CHAPTER 2
LITERATURE REVIEW

2.1 Biodiesel

Many researches have been done in the area of VO renewable fuel, not only in the process design, but also in finding the suitable VOs or fats as raw material and suitable chemicals for the reaction media design.

Due to environmental problems associated with the burning of fossil fuel and crisis, for the last 30 years the research interest has expanded into the area of biofuel. Since 1980, there has been increasing interests in methyl esters fuel since biodiesel has been found to have properties that make it an excellent substitution for petrodiesel. Many researches and uncountable publication papers have looked into the production of biodiesel using conventional and heterogeneous catalysts; to increase its economic competitiveness against petrodiesel by finding suitable cheaper raw materials, i.e. VOs and fats. The main obstacles in the current production methods that must be overcome before commercialization of biodiesel are improvement of the oil yields and finding a recyclable catalyst to make the process as economical and environmental friendly as possible [4, 15].

2.2 Overview of biodiesel production methods

2.2.1 Direct use

Although, numerous studies have shown that TGs hold promises as alternative diesel engine fuels [84-89], the direct use of VOs fail to pass the longer periods of time operating tests [2, 4, 13]. In addition, there are serious problems that appeared in the diesel engine; especially in direct injection engine type; these include:

- Coking and trumpet formation on the injectors to such an extent that fuel atomization does not take place properly or even prevented as a result of plugged orifices [13].

- Significant carbon deposits [1, 90].
- Oil ring sticking [2].
- Thickening or gelling of the lubricating oil due to contamination by VOs [13].

Another major obstacle encountered in substituting and revolutionizing the VOs (especially animal fats) for diesel fuel, is mostly related to their high viscosity in compression ignition [4], where most VOs have viscosities in the range of 27.2 – 53.6 mm^2/s which are 11–17 times higher than the viscosity of diesel fuel [2]. Castor oil has an even higher viscosity than most VOs that is more than 100 times greater than the diesel fuel [91]. Table 2.1 shows the kinematic viscosities of various VOs and that of their derivative methyl esters.

These problems are caused by the large TGs molecule and its higher molecular mass, and are usually avoided by modifying the engine. However, the modification depends on the conditions and type oil used but still there are other minor problems related to low volatility, and low flash point of the oil [1, 7, 21].

Table 2.1 Kinematic viscosities of VO and their methyl ester (ME) counterparts from methanolysis, determined at 38°C as mm^2/s [4]

Sample	Cottonseed	Hazelnut kernel	Poppyseed	Rapeseed	Safflowerseed	Sunflowerseed
VO	33.7	24	42.4	37.3	31.6	34.4
ME	3.1	2.8	3.5	3.3	2.9	3.2

2.2.2 Blending

The idea of blending lipids with fossil fuel, in various part ratios, primarily came out in the early 1980s. The viscosity, flash point, and volatility problems can be solved by blending oils and fats with petrodiesel in different percentages [13].

The description B2 for biodiesel blended with diesel is typically referred to a mixture of 2% biodiesel and 98% petroleum diesel (v/v %) [1, 4]. Though, the most common form of marketed biodiesel i.e. the blended VO alkyl ester with diesel fuel is BD20 (biodiesel 20%), which is 20% biodiesel to 80% petrodiesel. The blended fuels can be diluted by hydrocarbons, rather than petrodiesel, such as pure ethanol or another solvent [1, 4].

For instance, canola oil is highly viscous than other common VOs. At 40 °C a blend of 75/25 canola oil/diesel fuel has a viscosity of 40 mm^2/s; and for a 50/50 blend the viscosity is found to be 19 mm^2/s [87]; while the maximum specified ASTM D6751 (D445 based method) and EN 14214 (ISO 3104 based method) values are in the ranges of 1.9–6.0 mm^2/s and 3.5–5.0 mm^2/s, respectively [23].

Other researchers, Yuan *et al.* [92] reported that a 75% blend of soybean oil with no.2 diesel fuel has a viscosity of 3.78 mm^2/s at 40°C, with a 50% blend the viscosity is reduced to 3.41 mm^2/s, while a 25% blend has 3.11 mm^2/s at the same temperature. Strayer *et al.* [87] made a comparison between different oils blend with petrodiesel. A 75/25 blend of canola oil and fossil fuel has a lower viscosity of 40 mm^2/s compared to 60 mm^2/s of pure canola oil blend of 50/50.

Despite the reports that blending of VOs with diesel fuel has shown enhancement in terms of the former physicochemical properties, but the long term period of usage in diesel engine have been found to lead to a decrease in power output and thermal efficiency by carbon deposits and lubricating oil fouling [1, 88, 93].

2.2.3 Pyrolysis or thermal cracking

Pyrolysis or thermal cracking refers to the thermal cleavage of VOs by heat, usually in the presence of a catalyst and the absence of oxygen, to produce smaller molecules, such as alkanes, alkadienes, carboxylic acids and small amounts of aromatic and gaseous products [4, 13, 94]. Pyrolysis is the only technique used for converting the biomass into bio-oil, which can be used as a fuel directly [95].

The pyrolysis processes are categorized according to the operational conditions: conventional, fast and flash pyrolysis. These processes can be applied to animal fats, VOs, fatty acids and fatty acids methylesters.

However, the pyrolyzed VOs usually reveal large differences in their compositions [18]. The first pyrolyzed VOs, before the First World War, was aimed to synthesize products suitable for diesel engine.

