levels comparable to those produced without co-solvent and was more stable than other co-solvents. Aromatic hydrocarbons like toluene and THF are moderately polar with non-polar and polar molecules. As a result, they can enhance the methanol extraction in SET employing polar and non-polar compounds. Because of this, their extraction efficiency reduced as the reagent's methanol concentration increased. Toluene should be used at low concentrations to boost the non-polar solubility of methanol, allowing for better conversion into the triglycerides and FFA to esters. When toluene is added, however, it competes with methanol extraction since it is less polar than pentane. THF is more polar than alkane and toluene, removing both polar and non-polar molecules, lowering triglyceride and FFA methanol solubility. Increased THF content inhibits more triglycerides and FFA from dissolving in methanol and being converted to methyl esters. Moreover, increased N_2 in the SET process also results in the reduction of the extraction efficiency and AME generation. Even though CO_2 was utilized as co-solvent in the SET process, 10-50 Ey and Fy enhanced the CO_2 pressurization. Thus, CO_2 is an ideal co-solvent for the SET process because it enhances the overall solubility of jatropha oil and the subsequent conversion to methyl esters.

Kumar *et al*. [38] synthesized biodiesel from non-edible mahua and jatropha oils using methanol and KOH in the presence of THF as co-solvent. The effects of co-solvents on the transesterification were determined at 1 wt.% KOH, 1:6 oil-to-methanol molar ratio and 1.25:1 of THF-to-methanol ratio (v/v) at 28 ºC and 45 ºC. In 1 min reaction with mahua oil, the conversion of triglyceride was increased by 300% in THF at 28 ºC, but only by 45% at 45 ºC. Nonetheless, after 30 min of reaction, conversion with THF rose by just 5% at 28 ºC and 10% at 45 ºC. At 45 ºC, nearly the complete conversion (99%) was accomplished in 180 min with THF, whereas 95% was accomplished without THF. The THF effect was significantly smaller in the early phases of the reaction in the case of jatropha oil. Furthermore, there was no difference between the THF and non-THF distinction when the maximal degree of conversion (99%) was reached after 90 min at 28 ºC and 30 min at 45 ºC. Due to the high conversion degree (99%), even without THF at 45 ºC, it was reached roughly 30 min. Thus, given the expense of removing a large amount of THF from the reaction mixture at 45 ºC, THF was not required for the transesterification of jatropha oil. With mahua oil, the projected amount of complete conversion was accomplished entirely using THF at 45 ºC. Co-solvents, THF, had resulted in a steady increase in the rate of mahua oil methanolysis. At 28 ºC, the rate constant was increased from 0.08 to 1.17 L^2 mol^{-2} min^{-1}, whereas at 45 ºC, it was increased from 0.43 to 3.18 L^2 mol^{-2} min^{-1}. At 28 ºC, the corresponding values of jatropha oil ranged from 0.50 to 2.76 L^2 mol^{-2} min^{-1}, whereas at 45 ºC, they ranged from 1.26 to 4.56 L^2 mol^{-2} min^{-1}.

Cao *et al*. [39] transesterified soybean oil to supercritical methanol without a catalyst. A co-solvent was added to the reaction mixture to lower the operating temperature, pressure and molar ratio of alcohol-to-vegetable oil. As a co-solvent in the reaction system, propane considerably decreased the harsh conditions necessary for the supercritical reaction. It was observed that the critical points of the binary system were achieved at decreasing temperatures as the molar ratio of propane-to-methanol increased. The optimal reaction temperature decrease considerably when the ratio was exceedingly low as the number of propane increased. On the other hand, the optimal temperature remained constant when the ratio reached a specific number. This suggested a high energy barrier to the transesterification reaction and that the procedure cannot be done without either a high reaction temperature or the presence of a catalyst. The optimal temperature was 280 ºC, if the propane-to-methanol molar ratio was 0.05 or higher. The transesterification process of soybean oil were also performed to assess the influence of a change in the molar ratio of methane-to-oil on the formation of methyl esters at 280 ºC and a constant propane-to-methanol ratio of 0.05. At a reaction temperature of 280 ºC and a methanol-to-oil ratio of 24, 98% of soybean oil was converted to methyl esters in 10 min at a reaction pressure of just 12.8 MPa.

Muppaneni *et al.* [40] investigated the yields of fatty acid ethyl ester produced by non-catalytic transesterification of *Camelina sativa* oil utilizing supercritical ethanol (SCE) as a co-solvent. Due to the simplification of the separation and purification processes, this strategy enabled simultaneous trans-

esterification of triglycerides and ethyl esterification of fatty acids in a shorter reaction time, potentially lowering energy consumption. It was revealed that the co-solvent played a critical role in reducing the severity of the critical operational parameters and enhancing biodiesel production. Hexane was added to the reactant mixture to help in forming a single phase of ethanol and camelina oil and accelerate the reaction rate at supercritical temperatures. It was observed that the uncertain amount of hexane could considerably increase the formation of ethyl ester. The yield of ethyl ester was 44.6% without hexane but increased to 65.33% with 0.05 (v/v) co-solvent-to-oil ratio and 25:1 ethanol-to-oil molar ratio. The maximum yield was obtained at the co-solvent-to-oil ratio of 0.2 (v/v). Hexane was found to be an efficient solvent for vegetable oil, allowing for the formation of a homogeneous phase between the oil and alcohol at lower reaction temperatures and pressures, resulting in increased yield. Additionally, it was revealed that when the hexane-to-ethanol ratio increased, the optimum operating state of supercritical ethanol (SCE) reduced significantly, eventually approaching a constant value of 295 ºC. The experiments were conducted at temperatures ranging from 280 to 350 ºC and with varying molar ratios of co-solvent to ethanol. As a result, the study concluded that hexane had considerable potential as a co-solvent in supercritical alcohol technology.

Peña *et al.* [20] conducted the series of experiments to determine the effect of various variables on the methyl ester concentration, viscosity, acidity and water content of biodiesel made from castor oil. In this context, the study conducted a batch reactor methanolysis of castor oil at 60 ºC to determine the effect of three alkaline catalysts (CH_3ONa, NaOH and KOH) and co-solvent (hexane). It was found that CH_3ONa produced significantly more methyl ester than the other studied catalysts. This was due to a dramatic improvement in the interaction between oil and methanol. As proven, addition of hexane to the castor oil transesterification reaction increased the methyl ester generated. Additionally, the co-solvent kept the methyl ester concentration within the EN14214 standard range. The CH_3ONa sample containing 15% (v/v) hexane contained the highest methyl ester concentration in the range examined. A slight decrease in methyl ester concentration was observed when the hexane concentration was increased above 15% (v/v). This decrease, however, was not considered significant because it was within the error range. However, the phase separation was facilitated by the presence of co-solvent (biodiesel and glycerol). This showed that the glycerol-rich phase split from the free-co-solvent system more rapidly at the critical period. Additionally, when hexane was used as a co-solvent, the soap produced was significantly reduced. The castor oil-based biodiesel had a high viscosity and should be mixed with conventional diesel or low-viscosity biodiesel.

Ambat *et al.* [41] investigated biodiesel synthesis using low-cost feedstocks such as lard oil and waste cooking oil (WCO). The effects of acetone and THF as co-solvent for the transesterification process were studied and found that 5% THF generated the best results. The maximum yields of lard oil methyl ester and WCO biodiesel were 99.7% and 99.4%, respectively, in 45 min at 50 ºC and 60 ºC, using 0.9 wt.% catalyst and 1.0:5.5 oil-to-methanol ratio. The effect of co-solvent on the biodiesel production technique was determined by transesterifying each oil at 40 ºC for 40 min with 0.6 wt.% catalyst and 1:3.5 oil-to-methanol molar ratio in the presence of various weight percentages of acetone and THF. It was determined that samples containing 5% THF produced the maximum FAME when lard and WCO were combined. This indicated that 5% THF was adequate for increasing the solubility of methanol and oil, phase separation of FAME and glycerol and glycerol separation from the reaction mixture.

Le *et al.* [42] pioneered the use of fatty acid methyl esters (FAMEs) as a co-solvent in the transesterification of rubber seed oil with high levels of FFAs for biodiesel generation (35.6 wt.%). The homogeneous system of triolein (oil) and methanol (reagent) was also investigated to evaluate the influence on the transesterification process by employed methyl oleate as a typical co-solvent of FAME. When the FAMEs concentration was greater than 30% by weight, the homogeneous system (FAMEs/triglyceride/methanol) was achieved. The crude RSO produced after esterification was transesterified using 34% concentration of FAMEs as co-solvent. At 40 ºC, the reaction took 30 min to complete. The EN 14214/JIS K2390 requirements were met by biodiesel quality, which included 99.2% FAMEs.

Fu & Vasudevan [43] developed several solvent-co-solvent combinations to optimize enzyme activation and substrate mass transfer during the enzymatic transesterification of canola oil, which was catalyzed by *Candida antarctica* lipase. A hydrophobic solvent and a hydrophilic co-solvent were combined in the solvent-co-solvent combination. Isooctane was chosen as the hydrophobic solvent and six hydrophilic co-solvents (dimethoxyethane, methyl iso-propyl ketone (MIPK), *tert*-butanol, isopropanol, acetone and dioxane) were blended in various ratios with isooctane. The results indicated that by increasing the dispersion of methanol with the co-solvent at low co-solvent concentrations, biodiesel production might be improved. However, increasing the concentration of hydrophilic co-solvent significantly reduced the yield of biodiesel, implying that the hydrophobic solvent's protection of lipase was disrupted, resulting in the enzyme deactivation. It was also observed that the hydrophobicity and hydrophilicity of reaction mediums were polarity dependent.

Sahani *et al*. [44] synthesized biodiesel from a non-edible feedstock using a heterogeneous base catalyst (strontium lanthanum alloy oxide) in a two-step method utilizing DPE (diisopropyl ether) as co-solvent. The alcohol-to-oil molar ratio of 14:1, catalyst dose of 1.5% at 60 ºC alcohol-to-DPE of 1:1 at a stirring rate of 600 rpm for 40 min were identified as ideal conditions for promoting the optimum yields. To investigate the influence of co-solvent on biodiesel yield, various co-solvents *e.g. n*-Hexane, diisopropyl ether, acetone and toluene were utilized to attain the most excellent ester conversion. The DPE was determined to be the most effective co-solvent, owing to its ability to stabilize polar materials (methanol) in mixtures *via* hydrogen bonding and an alkyl group, which was easily incorporated with the oil phase. However, due to its high molecular weight, acetone demonstrated an efficiency comparable

to that of DPE. *n*-Hexane and toluene, which were ineffective and did not operate as co-solvents, lowered the ester's conversion efficiency. This was because oil dissolves in the co-solvent phase, resulting in the reversal reaction in the system upon applying the two co-solvents.

Chumuang & Punsuvon [45] optimized a heterogeneous calcium methoxide ($Ca(OCH_3)_2$) catalyzed transesterification process for the production of biodiesel from waste cooking oil (WCO) utilizing THF as a co-solvent. A quadratic model with an analysis of variance generated from the RSM was proposed to forecast FAME conversion and the model explained 99.43% of the observed variation. The RSM determined that the best conditions were 2.83 wt.% catalyst concentration, 11.6:1 methanol-to-oil molar ratio, 100.14 min reaction time and 8.65% (v/v) THF in methanol. The results indicated that the methanol-to-oil molar ratio and the THF concentration had no significant effect on the FAME conversion. The reaction, however, was impacted by the interaction between the catalyst and THF concentrations. No significant relationship was observed between reaction time, THF and FAME conversion. The production of WCO biodiesel without the use of THF as co-solvent was also investigated and the optimal conditions were determined to be 12:1 methanol-to-oil molar ratio, 3 wt.% $Ca(OCH_3)_2$ catalyst concentration, 180 min reaction time and 65 °C reaction temperature, which resulted in 99.06% FAME conversion and 97% FAME purity. On the other hand, biodiesel production using THF as co-solvent allowed for significant reductions in the methanol-to-oil molar ratio (12:1 to 11.60:1), $Ca(OCH_3)_2$ catalyst concentration (3 to 2.83 wt.%) and reaction time (180 to 100.14 min) while maintaining approximately the exact FAME conversion and purity. THF accelerated the catalyzed reaction by increasing the mixing of methanol, WCO and the $Ca(OCH_3)_2$ catalyst. Thus, the research addressed the issue of phase separation between hydrophilic methanol, hydrophobic oil and a solid catalyst, which was widely acknowledged as a significant challenge when using a heterogeneous catalyst in the production of biodiesel.

Sakthivel *et al*. [46] examined the effects of residence time and the reaction temperature on fatty acid methyl ester production with and without biodiesel as co-solvent. The study was tested batch and continuous transesterification of *Jatropha curcas* oil. The effect of residence time on yield in batch processes was studied with 5, 10 and 15% co-solvent addition. As a result of producing a single phase of reactants by co-solvent, which increased the oil miscibility. The rate of reaction raised with co-solvent concentration, owing to the increased contact surface between reactants and catalyst. Moreover, the reaction rate with co-solvent was substantially larger than without co-solvent. The biodiesel output improved to 8.1, 10.7 and 13.7% with 5, 10 and 15% co-solvent additions. The most excellent yield was obtained with 15% co-solvent. The inclusion of co-solvent increased methyl ester yield compared to co-solvent free procedure. Biodiesel production was increased at all reaction temperatures using co-solvents (5, 10 and 15 wt.%) in a packed bed reactor. Moreover, biodiesel yield increased linearly with temperature, both with and without co-solvent. The best yield was obtained with 15% co-solvent and 240 °C reaction

temperature. This was owing to faster phase separation caused by better miscibility of oil and methanol at temperatures below supercritical stages. The effect of residence time on yield in a continuous process was studied at 240 °C. The most excellent yield was observed at 30 min reaction time and 15% co-solvent addition. After 40 min, the yield somewhat reduces at 240 °C reaction temperature. The output of biodiesel increased initially, then decreased slightly with residence time. This suggested a reversal reaction due to longer residence time. The triglycerides generated from fatty acids reacted with the three hydroxyl groups on glycerol, resulting in water molecule splitting. The yield of fatty acid methyl esters obtained was nearly 20% greater than the co-solvent free method.

Bambase *et al.* [47] evaluated the use of OH-impregnated CaO as heterogeneous catalyst in converting the refined coconut oil to crude biodiesel in the presence of THF as co-solvent. The results indicated that 66.36% conversion to biodiesel could be accomplished in 10 min when a 20% (w/v) NaOH solution was employed during impregnation, followed by 2 h of calcination at 600 °C. The addition of THF as co-solvent further enhanced conversion to 81.70%, which was comparable to the 85.98% obtained when NaOH was used as catalyst under identical reaction conditions. Calculations were used to determine the effect of co-solvent on biodiesel synthesis. The amount of THF required to homogenize a 1: 6 molar ratio of coconut oil-to-methanol was determined that 1.15 mL THF per mL methanol was required to obtain a single-phase mixture or THF molar ratio of 3.45. The homogenization of coconut oil and methanol in the presence of the base catalyst yielded 81.70% biodiesel, comparable to the homogeneous NaOH purity of 85.98%. THF increased coconut oil and methanol miscibility, resulting in a faster reaction rate and increased conversion to biodiesel. The effect of employing OH-impregnated CaO and THF on biodiesel conversion over time was determined using time profiling. After 18 and 24 min, respectively, the percentage of biodiesel reached more than 90% and 96.33%, revealing that the reaction time for homogeneous catalysis might be cut in half. The reduced reaction time may result in a reduction in the cost of biodiesel production.

Hájek *et al*. [48] reported the transesterification of oil using methanol and co-solvents *viz.* ethyl acetate (ETAC), tetrahydrofuran (THF), hexane (HEX), acetone (AC) and diethyl ether (DEE) at the homogeneous base catalyst of KOH and heterogeneous catalysis of mixed oxides. Co-solvents combine oil and methanol into a single phase, accelerating the process. As a result, biodiesel manufacturing will be more environmentally friendly, as less energy will be consumed, enhancing sustainability. The entire binodal curve of ternary plots of oil, methanol and co-solvent was determined to estimate the molar ratio at which the reaction mixture forms a single phase. Because their electric dipole moment is similar to that of methanol, ethyl acetate and tetrahydrofuran have a comparatively limited heterogeneous zone. Tetrahydrofuran had the highest esters content in the ester phase when used as a homogeneous catalyst. The ester content of heterogeneous catalysts was lower with co-solvent than without co-solvent, most likely due to co-solvent dilution of reaction components or co-solvent bonding to the

active sites of catalyst. Ethyl acetate, THF and DEE had a smaller heterogeneous zone than hexane and acetone. The dipole moments of ethyl acetate, THF and DEE are comparable to that of methanol, indicating that these solvents were reasonably miscible, requiring only a little amount of co-solvent to form a single phase. The dipole moments of the co-solvents hexane and acetone are different from those of methanol, which has a smaller single area, implying that a significant amount of co-solvent must be added to the reaction mixture to ensure the homogeneity.

Transesterification with co-solvent addition was investigated utilizing KOH catalyst to optimize the ester content (more than 90 wt.% after 90 min of reaction). Due to the low temperature (25 °C), a complete oil conversion to ester was not possible. The ester phase created by transesterification with the co-solvents ethyl acetate and diethyl ether contained less ester than the ester phase formed in absence of co-solvents (~ 85 wt.%). Acetone and hexane had the lowest ester concentration because they required the greatest co-solvents to convert the combination to a single phase. This resulted in a decrease in the concentration of oil and methanol, which slowed the reaction. Compared to methyl esters produced without co-solvents, the presence of glycerides increased the viscosity of the ester phase (4.9 mm^2 s^{-1}). Transesterification was carried out heterogeneously employing Mg-Al mixed oxides with a molar ratio of Mg-to-Al 4. About 42 wt.% THF, 39.5 wt.% ethyl acetate and diethyl ether and 29.6 wt.% hexane and acetone were all smaller than the value obtained without the co-solvent (72 wt.%). The decline was significantly smaller than that observed with the homogeneous catalysts.

Todorovic *et al.* [49] demonstrated the use of crude biodiesel as a co-solvent in the methanolysis of sunflower oil catalyzed by calcined CaO. The optimal reaction conditions were determined by following a methanol-to-oil molar ratio of 7.1:1, a catalyst concentration of 0.74 mol/L, a reaction temperature of 52 °C and a co-solvent loading of 10 wt.% (based on oil weight). They ensured a maximum esters content of 99.8% over a 1.5 h reaction time, which was close to the reported experimental result of 98.9%. At 50 °C and 60 °C, the transesterification processes in the absence of crude biodiesel indicated an initial induction period which happened due to mass transfer constraints in the three-phase system. However, when crude biodiesel was used as a co-solvent, the FAME level increase continuously throughout the reaction. This was due to the excellent miscibility of the reactants, which facilitated their transport to the active sites of CaO and increased the reaction rate, as previously observed. Increasing the temperature from 50 to 60 °C only marginally improves the reaction, which implied that the FAME content measurement was very reproducible.