While the pyrolyzed fats have been known for more than 100 years, especially in countries where there is a lack of petroleum deposits [4, 13]. Soon after, in 1947, the tung oil was saponified with lime, pyrolyzed and then refined to yield diesel fuel and small amounts of gasoline and kerosene [13].

Many investigators have identified the total hydrocarbons from hydrolyzed soybean and safflower oils, and biogasoline from palm oil [96]. Schwab *et al.* [97] compared the pure to pyrolyzed soybean oil, having 79% carbon and 12% hydrogen, the pyrolyzed soybean oil showed a lower viscosity and higher cetane number.

Hydrocarbon materials of gases, liquids and solids with lower molecular weights were produced from cracked copra and palm oil in the presence of catalysts. A variety of catalysts have been used in pyrolysis, largely the metallic salts, but the common two catalysts are SiO_2 and Al_2O_3 [13]. However, the non-catalytic pyrolysis processes were also known [95].

Although; the pyrolyzed VOs offered acceptable amounts of cetane number, copper corrosion values, viscosity, water, sediments and sulfur; many problems intricate the hydrolysis technique usability:

- Demonstrated unacceptable ash contents, carbon residue, and pour point, which forced additional separation steps [1], that requires additional equipment in the overall process design [15].
- Removal of oxygen from the process eliminates the environmental benefits of the product [13].
- Hydrolyzed fuel properties are closer to that of gasoline, more than diesel [18].

2.2.4 Microemulsion

Technically microemulsions are defined as isotropic, clear or translucent, thermodynamically stable dispersions of oil, water, surfactant and small co-surfactant of amphiphilic molecule. The microemulsions with liquids, such as methanol, ethanol, and ionic or non-ionic amphiphiles have been studied as a means of reducing the VOs high viscosity problem. Microemulsion had a maximum viscosity required for D2 fuel when butanol and hexanol were used as solvents [4, 98].

Ziejewski *et al.* [99] reported higher cetane number, much lower viscosity, lower sulfur content, FFA, and lower ash content, when nonionic emulsions of 53.3% (v/v) alkali refined and winterized sunflower oil, 13.3% (v/v) of 190-proof ethanol and 33.4% (v/v) 1-butanol were applied. A microemulsion prepared by blending solution of soybean with aqueous ethanol, using short term performance, resulted in a product property as well as No.2 diesel, with the differences only in the cetane number and energy content, while the durability was not investigated [88, 100].

Although the microemulsion has been effective in lowering the viscosity of the VOs, laboratory test results showed that:

- Significant irregular injector needle sticking [13, 15].
- Heavy carbon deposit on piston and head of engine [99].
- Incomplete combustion, which led to more injector needle blocking and in-take valve sticking [18, 99, 101].
- Lubrication oil contamination, due to formation of polymers, which increased the viscosity of the lubricating oil [18].

However, as mentioned that the blending, microemulsion and catalytic cracking have been associated with some engine performance problems. On the other hand the transesterification was found to be more common, easier and is commercially preferred. It appears to be the best technique as the physical characteristics of the transesterified oils seem to be like those of diesel fuel, while some of the problems, mentioned above, were almost solved [7, 102, 103].

2.2.5 Biodiesel via transesterification

Chemical transesterification also called alcoholysis, means taking the fatty acid ligands, neutralizing the FFA, removing the glycerine backbone and forming three long monoesters chain, which is called biodiesel. Alcoholysis process is comparable to hydrolysis reaction, except that an alcohol is utilized instead of water [1, 4].

The transesterification reaction proceeds by using primary or secondary monohydric aliphatic alcohols having 1–8 carbon atoms. However, the commonly used ones include methanol, ethanol, propanol, butanol, and amyl alcohol. For instance, methanol and ethanol are employed most frequently, particularly methanol because of its lower cost, and physical and chemical properties [4, 15, 18].

Transesterification, also called alcoholysis, has been known for around 150 years by the scientists Duffy and Patrick [104]. In the past few years, alcoholysis method has been extensively studied in order to develop engine performance and to improve the production quality [11, 105]. It has been known to reduce the viscosity of oils and fats, and to enhance the physical properties of renewable fuels [106]. Table 2.2 presents some properties of VOs biodiesel fuel compared against the properties of diesel fuel [1].

Table 2.2 Physical and chemical properties of alkali-transesterified VO [1]

VO esters	Kinematic viscosity (mm^2/s) (ºC)	Cetane No.	Lower heating value (MJ/l)	Cloud point (ºC)	Flash point (ºC)	Density (g/l)
Peanut	4.9 (37.8)	54	33.6	5	176	0.883
Soybean	4.5 (37.8)	45	33.5	1	178	0.885
Babassu	3.6 (40)	63	31.8	4	127	0.88 (15ºC)
Sunflower	4.6 (37.8)	49	32.4	1	183	0.860
Tallow	–	–	–	12	96	–
Rapeseed	4.2 (40)	51–59.5	32.8	–	–	0.882
Diesel fuel	1.2-3.5 (40)	51	35.5	–	–	0.83–0.84(15ºC)

As a point of comparison, biodiesel produced from VOs have viscosities much closer to diesel viscosity. Their cetane numbers and flash points are higher, but they have, to some extent, lower volumetric heating values. Hence, the biodiesel has the potential to replace diesel, since their characteristics are quite similar. Other attractive advantages offered by the use of this fuel are:

- Reducing the dependence on imported fossil fuel which is becoming expensive day by day due to reserve depletion [19, 24].
- It is a renewable resource [4].
- Less environmental pollutants since biodiesel was found to be biodegradable like sugar [7] and greatly biodegradable in fresh water as well as soil environments [15].
- Does not contribute to ozone depletion [24, 107], hence reduces the current net levels in the atmosphere of carbon monoxide (CO), carbon dioxide (CO_2), sulfur dioxide (SO_2) particulate matters, and other unburned hydrocarbons [108,

109]. Only a minor increase in the nitrogen oxides (NO_x) generation has been reported. However, various strategies have been suggested to eliminate the NO_x emission of biodiesel [15, 110].