Laskar *et al.* [50] demonstrated that at room temperature transesterification of soybean oil to biodiesel utilizing CaO as a heterogeneous catalyst and 20% acetone as co-solvent. The optimal reaction conditions of 20% acetone in oil, a 2 h reaction time, a 3% catalyst loading and a 1: 6 oil-to-methanol molar ratio resulted in the 98% biodiesel generation. The influence of acetone loading and time on biodiesel yield was explored throughout 1 to 2.5 h in the 10 to 25% wt.% range. An increase

in the FAME conversion and an increase in acetone of up to 20% by weight was observed. Initially, the co-solvent was less soluble in methanol and oil, resulting in a low rate of FAME conversion. It was reported that as the acetone concentration increased, the phase separation duration decreased due to decrease in the viscosity of the reaction and the density difference between FAME and glycerol increased. A 1:6 molar ratio of oil to methanol, a catalyst concentration of 3% in 20% acetone and 2 h reaction duration resulted in the FAME conversion of 98%. As acetone was added to the reaction mixture, FAME conversion decreased, attributed to the dilution of the original reactants and the increased time required for FAME and glycerol phase separation. The concentrations of methanol and glycerol in the reaction mixture controlled the time necessary for separation, as collisions between glycerol and methanol are more common at low acetone concentrations, simplifying the separation process. Thus, 20% acetone and 11 h were picked as further transesterification parameters to optimize.

Jiang & Tan [51] used a batch autoclave to transesterify coconut oil with supercritical methanol in the presence of a co-solvent. Co-solvents such as CO_2, propane, *n*-hexane, heptane, cyclohexane, DME, ether and toluene were used to evaluate the influence of co-solvents on the transesterification of coconut oil with supercritical methanol. It was established that independent of the co-solvent utilized, adding co-solvent to the transesterification process increased the miscibility of coconut oil and methanol, meaning that adding a co-solvent could increase the miscibility of coconut oil and methanol. It should be emphasized that all yields were achieved after cleaning the autoclave with 1.5 M oxalic acid solution at 60 °C for 60 min prior to loading the reactants and co-solvent, which served as catalyst. The maximum yield of 77.2% was obtained with heptane as co-solvent, while ether yielded 72%. Both organic co-solvents outperform CO_2 and propane due to their inherent suitability as solvents for coconut oil, which benefits its miscibility in methanol. Although heptane produced the best yield, ether was chosen as co-solvent in this study because its boiling point (34.6 °C) was lower than that of heptane (98 °C) and methanol (64.7 °C), requiring less energy to remove the co-solvent from the methanol during transesterification. Additionally, when ether was used as co-solvent in the transesterification of coconut oil with methanol, stirring speed had no effect on yield when the molar ratios of methanol, coconut oil and ether were maintained constant at 30:1:3 and the temperature and pressure were maintained at 285 °C and 13.1 MPa, respectively. These findings implied that the co-solvent ether increased coconut oil and methanol miscibility, resulting in a nearly homogenous phase during transesterification.

Todorovic *et al.* [52] investigated the homogeneous and heterogeneous base-catalyzed methanolysis of sunflower oil in the absence and presence of co-solvents. Previously, KOH was used as a catalyst and THF as co-solvent and the reaction was carried out at 10 °C and a methanol-to-oil molar ratio of 6:1 was used. In the latter scenario, CaO and a variety of organic solvents such as THF, *n*-hexane, dioxane, ethyl acetate, diethyl ether, triethanolamine, and methyl ethyl ketone were used as solid catalysts and co-solvents, respectively and the reaction

was carried out at 60 ºC with a methanol-to-oil molar ratio of 6:1. The rate of methanolysis of sunflower oil catalyzed by KOH increased as the THF concentration was increased to 50% of the oil mass, which was attributed to self-enhancement of the interfacial area caused by reducing the mean drop size. THF had no effect on the rate of CaO-catalyzed methanolysis at a 20% concentration but slowed the reaction and lowered the yield of fatty acid methyl esters (FAME). Only *n*-hexane and THF accelerated the initial stages of methanolysis. Triethanolamine and ethyl acetate had no effect. However, diethyl ether, dioxane and methyl ethyl ketone slowed the process and reduced the yield of FAME. Compared to the reaction conducted without THF, the methanolysis reaction conducted with THF was exceedingly rapid, requiring only a few minutes at 50% THF concentration. THF and *n*-hexane were added to the reaction solution at 20% concentration, with CaO as solid catalyst and moderately favourable. Triethanolamine and ethyl acetate did not affect the methanolysis reaction, whereas diethyl ether, dioxane and methyl ethyl ketone significantly lowered the yield and rate of FAME production.

Ataya *et al.* [53] conducted the transesterification experiments on canola oil, adjusting the NaOH catalyst concentration (1 and 3 wt.%) in two-phase and single-phase processes. The single-phase was established by introducing a co-solvent. It was postulated that the reaction occurred at the interface of the two phases of two-phase reaction medium. The induction period was affected by agitation, the presence of two phases and the concentration of NaOH catalyst. Two separate regimes have been observed for the single-phase medium: one at short reaction durations related to reaction kinetics and another at longer reaction times that may be related to mass transfer. However, Conversions were much higher in the agitated single-phase system than in the agitated two-phase system during the trials. Because there was no contact between phases in a single phase, there were no limits imposed by interphase mass transfer. These findings were consistent with the assumption that the mass transfer affected the reaction rate when an interface was present. The notion of the "interface reaction" was used to explain why the ratio of monoglyceride to diglyceride yields varied between two-phase and single-phase processes.

Fadhil & Mohammed [54] investigated the influence of co-solvent on the transesterification of bitter almond oil (BAO), an inedible feedstock, with methanol. Hexane and KOH were used as co-solvent and catalyst, respectively. Biodiesel with yields of 97.88 wt.% and 98.50 wt.% ester content was obtained using 0.60 wt.% of KOH, a 5:1 methanol-to-oil molar ratio, a 1:1 hexane-to-methanol volume ratio at 32 ºC for 45 min of the reaction time. Compared to the non-solvent method, adding co-solvent decreased the catalyst concentration, temperature, methanol-to-oil molar ratio and time required to obtain the highest biodiesel yield. The influence of hexane-to-methanol volume ratio on co-solvent methanolysis of BAO was investigated through the experimentation with various hexane-to-methanol volume ratios. The biodiesel yield increased from 87.0 to 94.55% when the volume ratio of hexane-to-methanol was raised from 0.5:1 to 1:1. This could be explained by the fact that greater concentrations of hexane are required to over-

come the mass resistance induced by the poor miscibility of hexane with methanol and other volatiles. However, volume ratios of hexane-to-methanol that were greater than the ideal resulted in a reduction of the biodiesel yield because an excess of hexane dilutes the reactants, reducing the reaction rate. It was found that the addition of high boiling point solvents elevates the boiling point of the entire solution above the boiling point of methanol, allowing for a higher temperature reaction. Except for acetone, transesterification of BAO in the presence of any of the co-solvents examined yielded up to 90%. Hexane produced the most biodiesel (98.50 wt.%) because hexane dissolves oil more completely, resulting in the more homogeneous reaction mixture. As a result, the reaction of transesterification will be hastened.

Encinar *et al.* [19] investigated the rapeseed oil transesterification using a variety of co-solvents (diethyl ether (DEE), dibutyl ether (diBE), *tert*-butyl methyl ether (tBME), diisopropyl ether (diIPE), tetrahydrofuran (THF) and acetone). It was found that except for di-*n*-butyl ether, other co-solvents enabled conversions above 90%. After purification, some biodiesel had a strong co-solvent fragrance. The boiling temperatures are comparable to methanol, tBME, diIPE, THF and acetone can be removed together but not reused. DEE has a lower boiling point than methanol, allowing faster elimination and reuse. The immiscibility of oil and methanol lowered oil conversion, but excessive co-solvent addition reduced the transesterification rate due to a dilution effect on the reagents. In any case, the test results are not statistically significant. Addition of co-solvent (DEE) was increased conversion value and benefit in the early stages of growth (30 min).

Hsiao *et al.* [55] used acidic and alkaline catalysts to increase biodiesel output from the waste cooking oil to a two-stage catalytic reaction. To make a single-phase solution, THF as co-solvent was added to a mixture of vegetable oil and methanol. The entire device was placed in a microwave oven to speed up the biodiesel transesterification reaction. The first stage reaction took 7.5 min using a 9:1 methanol-to-oil molar ratio, 1% catalyst and a reaction temperature of 60 ºC. The second step used a 12:1 methanol-to-oil molar ratio, 1% catalyst loading, a reaction temperature of 60 ºC and a reaction time of 1.5 min. After 9 min, the biodiesel conversion rate was 97.38%, exceeding the EU EN14214 standard of 96.5%. The acid value declined somewhat after 2.5 min, from 4.36 mg KOH/g to 4.19 mg KOH/g. This was the reaction only occurred when the two immiscible phases interacted. However, when THF was introduced, methanol and waste cooking oil were efficiently mixed and reacted well. As a result, the acid value dropped faster during this time, from 4.36 mg KOH/g after 2.5 min to 2.22 mg KOH/g after 2.5 min and then to 0.96 mg KOH/g after 12.5 min. As the process progressed, the concentration of free fatty acids decreased, resulting in a fall in acid value over time.

Ehimen *et al.* [56] investigated the conversion of microalgae lipids to biodiesel using an *in situ* transesterification method resulted in increased alkyl ester conversions compared to the conventional two-stage oil extraction and transesterification process. To further increase the viability of *in situ* approach, this research analyzed improvements that would minimize the

process's substantial methanol consumption while potentially improving oil to methyl esters conversion and biodiesel yields. The results indicated that using ultrasound agitation for the *in situ* process and combining it with co-solvents (*n*-pentane and diethyl ether) considerably increased the conversion of chlorella oil to methyl esters while consuming less methanol. In comparison to *n*-pentane, using diethyl ether as *in situ* transesterification co-solvent increased the mass content of FAME in biodiesel for all methanol-to-oil molar ratios and reaction times. After 8 h reaction time, the most significant oil to FAME conversion of 79.9 ± 7.1 wt.% was obtained using methanol-to-oil ratio of 79:1 with diethyl ether as co-solvent. This result was comparable to the percentage mass FAME conversion of 77.8 ± 7.7 wt.% observed *in situ* employing a methanol-to-oil reacting molar ratio of 105:1. The use of diethyl ether co-solvent level and its integration into the *in situ* transesterification process resulted in a reduction in the amount of methanol required without impairing FAME conversion. The yields of microalgae-derived biodiesel and FAME in mechanically agitated *in situ* processes using co-solvents and lowered reacting methanol molar ratios were much lower than those achieved using methanol alone. It was discovered that using ultrasound and co-solvents, FAME yields from the *in situ* transesterification process could be enhanced by 15-17% compared to using methanol and acidic catalysts alone, with a reduction in the reacting methanol-to-oil molar ratios from 315:1 to 79:1.

Sawangkeaw *et al*. [57] investigated the transesterification of vegetable oil in supercritical methanol in a batch reactor and discovered a non-saponified product with a high methyl esters concentration and a high glycerol purity. The high viscosity of vegetable oil may cause flow system difficulties in the continuous reactor. THF and hexane were chosen as co-solvents in this investigation to lower the viscosity of the vegetable oil. The GC-MS chromatograms of mixed methyl esters standard and biodiesel products were obtained over a 10 min reaction time using THF at 350 ºC, a 42 methanol-to-vegetable oil molar ratio and a 5 THF-to-vegetable oil molar ratio to ensure that no reaction occurred between the co-solvent and other reactants. The composition of biodiesel produced utilizing the THF approach was nearly identical to the benchmark mixed fatty acid methyl esters. No THF or hexane peaks were detected in the chromatogram of biodiesel produced using the THF technique in 250 mL reactor for 10 min using crude palm kernel oil as reactant. As a result, the transesterification reaction was unaffected by co-solvents. The Redlich-Kwong equation of state and Lorentz-Berthelot-type mixing rules were used to compute the amount of methanol, co-solvent and vegetable oil at a given pressure using the critical properties of crude palm kernel oil, methanol, *n*-hexane and THF as parameters. Additionally, neither the addition nor the removal of co-solvent affected the methyl esters level.

Felícia *et al*. [58] applied chicken fat as feedstock in transesterification with co-solvent to produce biodiesel. The reaction of chicken fat with diethyl ether as co-solvent and NaOH as a catalyst was used. The influence of diethyl ether-to-methanol volume ratio on biodiesel yield was investigated in this study through a series of tests. Biodiesel output tended to decrease as more diethyl ether was utilized. The best biodiesel yield was obtained when diethyl ether-to-methanol ratio was 0.55:1. However, due to the dilution effect of reactants, excessive addition of diethyl ether in this study resulted in a decrease in biodiesel yield.

Gargari & Sadrameli [59] investigated the single-phase transesterification of linseed oil using a heterogeneous base catalyst (CaO) and hydrogel as water absorber. Co-solvents including diethyl ether (DEE), tetrahydrofuran, biodiesel and *n*-hexane were employed to improve the oil-methanol solubility. T-tests and F-tests indicated a substantial change in the transesterification results with and without co-solvent. Process parameters were optimized utilizing response surface methods. In order to achieve the highest FAME yield of 98.77%, the following conditions were used: methanol-to-oil ratio 9.41:1, DEE-to-methanol ratio 1.11:1, catalyst concentration 0.98 wt.%, temperature of 30 ºC, agitation rate of 650 rpm and reaction time of 60 min. A reasonable volume of co-solvent was shown to improve biodiesel output, but a large volume lowered yield. This work investigated co-solvents such as DEE, THF, *n*-hexane and biodiesel. DEE outperformed the other co-solvents therefore, it was used in the reaction. Using more DEE made manufacturing unprofitable. A lower concentration of catalyst reduces the efficacy of parameters. The co-solvent decreased reaction time and methanol usage in this study, resulting in lower costs. The molar ratio of DEE-to-methanol was varied from 0.5 to 2.0, with 1.11 being the best. Under ideal conditions, DEE, THF, biodiesel and *n*-hexane were investigated as co-solvents. Due to its polarity, DEE had the highest performance and may increase FAME yield up to 98.77%. Economically, biodiesel was a good co-solvent choice, but it did not considerably increase biodiesel output.

Çaglar [11] developed a one-phase technique using a mixing solvent such as tetrahydrofuran. As a result, complete conversion up to 99.89 wt.% can be accomplished within 10 min. The tests were conducted to ascertain the optimal operating conditions for this solvent. The findings would result in lower capital and operating expenses for biodiesel manufacturing. The first experiment used the molar ratio of oil-to-methanol-to-THF of 1:1:1. At 3, 5, 10 and 20 min, samples were obtained from the mixture. The reaction was so rapid that equilibrium was attained in less than 5 min, allowing for nearly complete conversion of tri- and di-glycerides. For reaction times of 3, 5, 10 and 20 min, 95.72% methyl ester yields were obtained. After 20 min, the reaction medium contained approximately 0.8% monoglycerides. The optimal THF concentration for homogeneous one-phase reaction mixtures was determined utilizing a range of THF values. The oil-to-THF volume ratios studied were 1:0.5 and 1: 0.25. The combination was sampled after 5 and 10 min. The only modification was to the THF volume ratio. When the volume ratio of oil-to-THF was 1: 0.25, the methyl ester conversion increase from 85.25 to 96.76% min for 5 and 10 min. When the reaction time was raised to 10 min, the conversion of mono-, di-, tri- and free glycerol was significantly decreased. However, the methyl ester conversion was higher when the volume ratios of oil to THF were 1:0.5 rather than 1: 0.15. Oil-to-THF volume ratios of 1:0.5 resulted in the highest methyl ester conversion of 99.89%.

Han *et al.* [60] transesterified soybean oil in supercritical methanol without catalyst. The addition of co-solvent decreased the reaction's temperature, pressure and molar ratio of alcohol to vegetable oil. By including CO_2 as co-solvent in the reaction system, the harshness of the reaction conditions was significantly reduced. At a reaction pressure of 14.3 MPa, a reaction temperature of 280 ºC, a methanol-to-oil ratio of 24 and a CO_2-to-methanol ratio of 0.1 resulted in 98% yield of methyl esters in 10 min. Additionally, the manufacturing process was environmentally beneficial. In comparison to methanol, CO_2 has a critical point of 31.0 8 ºC (Tc) and a pressure of 7.28 MPa (Pc). The critical points of the binary system were discovered to be at lower temperatures as the CO_2-to-methanol molar ratio increased. While increasing the CO_2-to-methanol molar ratio decreased the system's critical point, it did not affect the supercritical process's ideal temperature. When the molar ratio was low, the optimum reaction temperature fell as CO_2 concentration increased. Nonetheless, until the ratio reaches a specific value, the ideal temperature remains constant. A kinetic analysis revealed that adding the co-solvent to the supercritical system boosted the rate constant of the transesterification reaction. At 28 ºC, utilizing supercritical methanol and CO_2, soybean oil was transesterified to methyl esters without the use of catalyst. Methanol-to-oil and CO_2-to-methanol molar ratios were 24 and 0.01 in both cases. The GC analysis indicated that approximately 98% of the triglycerides were converted to methyl esters in less than 10 min.

Lam & Lee [61] explored using biodiesel as co-solvent in $SO_4^{2-}/SnO_2–SiO_2$ catalyzed transesterification process (solid acid catalyst). It was discovered that using biodiesel as a co-solvent resulted in a high FAME yield of 88.2% (nearly 30% higher than without co-solvent) in a shorter reaction time (1.5 h). Using biodiesel as a co-solvent helped speed up the conversion of waste cooking oil to biodiesel. The yield of biodiesel was generated by varying the amount of co-solvent utilized in two ways. (i) The catalyst was submerged in co-solvent for 2 h and filtered and (ii) the co-solvent was agitated for 2 h with both immiscible reactants. Using the correct amount of co-solvent, the yield of FAME increases from 59.9 to 80.3%. The solubility of biodiesel in both oil and methanol enhanced triglyceride (oil) dispersion in the methanol phase, thereby improving reactant molecule accessibility and diffusion to the catalyst-active sites. When a large quantity of co-solvent was added to the reaction mixture, the FAME yield decreased. As a result, a large amount of co-solvent in the first reaction mixture (which contains biodiesel) retarded transesterification, reducing the FAME yield. The quantity of co-solvent used in the first method did not affect FAME yield, save for a slight increase when the co-solvent-to-oil ratio was increased to 0.5. This unexpected outcome was attributed to the inadequate contact time of the catalyst in the co-solvent (2 h).