- It can be blended in any proportion with petroleum diesel fuel [4].

2.3 Kinetics affecting the transesterification reaction

Several researchers have presented that the molar ratio of alcohol to oil, catalyst type and concentration, reaction time, reaction temperature, agitation rate, and the FFA and water content in the oil are the main parameters affecting the transesterification reaction [4, 21, 111]. The effects of these parameters are discussed individually below.

2.3.1 The effect of molar ratio

The molar ratio of alcohol to TGs is one of the most effective variables affecting the yield of esters; the molar ratio determines the ability of the transesterification reaction to reverse its direction to the reactants side [15, 102, 111].

The stoichiometric ratio for transesterification reaction requires three moles of alcohol and one mole TGs to yield three moles of fatty acid alkyl esters and one mole of glycerol (GL) [13].

Freedman *et al.* [63] studied the effect of varying the molar ratio from 1:1 to 6:1 on esters conversion with soybean, sunflower, peanut and cottonseed oil, under the same reaction conditions. They found that those VOs behaved alike, with conversion ranged from 93 – 98%, at a molar ratio of 6:1. Likewise, 6:1 is the optimum operating molar ratio yielding high conversion of duck tallow Karanja oil [112, 113], and sunflower [114], to methyl esters using alkaline catalyst. It was observed that as the molar ratio was increased more than the theoretical stoichiometric ratio, 3:1, the ester yield increased too. On the other hand, in some cases, 6:1 molar ratio released significantly more glycerine than 3:1 [13]. Accordingly, a molar ratio of 6:1 is usually used in the commercial productions, to obtain methyl ester yields higher than 98% on a weight basis [18].

Meher *et al.* [2], Ma and Hanna [13], and Leung *et al.* [66] stressed the importance of the molar ratio between the reactants. However, they reported that excess molar ratio can lead to greater esters conversion in a short time, but will complicate the separation of glycerol, due to increase its solubility in alcohol. Thus, adding the alcohol recovery cost to the process.

Similarly many investigators have systematically studied the effect of molar ratio on yield ester. Ting *et al.* [76] reported that the addition of large quantity of methanol ratio, 15:1 to 40:1 in the presence of 5% of H_2SO_4 for 60 minutes, slowed down the separation of the ester and glycerol phases during the production of biodiesel. A 15:1 molar ratio was reported to be the optimum for transesterification of soybean.

Miao and Wu [115] varied the molar ratios of the methanol/ microalgal oil up to 84:1. In the acid catalyzed transesterification, 56:1 was reported to be the optimum molar ratio. Encinar *et al.* [116] studied the cynara oil ethylesters conversion when the ratio ranged from 3:1 to 15:1. The reaction was incomplete for molar ratio less than 6:1 and the best results were found between 9:1 to12:1, while the highest yield was achieved at a molar ratio 9:1. The same authors in another work [111] tested a range of molar ratios 6:1 – 12:1 of ethanol/UFO. Their results showed that the best biodiesel properties were obtained when a ratio of 12:1 was used. In a study conducted by Wang *et al.* [22], using two catalyzed step for the transesterification of WCO, the yield increased from 91.6 to 97.22% when the ratio was varied from 3:1 to 10:1. Liu *et al.* [116] conducted experiments in order to study the best molar ratio for the transesterification of soybean oil by varying the molar ratio from 6:1 to 18:1. Their results revealed 12:1 as the best an economically feasible molar ratio.

Varma and Madras [103] varied the molar ratio from 10:1 to 70:1 and found the highest conversion of linseed oil methylesters at molar ratio of 40:1 was applied. In one study, soybean oil was transesterified with methanol using CaO as catalyst and the ratio was varied from 12:1 to 18:1 [118]. The ester yield increased as the molar ratio was increased, with the best yield of 97% obtained for a molar ratio 12:1. However, they found that increasing the molar ratio to 18:1 did not produce an increase in the yield; instead a lower yield of 90% was obtained.

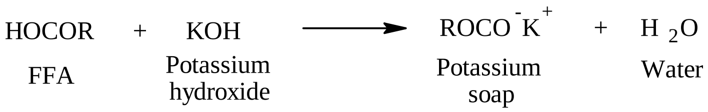
Alamu *et al.* [119] conducted their experiments at molar ratios ranging from 10:1 to 25:1. The maximum yield was 96% with ethanol/oil ratio of 20:1. The biodiesel yield dropped gradually when the ratio was increased under the typical reaction conditions. Phan and Phan [120] studied the effect of ratio at 30 °C in the presence of KOH, where they observed an increase in the conversion from 50% to 64% when the ratio was increased from 5:1 to 8:1, respectively.

Leung and Guo [21], during their transesterification of neat canola oil, reported that the esters content increased from 80.3 to 98%, and the yield rose from 78.7 to 90% when the molar ratio was increased from 3:1 to 6:1. Their study on used frying oil (UFO) showed increases in the ester content from about 80 to 94%, and yield from 77 to 87.5%, with increasing the molar ratio from 3:1 to 7:1.

From the literature review, it can be concluded that excess alcohol results in greater ester conversion; however, exceeding the optimum ratio can lead to Glycerol separation difficulties and reducing the final product yield.