A study was conducted to identify the optimal period for co-solvent to be adsorbed entirely inside the pores of catalyst (case 1) or fully soluble in the reactants (case 2) to maximize FAME production. The soak/stir time was ranged from 1 to 10 h. Surprisingly, increasing the co-solvent contact time with the catalyst (before transesterification) boosted FAME yield

from 51.2% to 88.2% (contact time 10 h) (contact time of 1 h). Depleted co-solvent pores enabled the faster transesterification reaction, if co-solvent and catalyst contact time were long enough. As noted earlier, co-solvent (biodiesel) enhanced oil-methanol miscibility. The catalyst pores can then be filled with co-solvent, allowing more accessible access to the active sites for triglycerides and methanol molecules. Furthermore, the quantity of co-solvent did not affect the FAME yield when the immersion duration between catalyst and co-solvent was set at 2 h. As the contact duration between the catalyst and co-solvent was kept at 10 h, as increasing it would not benefit the industry. However, an entirely different outcome was achieved when the co-solvent was initially mixed with the reactants. After 3 h of co-solvent interaction with the reactants, the FAME generation was reduced. The high quantity of free fatty acids (FFA) in waste cooking oil likely accelerates co-solvent breakdown. If the co-solvent (biodiesel) and the high FFA oil are not in touch for an extended period, the FAME will become unstable and produce an acidic and viscous mixture. Adding biodiesel as a co-solvent to the reactants and stirring for a long time did not increase the transesterification rate but decreased yield.

In contrast, at higher reaction temperatures (> 100 ºC), the presence of co-solvent increased FAME yield, especially when the catalyst was immersed in it. The FAME yield was 88.2% when the co-solvent was mixed with the catalyst and 80.33% with the reactants. As a result, the role of co-solvents in accelerating heterogeneous transesterification was proven. The methanol-to-oil molar ratio affected FAME production. Initially, higher methanol-to-oil molar ratios increased FAME production up to approximately 15. The yield dropped when the methanol-to-oil molar ratio was raised. Decreased FAME yield with reaction, increasing the reaction time from 0.5 to 3 h increased FAME production. After 1.5 h, when the co-solvent was added to the catalyst, the yield of FAME (88.2%) did not rise appreciably, suggesting that reaction equilibrium had been established. Apart from that, using co-solvent initially took 2.5 h to reach equilibrium, whereas without using co-solvent took 3 h. This data clearly shows that adding a co-solvent increases FAME yield while decreasing reaction time.

Tan *et al.* [62] synthesized biodiesel from palm oil using the non-catalytic supercritical methanol (SCM) method. The use of co-solvent to reduce the number of operating conditions required in SCM was studied. The findings suggested that non-polar solvents, such as heptane can reduce the reaction temperature. When heptane was employed as co-solvent, a substantially greater yield of biodiesel may be produced at a lower temperature (360 ºC) without co-solvent with an 80% yield. However, at lower temperatures and pressures of 280 ºC and 15 MPa, a considerable amount of 66% could be produced when a small amount of 0.2 molar ratio of heptane-to-methanol was applied. The optimum working state of SCM falls significantly as the molar ratio of heptane-to-methanol rose until it approached a constant temperature of 280 ºC. Consequently, it was reasonable to conclude that heptane had a lot of promise in supercritical alcohol technology as co-solvent.

Trentin *et al.* [63] investigated the production of fatty acid ethyl esters (FAEE) from continuous catalyst-free transesteri-

fication of soybean oil in supercritical ethanol with CO_2 as co-solvent. The experiments were conducted in a microtube reactor at temperatures ranging from 523 to 598 K, pressures ranging from 10 to 20 MPa and oil-to-ethanol molar ratios ranging from 1:20 to 1:40 co-solvent-to-substrate mass ratios ranging from 0.05:1 to 0.2:1. As the amount of CO_2 supplied to the system grew, the yield of ethyl esters increased. Effective reaction yields were achieved at 598 K, 20 MPa, a 1:20 oil-to-ethanol molar ratio and a CO_2-to-substrate mass ratio of 0.2:1. The influence of changing the co-solvent, CO_2-to-substrate mass ratio from 0.05:1 to 0.20:1 on FAEE yield was studied. The greatest FAEE yields were found with a co-solvent-to-substrate mass ratio of 0.2:1. At 598 K and 0.8 mL/min, co-solvent-to-substrate mass ratios of 0.05:1, 0.1:1 and 0.2:1 provide 60%, 61% and 78% FAEE yield, respectively. At 523 K and a co-solvent-to-substrate mass ratio of 0.2:1, yields of 26% were obtained, whereas, at 598 K, yields of the order of 78% were produced.

Yin *et al*. [64] tested the supercritical and subcritical methanol biodiesel synthesis from soybean oil in 250 mL high-pressure tank. The most significant methyl ester synthesis was achieved at a 42:1 methanol-to-oil molar ratio and reaction temperatures ranging from 260 ℃ to 350 ℃. A co-solvents (hexane, carbon dioxide, KOH) was added to the reactants to reduce the operating temperature and pressure and improve methanol conversion efficiency. The findings showed that adding hexane or CO_2 enhanced the methyl ester synthesis. Using CO_2 or hexane as a co-solvent in the reaction system at 300 ℃ improved the yield of methyl esters. A 98% yield of methyl esters was obtained in 20 min at 160 ℃ with a methanol-to-oil ratio of 24 for KOH. Addition of hexane to the mixture may help with conversion. Hexane, 2.5 wt.%, increased the methyl ester production from 67.70 to 85.55%. The most significant yield was over 67.7% when the quantity of hexane was increased. The addition of hexane increased the mutual solubility of methanol and soybean oil, which accelerated the process. On achieves 90.6% methyl ester production in 30 min at 300 ℃, 0.2 CO_2-to-methanol ratios and 42 methanol-to-oil ratios. CO_2 was also easily added and removed by depressurization.

The presence of KOH as co-solvent can affects methyl ester production. The molar alcohol-to-oil was 24:1 at various temperatures (120-240 ℃). The KOH-to-oil mass ratio ranged from 0 to 0.25 wt.%. A small yield (less than 5%) was obtained without a catalyst under subcritical conditions. Adding KOH to the reaction mixture increased the methyl ester yield significantly. The reaction yielded 98% methyl ester when KOH mass ratio was 0.1% and the reaction temperature was 160 ℃. The system pressure at this temperature, which should be subcritical, was just 10 MPa. The reaction temperature was lowered from 350 ℃ to 160 ℃ to get the exact yield as supercritical methanol. Unlike the alkali catalysis technique (ACM), the subcritical methanol utilized 10% of the ACM's catalyst. Catalysis at subcritical circumstances reduces the catalyst quantity while lowering the operating conditions.

Najafabadi *et al*. [65] used supercritical methanol to convert wet algal biomass into biodiesel directly. Microalgal lipids were extracted and converted to biodiesel simultaneously under high pressure and temperature conditions without the need for a catalyst. The most significant outcomes were observed when an 8:1 methanol-to-wet biomass ratio was used. The effect of numerous co-solvents on improving the efficiency of the super-critical process was investigated. Compared to wet biomass, hexane was shown to be the most efficient co-solvent with a 6:1 ratio. According to the findings, the direct conversion approach yielded somewhat more fatty acid methyl esters (FAMEs) than the usual extraction plus transesterification reaction. Several co-solvents were used to test the efficacy of direct supercritical transesterification. The co-solvent-to-biomass ratio was investigated at three levels: 4:1, 6:1 and 8:1. The addition of diethyl ether in a 4:1 ratio resulted in a crude extraction yield of 15.98 ± 1.93% (control). The extraction yield increased to 18.26 ± 1.23% using a 6:1 ratio. By raising the diethyl ether-to-biomass ratio to 8:1, the extraction efficiency was enhanced to 19.49 ± 1.05%. The yield of FAMEs was improved by adding diethyl ether in a 4:1 ratio, which was then increased to an 8:1 ratio, similar to crude extraction. Compared to the control, utilizing diethyl ether as co-solvent considerably enhanced FAMEs yield in all ratios. The crude extraction yield was raised to 20.79 ± 1.01% with a 6:1 hexane ratio, much higher than the control. When the hexane ratio was increased to 8:1, the result was 20.95 0.76, similar to the previous ratio. The FAMEs yield, like the crude extraction yield, exhibits a significant difference in all ratios compared to the control. Chloroform, unlike the other co-solvents, lowered extraction yield. When chloroform-to-biomass ratio was 4:1, it was significantly lower than the control at 12.20 ± 1.89%. With rising, the yields of crude extraction and FAMEs dropped. As a result, chloroform was ruled out as a viable co-solvent for boosting methanol transesterification. When hexane and diethyl ether were utilized as co-solvents, hexane performs somewhat better in improving the direct-supercritical conversion process efficiency. The most efficient and cost-effective ratio was chosen because raising the hexane/biomass ratio did not improve efficiency. Because the critical temperature and pressure of diethyl ether are lower than hexane, it has a more significant impact on diminishing the combination's critical characteristics. As a result, the severity of the reaction was greater. In contrast, hexane was more successful at dissolving lipids.

Mahangani *et al*. [66] utilized ZnO/TiO_2 catalysts to make biodiesel from waste vegetable oil and studied the effects of co-solvent (hexane), reaction temperature and time on the conversion. The technique of making biodiesel from waste vegetable oil using TiO_2-supported ZnO catalyst was studied with and without hexane as co-solvent. It was identified that the temperature and response time impacted waste vegetable oil conversion. After 15 min at 200 ℃ using hexane as co-solvent, the highest conversion was 99.1%. Using hexane as a co-solvent enhanced oil conversion at lower temperatures but had little effect at higher temperatures. Waste oil to biodiesel conversion time at 150 ℃ and 200 ℃ with and without a co-solvent (hexane) was investigated. In the absence of co-solvent, waste vegetable oil conversion increased with reaction time at 150 ℃. After 15, 30, 45 and 60 min of response, conversions were 65.5, 70.3, 83.3 and 97.9%, respectively. With hexane as co-solvent, the

waste oil conversion rose with reaction time, reaching 92.9% after 30 min. However, it was reported that increased reaction time was further 30 min and reduced conversion due to side reactions like glycerolysis. When side reactions influenced the co-solvent run, the reaction with hexane exhibited higher waste oil conversions than the reaction without co-solvent for up to 45 min. The enhanced mass transfer in the reaction medium due to the co-solvents inclusion can explain the increased oil conversion with hexane. The reaction temperature was increased to 200 °C, increasing waste oil conversion. After 15 min of reaction without or with hexane, 95.9% and 99.1% conversions were recorded, compared to 65.5% and 86.4% at 150 °C. Longer reaction times were unnecessary at 200 °C when conversions near 100% were achieved in 15 min. Raising the reaction temperature reduced oil viscosity and sped up the process. The co-solvent effect of hexane decreased as the reaction temperature rose. The use of hexane as a co-solvent in waste oil conversions was comparable to that without hexane. The improvement in reaction rate was explained by a decrease in the reacting medium's viscosity. The reaction appeared mass transfer-controlled at lower temperatures and a co-solvent improves waste oil conversion. Mass transfer limitations seemed to be reduced at high temperatures and adding a co-solvent did not affect the waste oil conversion process. It was recorded that using hexane as co-solvent in the conversion of waste vegetable oil to biodiesel significantly influenced the oil conversion only when the mass transfer was controlled.

Fadhil *et al*. [67] transesterified radish oil (RO) with co-solvents (*n*-hexane, petroleum ether, cyclohexane, diethyl ether and acetone) at room temperature (32 °C). Under the optimal conditions, the yields of methylic, ethylic and mixed methylic/ethylic biodiesels were 97.55 ± 2.0%, 97.33 ± 2.0% and 97.0 ± 1.0%, respectively. The co-solvent alcoholysis method resulted in the isolation of high-quality and yielded biodiesels from the radish oil. Hexane was shown to be the best co-solvent for the alcoholysis process of radish oil followed by petroleum ether. Because of their lower molecular masses, acetone and DEE had lower biodiesel yields than petroleum ether and hexane. The alcoholysis reaction of radish oil was studied using different co-solvent-to-alcohol volume ratios (0.5:1-2.5:1 co-solvent-to-alcohol (v/v)%. According to the data, the biodiesel yield increased as the co-solvent-to-alcohol ratio increased. This success was since when the ratio of co-solvent to alcohol increases, the oil viscosity decreases, resulting in increased oil solubility and consequent mass transfer. Nonetheless, the optimum co-solvent-to-alcohol ratio was 1:1, since this resulted in the highest biodiesel yields, whereas a higher co-solvent resulted in reactant dilution, decreasing the biodiesel result.

Fadhil *et al*. [68] used an alkali-catalyzed transesterification process in the presence of ethanol and co-solvent to produce fatty acid ethyl ester (FAEE) from chicken waste oil using hexane as co-solvent. At 0.75 wt.% KOH, an ethanol-to-blend molar ratio of 8:1, a hexane-to-ethanol volume ratio of 1.5:1, a temperature of 60 °C and a reaction period of 60 min, the best yield of FAEE (96.94-96.78 wt.% ester content) was obtained. When compared to FAEE made without a co-solvent, the inclusion of co-solvent boosted the yield and improved the

characteristics of FAEE. Using molar ratios of 3:1-10:1, the effect of the ethanol-to-blend molar ratio was examined. When the ethanol molar ratio was increased, the yield of FAEE increased. At an ethanol-to-blend molar ratio of 8:1, the highest yield of FAEE (92.41-91.89% ester concentration) was observed. The use of an emulsion boosted the yield while lowering the costs of production. Throughout the ethanolysis of the combination, six different hexane-to-ethanol volume ratios were tested. As the hexane-to-ethanol ratio was increased, the yield of FAEE was also increased. Using 1.5:1.0 hexane-to-ethanol volume ratio, the maximum yield of FAEE (94.82-94.10%) was produced. Due to reagent dilution, increased hexane-to-ethanol ratios resulted in lower FAEE production. The following experiments were carried out with a 1.5:1 hexane-to-ethanol ratio. The waste mixture was co-solvent ethanolyzed at 40-78 °C. The conver-sion rate rose when the reaction temperature was raised. At 60 °C, well below the ethanol boiling point, the maximum FAEE production (96.94-96.78% ester concentration) was produced. This was due to the presence of co-solvent, which increased ethanol miscibility and, as a result, mass transfer. As a result, ester production increases. The mixture was exposed to co-solvent ethanolysis at intervals of 15 to 90 min. The yield of FAEE increased with reaction time and 60 min was shown to be the ideal period. The most FAEE was produced by hexane (96.94% ester concentration). Hexane can be dissolved in ethanol since its boiling point is nearly same that of ethanol. FAEE concentration was lowest in acetone and diethyl ether. The reaction temperature was higher than the boiling point of the solvents. Evaporation removes a portion of them as a result, lowering production.

Saeed *et al*. [69] synthesized biodiesel using milk thistle seeds oil (MTSO) as esterification-transesterification precursor in the presence of hexane as co-solvent. The high acid value of extracted oil (11.90 mg KOH/g) favoured pre-esterification in the presence of hexane. The esterified oil was processed with methanol using hexane as a co-solvent to create methylic biodiesel and methylic/ethylic biodiesel. The best reaction conditions resulted in the methylic biodiesel concentration of 96.23% and a methylic/ethylic biodiesel concentration of 95.63%. Pre-esterification was required to bring MTSO's acid value (11.9 mg KOH/g) within the response limits. The addition of HCl decreased the acid value of parent MTSO. Co-solvent esterification decreased the acid value by 0.75%, but non-solvent esterification increased by 1.25%. The effectiveness of MTSO esterification increased with co-solvent in the reaction medium. The most significant decrease in acid value was seen at a ratio of 1.5:1 hexane-to-methanol and decreasing the conversion efficiency as co-solvent concentrations increased. Methanol-to-MTSO molar ratios improved conversion. As the esterification temperature increased, the acid value of parent MTSO decreased. The co-solvent technique resulted in a decrease in the acid value of pure MTSO (60 °C). The conversion was unaffected by increasing the esterification temperature. The temperature increase may result in the evaporation of methanol and co-solvents. These were conducted in various solvents and across a range of periods. For both methods, increasing the esterification period increased the acid value of MTSO. The

co-solvent technique required less time due to the increased conversion rate (60 min). Additionally, the co-solvent assisted in the dissolution of the FFA in the methanol/HCl solution, resulting in a more homogeneous solution. The properties of the parent MTSO were likewise improved during co-solvent esterification, showing that FFA was converted to FAME. The improved properties were substantiated by reducing the parent MTSO's mean molecular weight. After reducing the acid value of the original MTSO, it was transesterified optimally using methanol or a methanol-to-ethanol mixture.

Kirubakaran and Selvan [70] synthesized biodiesel from waste chicken fat using a nano-eggshell heterogeneous catalyst and isopropyl ether as co-solvent and investigated the effect of transesterification factors on biodiesel yield. The practical value of the methyl ester yielded obtained by RSM was identical to the experimental value (98.1%), indicating that the model is statistically significant at the 97% confidence level. The trials were done twice under ideal conditions, utilizing Design expert software and a point prediction tool and resulted in a 97.2% biodiesel output. According to the studies, adding isopropyl ether increased biodiesel output while decreasing reaction time from 4 to 1.5 h. Consequently, isopropyl ether-assisted transesterification method enhances the reaction by increasing the mixing efficiency and mass transfer between the catalyst, methanol and chicken oil. Concentrations of co-solvents varied from 0.5 to 1 wt.%. Without the co-solvent, only 90.4% biodiesel could be generated.

Djokic-Stojanovic et al. [71] used triethanolamine (TEOA) as an effective "green" co-solvent in the CaO catalyzed ethanolysis of sunflower oil to produce biodiesel. The reaction temperature (61.6-78.4 °C), the ethanol-to-oil molar ratio (7:1-17:1) and co-solvent loading (3-36 wt.%) were all optimized utilizing a rotatable central composite design (RCCD) and response surface approach in a batch stirred reactor (RSM). The optimal reaction conditions were discovered to be a 9:1 molar ratio of ethanol-to-oil, a reaction temperature of 75 °C and a 30 wt.% co-solvent loading to oil yielding predicted and actual fatty acid ethyl ester (FAEE) contents of 98.8% and 97.9 ± 1.3%, respectively, after only 20 min of reaction. To obtain substantial FAEE concentrations, researchers used expired sunflower oil, hemp-seed oil and waste lard. Due to the mass transfer constraints imposed by the three-phase system, the reaction rate of CaO-based catalysts was reduced, particularly during the early stages of the reaction. Generally, the ethanolysis of sunflower oil by CaO calcination takes a long time. The eventual phase separation of the reaction mixture took more than a day to accomplish. Due to the presence of TEOA, the FAEE content has risen since the response began. After only 20 min, the FAEE content had increased to 79.3 ± 6.5%, much higher than the value obtained without TEOA (2.3 ± 1.6%). TEOA alone had no catalytic effect since the FAEE concentration was low after 6 h (0.5%). TEOA improved the reaction rate and yield of FAEE by reducing the viscosity of the reaction mixture due to the reactants' improved mutual miscibility in the early stages of the reaction. Additionally, hydrophilic TEOA reacted favourably with ethanol and entered CaO pores more quickly, facilitating the diffusion of oil and ethanol to the catalyst active sites

and accelerating the reaction rate. To raise the concentration of FAEE and shift the equilibrium to the right, TEOA can be combined with glycerol to form a deep eutectic solvent (byproduct). Due to the TEOA's strong water affinity may be challenging to get sufficient water for triacylglycerol hydrolysis and soap formation. Additionally, the esters acted as co-solvents, enhancing the miscibility of the reactants.