2.3.2 The effect of moisture and FFA content

For the selectivity of alcoholysis catalyst, the TGs have to meet certain specifications [63]. For example, as shown in the reaction below, the presence of moisture and high FFA in the feedstock can easily react with an alkali catalyst producing soaps and water. As a consequence, the downstream recovery and purification of the product is complicated by the formation of soaps, which resulted from the reaction between the FFA and the catalyst [24, 121].



$$\mathrm{HOCOR} + \mathrm{KOH} \longrightarrow \mathrm{ROCO^{-}K^{+}} + \mathrm{H_2O}$$

Figure 2.1 Undesired saponification formation [19]

As mentioned above, the use of alkali catalyst is associated with the oils having lower FFA content of <0.5% [13, 20, 24, 67, 68]. For oils with high FFA, previous works in this area have shown that single step acid catalyzed transesterification reaction can be employed [122, 123]. Some researchers have also demonstrated the use of two step base – base [124], acid – base [24], acid – acid [125] catalyzed reactions. Details of the single and two step reactions are given in the following subsections.

2.3.3 The effect of reaction time and temperature

Other than molar ratio, reaction temperature is another significant variable affecting the transesterification reaction of oil. The reaction temperature always depends on the reaction time, and increasing the time will allow the temperature to be lowered, even to room temperature for the biodiesel production [2]. In most cases, the conversion rate increases with time.

In view of these variations in time and temperature as reported by earlier investigators, Freedman *et al*. [63] transesterified peanut, cottonseed, sunflower, and soybean oils at the conditions of methanol to oil ratio of 6:1, 0.5% sodium methoxide catalyst, and 60 ºC. A yield of 80% was gained after 1 minute for soybean and sunflower oils. Then, after 60 minutes, the conversion for all four oils ranged in 93 – 98%. Ma *et al*. [126] conducted a similar study on beef tallow methyl ester production. During the first minute the reaction was very slow. Then the reaction started to proceed very fast to reach its highest yield after 15 minutes.

Abundant data can be found in the literature on the effect of reaction temperature on biodiesel production. Chongkhong *et al*. [127] tested the effect of reaction temperature on palm fatty acid distillate. The FAME content increased when the reaction temperature was increased from 70 to 100 ºC. However, the conversion rates were reduced in the range of 90–100 ºC. Han *et al*. [128] investigated the effect of temperature on the reaction of waste oil biodiesel using [HSO_3-bpyr][HSO_4] as the catalyst. Their results showed increasing methyl esters content with temperature, as the yield increased to about 60% when the temperature increased from 80 °C up to 180 °C.

Although, Meher *et al*. [112] suggested different temperature to be used while different types of oils can be applied, and Leung and Guo [21] agreed that the reaction rate of transesterification increases with increasing temperature. However, there are several authors who suggested that reaction temperature above 60 °C should be avoided because saponification of glycerides will take place before completion of the reaction, particularly in alkaline catalyzed reaction [15, 111, 114, 129].

Also, Chung *et al*. [113] discovered that increasing the temperature from 55 – 85 °C has no effect in the FAME content of transesterified duck tallow oil. Phan and Phan [120] tested three different temperatures on the waste cocking oil. Their results showed a trend of increasing yield from 30 to 50 °C. However, the lowest yield was obtained when the temperature was increased to 70 °C.

Oliveira *et al.* [130] varied the reaction time from 30 minutes to 2 hours, and temperatures of 25, 55, 60 °C for trans- and esterification of coffee oil and soybean oil. At all of the reaction conditions, coffee oil yielded lower esters content than soybean oil. Their results revealed that increasing the reaction time promoted higher ethyl ester conversions at room temperature, and no effect was seen on conversions at 60 °C.

2.3.4 The effect of mixing intensity

Agitation is a very important in transesterification reaction. Often low molecular weight alcohols, like methanol and ethanol, are used for biodiesel production. However, they are immiscible with oil at room temperature. Thus the reaction is described as a heterogeneous reaction [126]. Therefore, the reaction mixtures are frequently agitated to assist the mass transfer of alcohol into the oil [126, 131].

Ma *et al.* [126] and Noureddini and Zhu [132] studied the effect of mixing on the transesterification of beef tallow. Their results showed that, without mixing, the reaction occurred only at the interface of the layers. However, when NaOH-methanol mixture was added to the melted beef tallow with high mixing, the reaction between the melted beef tallow and the mixture increased, indicating that the chemical reaction was facilitated. During the methanolysis of soybean, used frying and tallow oils, Alcantara *et al.* [133] found that agitation had a significant effect during alcoholysis of soybean when two agitation speeds were tested. A higher conversion of the oil in a shorter time was observed at higher agitation speed. Vicente *et al.* [134] recommended agitation speed of 600 rpm as sufficient to overcome the mass transfer limitation during biodiesel production process.

2.3.5 The effect of catalyst type and concentration

Since most of the recent biodiesel production is from neat oils which contain 90-95% TG [102] and very little FFA, the basic catalysts are more effective for alcoholysis process [18, 21].

2.3.5.1 Alkaline homogeneous catalyst

The most common alkaline used are sodium hydroxide [135], potassium hydroxide [136], sodium methoxide [5, 130], potassium methoxide [137], barium hydroxide, calcium oxide [20], calcium hydroxide, magnesium oxide [2], calcium methoxide, magnesium methoxide [138], sodium amide [13], sodium hydride, potassium amide, potassium hydride [13], sodium peroxide, sodium ethoxide and sodium propoxide [63, 139], sodium butoxide, and many more [13, 18]. Among those, NaOH, $NaOCH_3$, KOH and $KOCH_3$ are most effective [2]. Basic methoxide catalysts are promising base catalysts and do not form like hydroxide soaps, however, they are hygroscopic and expensive [63].