Rahimi et al. [72] investigated the conversion of soybean oil to fatty acid methyl ester (FAME) using various four-way micromixers. Hexane was introduced into the reaction system as co-solvent to enhance mass transfer. The optimal transesterification combinations for achieving a projected maximum FAME of 97.67% were identified. In this study, the residence time was decreased by 3-15 s, which was not accomplished in earlier efforts. The ideal volume ratio of co-solvent-to-methanol for this research was 0.4, resulting in the 88% FAME concentration. Additionally, increasing the ratio resulted in a decrease in the FAME content. This is most likely owing to the reactants being diluted.

The effect of hexane on biodiesel synthesis was first shown using a batch reactor. The reaction was carried out at 57.2 °C with a 3 oil-to-methanol volumetric ratio. The higher FAME content was produced quicker utilizing co-solvent. The transesterification reactions were carried out in both microreactors and batch reactors to show the benefits of using microscale continuous reactors. At 57.2 °C reaction temperature, 0.45 hexane-to-methanol volumetric ratio and 3 oil-to-methanol volumetric ratios, the microreactor with E1 mixer produced 98.8% FAME content in 9.05 sec. The reaction generated an 84% FAME concentration in the microtube reactor without co-solvent. The use of microreactor technology eliminated the need for a mass transfer-controlled regime. Microreactors' short diffusion lengths allowed reactant molecules to diffuse quickly over the reaction interface. The study was an effort to reduce residence time to seconds (3-15 s).

Jinsii et al. [73] explored another route for the biodiesel production from cottonseed oil with ethanol utilizing THF as co-solvent. The finding indicates that triglycerides and ethanol may easily dissolve in a reaction mixture containing THF. After l.5 h, the maximum conversion of 88.73% was recorded with an ethanol-to-oil ratio of 14:1, a reaction temperature of 78 °C, a KOH concentration of 0.25 wt.% and a THF-to-oil ratio of 1:1. Conversion increased rapily as the ratio of THF-to-cottonseed oil increased. However, conversion reduced significantly when the ratio of THF-to-cottonseed oil surpassed 0.75:1. The greatest conversion rate of 85.92% was found when THF was used in a ratio of 0.75:1 with cottonseed oil. KOH was present in the combination at a concentration of just 0.25 wt.%. However, the trial revealed a high conversion rate. THF was shown to speed the transesterification reaction and enhanced triglyceride conversion in the test.

Akkarawatkhoosith et al. [74] presented a straightforward process that results in high biodiesel production and quality. As raw materials, palm oil and ethanol were employed while ethyl acetate was used as a co-solvent to increase biodiesel synthesis in a microtube under supercritical conditions. The interaction between the ethyl acetate-to-oil mass ratio was

determined to be insignificant. The biodiesel had a good quality and yield due to the short residence time and ethanol-to-oil molar ratio requirements. With the reactive co-solvent (ethyl acetate, 55 wt.%), the synergistic impact of ethanol and ethyl acetate on the FAEE% was studied (either ethanol or ethyl acetate). At 350 ℃ and 4 min, addition of reactive co-solvent yielded 75.3% FAEE, whereas ethanol and ethyl acetate yielded 55.6% and 49.4% FAEE, respectively. For ethanol, ethyl acetate and ethanol-ethyl acetate combination, the percent FAEE was 97.2, 83.9 and 99%, respectively, at 375 ℃ and 6 min. Using ethanol or an ethanol-ethyl acetate combination with a long residence time (6 min) and high reaction temperature (375 ℃) may produce a 96.5% biodiesel content. More FAEE was obtained with the same solvent type, higher reaction temperature and longer residence time. Thus, employing reactive co-solvent had a beneficial synergistic impact. The effect of reactive co-solvent and other variables on FAEE was investigated. It was concluded that the interaction effect was statistically negligible (P-value > 0.05). At low and high ethanol-to-oil molar ratio, the reactive co-solvent addition did not affect the % FAEE. The addition of reactive co-solvent at high temperature enhanced the FAEE % at low temperatures.

Escobar *et al.* [75] used co-solvent-assisted transesterification reaction to accelerate the synthesis of biodiesel from *Jatropha curcas* oil. The synthesis of methyl ester using NaOH as catalyst and hexane as co-solvent was optimized in four process variables. Using the minimum methyl ester purity of 96.5% as a criterion, the optimal volumetric ratio of co-solvent-to-methanol was 2:5. When performed at ambient temperatures (25-30 ℃), the required minimum methyl ester purity of 96.5% can be achieved in approximately 10 min; when performed at a temperature (60 ℃) near the boiling points of hexane and methanol, the required minimum methyl ester purity can be achieved in approximately 7 min.

Experiments without hexane were also conducted to investigate the effect of hexane on the transesterification of *J. curcas* oil. During a 60 min monitoring period, reactions without a co-solvent result in low methyl ester concentrations and an abundance of unwanted species in the ester phase. With chemicals, globules (probably methanol) developed, which stayed in the oil despite intense spinning. The study was that adding hexane to the reaction mixture improved methyl ester purity. After 10 min, reactions with hexane as co-solvent produced over 90% methyl ester. The results also showed that the amount of co-solvent used enhanced the purity of methyl ester in the ester phase. After roughly 20 min of reaction at high co-solvent-to-methanol volumetric ratio, methyl ester purity was 96.5%. This finding was expected because hexane helped produce a pseudo-homogeneous reaction mixture, allowing the methanol to enter the oil phase. Hexane was used to disperse the oil, not actively participate in the process. All volumetric hexane-to-methanol ratios can successfully convert oil to methyl esters, but production economics dictate that an optimum ratio be found. The ratio of the least amount of hexane injected that produces the desired minimum in the quickest time was 2:5. The ester and glycerol layers were instantly distinguishable after settling. For physical reasons, the glycerol component should easily be separated from the ester phase. Because glycerol is polar and hexane is non-polar, it is insoluble in hexane. The ability of methyl esters and methanol to hold glycerol is reduced when combined with hexane because hexane repels glycerol. The lack of soap particles between the ester and glycerol phases facilitates glycerol transfer from the ester phase to the glycerol layer.

Ayegba *et al*. [76] synthesized cotton seed oil methyl ester (CSOME) in a tubular reactor utilizing THF as co-solvent and KOH as catalyst. The feed was pre-mixed in a feed tank and fed into the reactor at varied flow rates using a fuel pump. The yield of CSOME increased from 93.3% after 6 min to 99.5% after 14 min. The reaction was carried out at room temperature with a methanol-to-oil ratio of 6:1 and a methanol-to-THF volume ratio of 1:1.

Taherkhani & Sadrameli [77] studied *in situ* transesterification of linseed oil with methanol and KOH to produce biodiesel. In the presence of 6.8% KOH as catalyst, a solvent-to-solids ratio of 10 and co-solvent-to-solvent ratio of 0.3, the maximum methyl ester concentration was 93.15% after 90 min of reaction at 40 ℃ with 700 rpm agitation. The SSR was varied from 1 to 15 in this research while the other variables were maintained constant. Increased SSR improved biodiesel output due to the reversibility. After the ideal point, the yield declined to dilute the catalyst concentration by high amounts of solvent and co-solvent. The co-solvent-to-solvent ratio was studied. The maximum percentage yield achieved without a co-solvent was 84.3%, whereas the best percentage yield achieved with a co-solvent was 93.15%. As a result, even a little increase in co-solvent enhanced yield. A trace of co-solvent improved methyl ester output by 8.85%. Increasing the solvent concentration to 0.25 enhanced the yield due to the decreased solubility of the solvent and extracted oil at low co-solvent concentrations. Using too much co-solvent during the separation process may make it difficult to separate the biodiesel from the glycerol. The yield declined significantly when the co-solvent content was raised over the optimal threshold.

Gargari & Sadrameli [78] reported the continuous transesterification of linseed oil using diethyl ether (DEE) as co-solvent to boost the formation of fatty acid methyl esters (FAMEs). The reaction was conducted continuously in a packed bed reactor using calcium oxide as heterogeneous catalyst. Under optimum conditions, a yield of 98.08% FAMEs was produced. This study studied the influence of DEE on FAME production. The purpose of co-primary solvent was to create a single-phase in a methanol-oil mixture. Mass transfer between the oil and methanol is improved by adding a suitable amount of DEE, which needs speeding up the process. This probe adjusted the volume of DEE at which the reaction yield could reach its maximum. The amount of DEE was investigated in a range of 0.5-2.0 for the optimization purposes. As a result, the heterogeneous catalyst particles packed in the reactor may be brought into proximity to a homogeneous methanol and oil solution. According to the results, the optimal condition was 1.19:1 molar ratio of DEE-to-methanol.