Considerable data on the different types of conventional basic catalyst, their range of concentrations and their applications with different types of oils are available from previous research works [5, 63, 112, 130, 135, 136, 137, 138]. Rashid *et al.* [114] investigated the effect of NaOH amount on sunflower methylesters production by designing seven experiments with catalyst concentrations of 0, 0.25, 0.5, 0.75, 1.0, 1.25 and 1.5% (w/w). The optimum yield (97.1%) was achieved with a concentration of 1.0%, while no product was obtained without catalyst (0%).

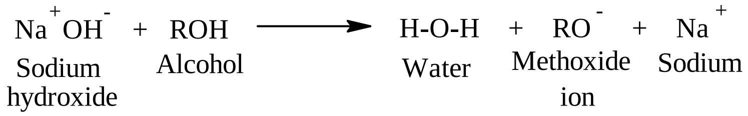
Meher *et al.* [112] conducted experiments on pongamia pinnata oil methylesters using KOH as catalyst with concentrations from 0.25 to 1.50%; the highest yield reported was 97-98% when 1.0% KOH was applied. Phan and Phan [120] tested KOH in the range of 0.5 – 1.5 wt% of WCO. The conversion was 82% and 90% at 0.5 wt% KOH and 0.75 wt% KOH, respectively. However, the conversion was reduced to 75% in the case of 1.5 wt% KOH.

Meneghetti *et al.* [137] studied the methanolysis of castor oil by carrying out the reactions at 60°C, in the presence of $NaOCH_3$, NaOH, $KOCH_3$ and KOH. After 10 hours of reaction, $KOCH_3$ was found to be more effective leading to a FAMEs yield of more than 75%, followed by $NaOCH_3$ (75%), KOH (70%) and, surprisingly, NaOH was less than 70%. In the same work, during the ethanolysis of castor oil at 80°C, after 10 hours of reaction, the highest yield was obtained by $KOCH_3$, followed by KOH, NaOH and lastly $NaOCH_3$. Another author also discovered that NaOH is more superior compared to $NaOCH_3$ and KOH [21].

Using duck tallow oil as feedstock, Chung *et al.* [113] evaluated the transesterification on various alkali catalysts with alcohol. The highest FAME content (97%) was obtained with KOH at 65ºC as compared to 83.6% and 81.3% when $NaOCH_3$ and NaOH were applied respectively, using similar parameters. Further, Ma *et al.* [140] found that NaOH gave the highest conversion compared to $NaOCH_3$, when the same concentrations of 0.3 wt% were applied.

The transesterification of rapeseed oil also has been investigated using magnesium oxide, calcium oxide, calcium hydroxide, barium hydroxide, and sodium hydroxide as catalysts. After 30 minutes of reaction, NaOH led to a conversion of 85%, $Ba(OH)_2$ 75%, and $Ca(CH_3O)_2$ 55%. A very slow reaction was observed when CaO was used, and there was no catalytic activity at all when MgO and $Ca(OH)_2$ were used [2]. Leung and Guo [21] and Georgogianni *et al.* [141] also studied the effect of NaOH concentration on biodiesel production from used cooking oil and neat canola. Their results revealed that the optimum catalyst concentration was 1.1 wt% and 1.0 wt%, respectively.

Currently alkaline and acidic catalysts have been proven to be more practical [24, 142], because they lead to much faster reaction rates than heterogeneous catalysts in transesterification of oils. However, alkali ones can achieve higher yield and purity of biodiesel within 30–60 minutes [129]. However, the constraints of the alkali catalysts is that they are highly sensitive to the purity of the reactants (oil and alcohol), i.e. the presence of high FFA and water [24]. The presence of water in the reactant causes saponification and affects the ester yield by increasing the mixture viscosity; as a result makes the separation of esters very difficult [2, 121, 143]. During alcoholysis, water can form as follows:



$$\underset{\text{Sodium hydroxide}}{Na^{+}OH^{-}} + \underset{\text{Alcohol}}{ROH} \longrightarrow \underset{\text{Water}}{H\text{-}O\text{-}H} + \underset{\text{Methoxide ion}}{RO^{-}} + \underset{\text{Sodium}}{Na^{+}}$$

Figure 2.2 Undesired water formation [121].

In addition, the removal of these catalysts from the completed reaction is technically difficult and a large amount of water is required to clean the organic phase (esters) from the catalyst [18, 70, 144]. In general, it is considerably costly to separate homogeneous catalyst from products [74]. For these reasons, an acidic catalyzed process is preferred [13].

2.3.5.2 Acidic homogeneous catalyst

Since many feedstocks contain high amount of FFA, many researchers reported that it was necessary to perform the reaction using acidic catalyst [13, 18, 24]. Strong liquid mineral acids, such as sulfuric acid [145], phosphoric acid, hydrochloric acid [146], sulfonic acid and organosulfonic acid, are commonly used for the esterification of FFA with alcohol [76].

Acidic transesterification reaction always proceeds slowly in the presence of non-strong acid. However, strong acid catalysts will not be effective in the transesterification either, because the strong acid will preferentially catalyze the esterification of FFA [18]. Several researchers have suggested the use of higher molar ratio, acid concentration, higher reaction temperature (≥100°C), and longer reaction time (≥48h) in order to obtain high esters yield [147, 148].

Acid catalyzed transesterification was studied by several researchers. Mohamad and Ali [146] investigated two acidic catalysts, H_2SO_4 at a fixed concentration of 2.25 M and HCl at different concentrations (0.5, 1.0, 1.5 and 2.25 M) in the presence of excess alcohol. Their results showed that H_2SO_4 is more superior than HCl. Meneghetti *et al.* [137] transesterified castor oil with methanol and ethanol using 2% concentrated H_2SO_4 and HCl. Similar yields of FAME were obtained after 4 hours of reaction. However, after 5 hours of reaction, the FAME yield started to increase with H_2SO_4 but decreased with HCl although the yields of FAEE were the same. Ting *et al.* [76] conducted esterification experiments to study the effectiveness of various acids; sulfuric, acetic, nitric, hydrochloric, and phosphoric acid; at the same concentration (5% v/v) and 1:20 of soybean oil/methanol ratio. The highest ester conversions of 86, 81.7 and 77.3% were obtained when H_2SO_4, HCl and HNO_3 were used, at 50 °C for 60 minutes of reaction time. Weak acids such as CH_3COOH and H_3PO_4 exhibited lower catalytic activity compared with strong ones. Tashtoush *et al*. [149] employed H_2SO_4 for WCO with high excess of alcohol (200%), but the reported conversion was too low (82%).

Although acidic catalysts are favored for esterification of feedstocks having high FFA, they demand the usage of high amount of alcohol and require expensive equipment. High amount of alcohol usage requires increasing the reactor size, and necessitates extensive conditioning and purification steps for alcohol recovery, and catalyst removal from the reaction products, i.e. esters and byproduct. In addition, excess alcohol will complicate the removal of Glycerol due to its high solubility in alcohol [11, 25]. Moreover, the yield is unexpectedly low when more superior acidic catalyst such as sulfuric acid is applied [149, 150].

To solve these problems, Basu and Norris [143], in their patent, proposed a mixture of calcium and barium acetate to be used as catalysts, as a possible solution to produce biodiesel from high FFA oil source. But their reaction required high temperature (200 – 250 ºC) and high amount of catalyst, which contributed to increasing the production cost in terms of increased power and catalyst consumptions.

Lately, a new combined catalyzed process for different feedstocks with high FFA, such as WCO, has been investigated. Zhang *et al*. [22], Canakci and Gerpen [151], Ghadge and Raheman [152], Veljković *et al*., [153], and Wang *et al*. [154] developed a combined process by using acidic catalyzed esterification in the first step to lower the FFA to an acceptable range, followed by the introduction of an alkali catalyst after the removal of the acidic catalyst, to complete the transesterification [121, 151, 154]. They reported a much higher conversion (97%) with an excess of alcohol ratio. Even though their new process showed high efficiency, the combined process still have many draw backs in particular difficulties related to catalyst recovery and high cost of stainless steel equipment needed for the acidic reaction media. Another author, Çayli and Küsefoğlu [124] transesterified the WCO by a two step process using alkali catalyst, but, their results still favors the use of problematic alkali catalyst. Due to the many problems associated with homogeneous catalyst, many researchers have resorted to using heterogeneous catalysts which could potentially solve those problems.

2.3.5.3 Heterogeneous catalyst

Heterogeneous catalyst is an ecologically important area in catalysis. Their processes considered as non–corrosive, higher activity, environmentally receptive, easier to separate from esters product giving higher conversion and longer life time [155]. In addition, the removal of heterogeneous catalysts is more easier that makes product purification easier too [156]. Consequently, considerable efforts have been made into developing new basic and acidic heterogeneous catalysts that could replace the conventional catalysts.

Different heterogeneous catalysts have been used to catalyze the transesterification of VOs, included the solid metal oxides; such as magnesium [73], calcium [75], strontium [117], and tin and zinc oxides [144; 157], WO_3/ZrO_2 ([107]), and modified zeolites; such Li/CaO, $CaCO_3$, $Na/NaOH/-Al_2O_3$ and EST-4 [82]. To a certain extent these catalysts behave in a similar mechanism as the homogeneous catalysts, since Glycerol and soap are produced in the process too [158].

Bournay *et al.* [158] provided a new method of using a mixture of zinc and aluminum oxides. The reaction was performed at high temperature and pressure with an excess of alcohol. An overall conversion of 98.3% was achieved.

For the transesterification of soybean oil, Xie and Huang [82] used 15% of ZnO loaded with KF at 600 ºC for 5 hours to obtain a yield of 87%, while Kim *et al.* [74] produced 95% of yield using $Na/NaOH/Al_2O_3$ in the presence of n-hexane as co-solvent, and alcohol to oil molar ratio of 9:1.

Some calcium compounds have been used as solid base catalyst for transesterification of VO with methanol. Demirbas [75] prepared methyl esters from sunflower oil using 1.0 wt % CaO. The catalyst showed weak catalytic activity at ambient temperature and even at 62 ºC. However, when 3.0 wt% CaO and 41:1 molar ratio were used and the temperature was increased to 252 ºC, the transesterification was completed within 6 minutes. Kouzu *et al.* [159] investigated the catalytic activities of calcium compound as catalyst for soybean oil. For 1 hour of reaction time, the FAME yield was 93% for CaO, 12% for $Ca(OH)_2$, and 0% for $CaCO_3$, respectively. Nonetheless, there are several factors that have to be clearly investigated such as Glycerol recovery, ability of the catalyst to catalyze feedstocks containing high FFA and the quality of biodiesel produced.