Djokic-Stojanovic *et al.* [79] explored 10 organic solvents (triethanolamine, diethanolamine, ethylene glycol, methyl ethyl

ketone, *n*-hexane, triethylamine, ethylene glycol dimethyl ether, glycerol, tetrahydrofuran and dioxane) as co-solvents in a batch stirred reactor for CaO-catalyzed sunflower oil ethanolysis. In the absence of co-solvent, the reaction was slightly slow, providing an FAEE content of just $89.7 \pm 1.7\%$ after 4 h. The only co-solvents that significantly accelerated the ethanolysis process were diethanolamine, triethanolamine and ethylene glycol, with the latter two producing a final FAEE content of $93.1 \pm 2.1\%$ and $94.1 \pm 1.5\%$, respectively, within 0.5 h. Due to its safety profile, triethanolamine was chosen as the optimal co-solvent for the ethanolysis of sunflower oil catalyzed by calcined CaO. It was reported that co-solvents lack catalytic activity without CaO, inhibiting oil-to-ethanol contact. The co-solvents were classed as stimulative or inhibitory. On the surface of solid catalyst particles, kinetics and reactant miscibility were varied, impacting the partition equilibrium. Diethylamine, triethanolamine and ethylene glycol co-solvents increased the reactants' mutual miscibility by speeding up the process and increasing the final concentration of FAEE. It outperformed ethylene glycol and diethanolamine as co-solvents. In addition, deep eutectic solvents like glycerol and water can be used to shift the reaction to the right and raise the FAEE concentration. Due to the toxicity of ethylene glycol, triethanolamine may be used as a co-solvent in CaO-catalyzed sunflower oil ethanolysis. After 20 min, the FAEE content reached $79.3 \pm 6.54\%$, much above the control response. After 0.5 h, the FAEE level was $93.1 \pm 2.07\%$, compared to 6 h in the control system. During the soybean oil methanolysis, glycerol hindered Ca-diglyceroxide catalysis. Glycerol excess facilitated reversal by lowering FAEE levels. Nevertheless, unlike hydrophilic co-solvents, hydrophobic co-solvents did not influence the initial ethanolysis step. Hydrophobic co-solvents varied activities during ethanolysis might explain their putative inhibitory impact. These co-solvents could not homogenize the alcohol and oil phases and had no influence on mono- and diacylglycerol production rates. The blockage of active sites on the catalyst surface prevented the production of catalytically active calcium alkoxide. This was done with CaO catalysts to generate ester-amines, cationic surfactants that helped homogenize the alcohol and oil phases. The polarity of hydrophilic co-solvents in alcohol but not in sunflower oil reduced FAEE levels.

Bertoldi *et al.* [80] examine the influence of CO_2 as co-solvent on the generation of fatty acid ethyl esters in a continuous catalyst-free process from the soybean oil transesterification in supercritical ethanol. The effect of various amounts of CO_2 on the yield of ethyl esters was investigated while maintaining a constant oil-to-ethanol molar ratio of 1:40, a constant pressure of 20 MPa and at 573 K and co-solvent (CO_2)-to-substrate mass ratio ranging from 0:1 to 0.50:1. When the mass ratio of CO_2-to-substrate is more significant than 0.05:1, the synthesis of ethyl esters drops. In this work, 98.5 wt.% yield was produced after 10 min of reaction at CO_2-to-methanol molar ratio of 0.1 at 553 K, a pressure of 14.3 MPa and a ratio of oil-to-methanol of 1:24. The findings obtained with CO_2-to-substrates mass ratio of 0.05:1, 36.9 wt.% in a flow rate of 1.5 mL/min were almost identical to those obtained with a CO_2-to-substrates mass ratio of 0.05:1. The phase

equilibrium measurements for the binary system ethanol-CO_2 indicated a significant mutual solubility between these compounds. On the other hand, CO_2 solubility in soybean oil had been reported to be exceedingly low. As a result, the co-solvent was likely to extract some ethanol from the oil phase, forming a two-phase flowing system and reducing the concentration of ethanol in contact with the vegetable oil, hence limiting reaction conversion.

Encinar *et al*. [81] investigated the transesterification of rapeseed oil under subcritical methanol conditions with *n*-hexane as co-solvent in a subcritical methanol reactor. The presence of *n*-hexane had a substantial effect on the reaction only during the first few minutes. In addition, it was discovered that the studies that employed *n*-hexane as co-solvent produced marginally lower values than the others, including density and viscosity.

Elkady *et al*. [82] investigated the biodiesel production from waste vegetable oils by pretreatment followed by transesterification in the presence of methanol in a KM micromixer reactor. According to the study, the primary stumbling block to the methanolysis of waste vegetable oil is the presence of two immiscible phases, which significantly slows the reaction. In this case, an organic co-solvent has been suggested to facilitate the diffusion of two immiscible reactant fluids and conduct the transesterification reaction in a single phase. THF was chosen over other co-solvents because its boiling point is close to that of methanol, allowing for easy separation from any excess methanol. However, using large amounts of THF in the transesterification process is not recommended due to the possibility of reagent dilution, which reduces the transesterification rate. The effect of the volumetric ratio of co-solvent to methanol on the yield of biodiesel was investigated in this regard over the studied range of 0.2 to 1.0. When a small amount reduced the THF-to-methanol ratio, a noticeable increase in production yield was observed. Additionally, biodiesel production increase as the volumetric ratio of THF-to-methanol increased. This behaviour suggested that the co-solvent had a favourable effect on the transesterification reaction. When the volumetric ratio of THF-to-methanol was 0.3:1, the optimal yield of biodiesel was 97.3%. Increased in the volumetric ratio of THF-to-methanol above the optimal selected value had no discernible effect on biodiesel yield.

Liu *et al*. [83] successfully developed a process for transesterifying epoxidized soybean oil (ESBO) to produce epoxy methyl esters (ESBOME) at room temperature (25 ℃) using 1.1% of NaOH as catalyst. The transesterification reaction may be completed in less than 5 min without losing the epoxide function. Due to the oil's limited solubility in methanol, the study notes that the transesterification reaction between oil and methanol begins as a heterogeneous reaction. As a result, mass transfer between the two phases had a substantial effect on the transesterification reaction rate. Incorporating a co-solvent into the transesterification reaction was an effective technique for overcoming this issue and minimizing the amount of methanol utilization. The study has investigated the effect of co-solvents such as acetone, ethyl acetate, THF and diethyl ether. Acetone and diethyl ether provided the highest ESBOME yields, both above 99%. The efficiency of ethyl acetate and

THF was lower than that of acetone and diethyl ether. Consider using diethyl ether as highly hazardous solvent and more expensive solvent than acetone as co-solvent. By employing acetone as a co-solvent in the transesterification process, methanol and epoxidized soybean oil were able to integrate better and the reaction rate was raised. On the other hand, the amount of co-solvent used in the reaction system was affected the substrate concentration. As a result, the amount of co-solvent (acetone) examined ranged between 0% and 25% of the total weight of the oil. After 1 h of reaction, when 5 wt.% acetone was added as co-solvent, the yield of ESBOME was marginally enhanced (99.5% *vs.* 99.7%). The acetone content was steadily increased (10-25%), the production of ESBOME remained constant (> 99.5%).

Miyuranga *et al.* [84] synthesized biodiesel from the waste cooking oil (WCO) using acetone as co-solvent to overcome the mass transfer barrier. The direct transesterification of WCO was investigated with and without adding acetone as co-solvent using methanol and KOH as homogeneous catalysts. Direct transesterification with acetone produced 98.46% of the maximum amount of biodiesel compared to transesterification without acetone (66.28%) under the same reaction conditions. Addition of acetone decreased the time required for the acetone to separate from the glycerol mixture following the termination of reaction. The study was observed that improving reaction conditions in the absence of co-solvent was necessary to achieve yields comparable to those obtained with a co-solvent. As a result, all of these findings demonstrated that co-solvent had a beneficial effect on methanol and oil miscibility. It was capable of increasing the mass transfer rate between the reactants during the transesterification reaction, allowing for a high yield of biodiesel under mild reaction conditions, resulting in cost savings. This finding demonstrated that by including acetone as co-solvent, the miscibility of WCO and methanol was enhanced, resulting in a practically homogeneous transesterification process. As a result, in the experiments conducted, stirring speed did not affect transesterification in the presence of co-solvent.

Conclusion

The yield of biodiesel produced *via* transesterification had been influenced by several critical elements, including the methanol-to-oil molar ratio, the amount of catalyst used, the reaction time, the reaction temperature and the agitation speed of the reaction. While those components were upgraded to maximize biodiesel yield, mass transfer resistance remained a critical factor limiting the biodiesel yield. Mass transfer resistance developed due to the immiscibility of oil and alcohol. A co-solvent could be added to the reaction medium to promote the miscibility between non-polar oil and polar alcohol. Acetone, hexane, diethyl ether, THF, benzene and toluene were frequently used as co-solvents. The co-solvent assisted the formation of a single-phase by increasing the miscibility of each reactant and overcoming mass transfer resistance. The presence of a co-solvent can facilitate the transesterification reactions results in a higher output of biodiesel with a shorter reaction time and lower temperature than the non-solvent process, hence improving the total energy balance of biodiesel production. In comp-

arison to the standard transesterification reaction, the inclusion of co-solvent accelerated the reaction and reduced methanol consumption. Biodiesel production was boosted at low co-solvent concentrations due to the better dispersion of methanol. However, at greater co-solvent concentrations, enzymes deactivation, the operating cost increased, lowering biodiesel production resulted. It was feasible to alter the physico-chemical properties of biodiesel fuel by selecting an appropriate co-solvent prior to transesterification. The supercritical methanol/co-solvent method outperformed the conventional supercritical methanol method. Addition of co-solvent, the density difference between FAME and glycerol was increased, resulting in a shorter phase separation time.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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