Recently, several studies have been conducted on the use of enzymes, such as lipase, for the transesterification process by immobilizing them in a suitable support. They became more attractive than the other catalysts due to ease of Glycerol recovery, simpler purification of esters, and their ability to be reused without separation. Besides, the operating temperature of the process is as low as 50 ºC [18, 160].

Selmi and Thomas [161] reported a conversion yield of 83 % when sunflower oil was transesterified with ethanol using M. meihei (Lypozyme) without any solvent. Nelson *et al.* [162] performed batch experiments for the tallow, soybean and rapeseed oils with different alcohol using M. meihei (Lypozyme IM60), both in the presence and absence of solvent. They reported conversions in the range of 95.0% with primary alcohols and hexane as a co-solvent. Comparing the efficiencies of methanol and ethanol in the absence of solvent, methanol showed less efficiency of 19.4% while ethanol led to a conversion of 65.5%. Abigor *et al.* [163] also used methanol and ethanol for the transesterification for palm kernel oil catalyzed by P. cepacia (Lipase PS-30), in the absence of solvent. They reported conversions of 15% and 72% for methanol and ethanol, respectively. Mittelbach [164] used methanol and ethanol for the transesterification of sunflower in the presence of P. fluorescens and reported conversions of 79% and 82% for methanol with petroleum ether and ethanol without solvent respectively.

Ting *et al.* [76] investigated new commercial lipase solution from Candida antartica (Lipozyme) encapsulated in silica aerogels and reinforced with silica quartz fibre felt. The biocatalyst was used for transesterifying sunflower oil with methanol, and without any other solvent. Under optimal conditions of molar ratio 1:1, the encapsulated enzyme achieved biodiesel conversion of about 90% after 5 hours at 40 ºC.

Even though previous works have shown that it is possible to produce biodiesel through enzymatic catalysis, there are several disadvantages associated with this process that requires further research in order to make it feasible.

Some of the disadvantages are similar to those identified for the metal oxide compounds. In addition to those, there are factors related to the enzyme itself, which become the main obstacle of this process i.e. the high production cost of enzyme, expensive product purification due to difficulties in the separation of the recombinant or natural enzymes, and enzyme deactivation by methyl alcohol, and also a much longer reaction time is required [71, 162, 165]. Due to the drawbacks associated with catalyzed transesterification reaction, several researchers have suggested transesterification reaction via non-catalytic supercritical alcohol [166, 167].

2.3.5.4 Catalyst-free process

The transesterification reaction can occur in the absence of a catalyst when the alcohol is subjected to conditions of supercritical temperature and pressure.

Song *et al.* [109] successfully produced 93.0% from the transesterified refined bleached deodorized (RBD) palm oil using supercritical methanol at 350 °C and molar ratio of 30:1. Saka and Kusdiana [168] studied the transesterification reaction of rapeseed oil in supercritical methanol with free catalyst. This process was performed in a vessel preheated at 350 ^{o}C, 42:1 molar ratio of oil to methanol, pressures between 45–65 MPa and set interval time of supercritical treatment ranging from 10–240 s. Their results concluded that in a maximum reaction time of 240 s, this process was able to convert all the TGs into ester.

In another work, Kusdiana and Saka [169] investigated various supercritical alcohols of methanol, ethanol, 1-propanol, 1-butanol, or 1-octanol to study the transesterification of TGs at 302 °C. The results showed that transesterification was faster for alcohols with shorter alkyl chains, for example the yield of conversion increases from 50–95% in the first 10 minutes when methanol was used.

Rapeseed oil can be converted into high content of FAME in a very short time (2–4 mins) at 350 °C and 19 MPa. This was mainly due to the existence of a single phase supercritical methanol/oil [168]; the supercritical methanol may easily solvate the non-polar TGs [18]. Madras *et al.* [94] conducted experiments at various temperatures (200–400 °C) with sunflower oil/alcohol molar ratio of 40:1, and a fixed pressure of 200 bar. High conversions between 80–100% were obtained when the reaction was conducted in supercritical methanol and ethanol.

Table 2.3 Comparison between conventional alkali catalyst and supercritical alcohol methods for biodiesel production [168, 170]

	Catalyst type	
	Conventional alkali	Supercritical alcohol
Reaction temperature, ºC	30–65	250–350
Reaction time, h	1–6	0.067
Reaction pressure, MPa	0.1	10–65
Catalyst	Alkali	None
FFA	Saponified product	Alkyl ester
Yield, %	96–97	98
Compounds to be removed during purification	Methanol, catalyst and saponified products	Methanol

Meanwhile, the transesterification by supercritical methanol, ethanol, propanol and butanol seems to be the most promising process. Among those, supercritical methanol has high potential for transesterifying both high and low quality oils/fats to methyl esters. This new method requires shorter reaction time, simpler purification procedure, and separation of methyl ester and Glycerol since no separation of catalyst is needed, compared to traditional alkali catalyst [4].

Table 2.3 presented a comparison of the production of biodiesel by supercritical alcohol and homogeneous alkali-catalyzed transesterification methods. Similar to enzymatic processes, the supercritical alcohol method also has several disadvantages that do not render the process economically feasible even though it has been shown as a better method technically [9, 171].

This technique requires high amount of alcohol [103] and large plant capacity, which contributed to increase the operation cost. Besides, the reaction requires high temperature of 350 ºC and high pressure of 45 MPa [18]. However, at higher temperature, i.e. >300 ºC, the content of FAME can be affected by thermal decomposition of the oil and esters [109].

As discussed above, most of the existing transesterification processes either homogeneous or heterogeneous processes, or catalyst free process have several disadvantages that restrict the commercial production of biodiesel, therefore a new method that eliminates or reduces those disadvantages is highly desirable.

2.3.6 Ionic liquid as catalyst

Efforts have been made on designing acidic ionic liquids to replace homogeneous and heterogeneous acids in a variety of chemical applications [42], such as catalysis in supporting enzyme catalyzed reactions [44], [172], homogeneous and heterogeneous catalysis [43], purification [173], photo-isomerization [174], and electrochemistry [175], due to the environmental friendly nature of ILs, which is also known as green catalyst [45], [172].

The major impetuses in reaction catalysis concerns the development of systems in which easy separation of products and reuse of catalyst is viable, along with high reactivity and selectivity [176]. Ionic liquid is viewed as the prospective catalyst for biodiesel production that addresses both the economical and environmental aspects owing to their properties of less corrosion effects, ease of separation, recyclable, continuous processing, and less waste water production [30], [45]. Moreover, ILs catalysis could decrease the number of reactions and purification steps required in the biodiesel preparation and separation, which might allow for a more economically competitive processing and higher purity yield of esters.

Brønsted acidic task-specific ionic liquids, which possess the advantageous uniqueness of solid acids and mineral acids, have been designed to substitute the traditional mineral hazardous liquid acids, such as H_2SO_4 [177]. The applications of Brønsted acidic functional ILs are widely known in the area of esterification with excellent yields and selectivity [178, 179], after the first Brønsted acidic IL was synthesized in 2002 by Cole and co-workers [180]. Yet, most of the works dealt with aliphatic or arylic esters and very little information on fatty acid alkyl esters preparation using acidic ILs can be found in the literature [128], [181] and no articles about transesterification of crude palm oil in the presence of IL came into view.

Promising ILs have the ability to answer the drawbacks associated with product separation and catalyst recycling [182]. In most cases, it is hard or unfeasible for the reaction to reach 100 % conversion with 100 % selectivity due to thermodynamic complications and the competition of parallel reactions [183].

In view of the fact that ILs are an excellent substitute for traditional solvents in organic synthesis and catalysis, their use as either solvents or catalysts has been growing and gaining considerable attentions because of their prospects as green catalysts [176]. Hence, within the last decade, their applications in the chemical processes have taken a new turn [183]. For example, ILs have been used as catalysts in hydrogenation, isomerization, C–C and C–O cleavage reactions such as catalytic cracking of polyalkenes and C–C coupling reactions such as Friedel–Crafts reaction with excellent yields and selectivity [183]. Yet, the use of ILs as catalyst for transesterification of CPO to biodiesel has not been investigated.

Information on the use of ILs for transesterification of oil into biodiesel is scarce in the literature, but the attractive properties of ionic liquids have been the motivation to use ionic liquid in this research area. Abreu *et al.* [184] studied the activity of two multi-phase systems, for soybean oil alcoholysis based on tin compounds. The two systems were prepared from the complex Sn(3-hydroxy-2-methyl-4-pyrone)$_2$(H_2O_2) by dissolving it in 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]) and supporting it in acidic resin. On the other hand, their recyclability run results showed that the multi-phase systems failed to achieve more than 1.0% yield.

Later, DaSilveira *et al.* [182] immobilized a complex of Sn(3-hydroxy-2-methyl-4-pyrone)$_2$(H_2O)$_2$ in 1-n-Butyl-3-methylimidazolium tetrachloro-indate ($BMIM^+.InCl_4^-$), and compared it with different catalysts. Their idea, of preparing these biphasic systems in ILs, seems to be based on the advantages of both ILs and heterogeneous catalysis. The catalysts tested in their work were lanthanide(III) chloride, cerium(III) chloride, barium(II), titanium(III), zirconium(IV), copper(II), magnesium(II), zinc(II), cadmium(II), platinum(IV), platinum(II), nickel(II), tin(II) and indium(III) chlorides, aluminum (III) and germanium(IV) oxides, copper(II) bromide, copper(I) iodide, $Na_2O_5(H_2O)$, Na_2SiF_6, and $BF_3.OEt_2$. However, all of these catalysts showed very low efficiency or almost failed to promote the reaction, giving only traces of biodiesel. When the tin complex was used in replacement of these catalysts, the highest conversion obtained was 83% after a 4 hour reaction, using 1.0% catalyst. From the work of Abreu *et al.* [184] and DaSilveira *et al*. [182] it seems that the use of biphasic systems is expensive because of the number of chemicals used for synthesizing the ILs and for the preparation of the complex mixtures.

Wu *et al.* [181] reported the first example of direct use of ILs as transesterification catalyst particularly acidic ones, such as 1-(4-sulfonic acid) propylpyridinium hydrogensulfate [HSO_3-PPyr][HSO_4], 1-(4-sulfonic acid) butylpyridinium hydrogensulfate [HSO_3-BPyr][HSO_4], 1-(4-sulfonic acid) propyl-3-methylimidazolium hydrogensulfate [HSO_3-PMIm][HSO_4], 1-(4-sulfonic acid) butyl-3-methylimidazolium hydrogensulfate [HSO_3-BMIm][HSO_4], and N-(4-sulfonic acid) propyl triethylammonium hydrogensulfate [HSO_3-PEt_3Am][HSO_4].

A well refined cottonseed oil was catalyzed by various Brønsted acidic ILs with pyridinium, imidazolium and ammonium cations, having butyl and propyl sulfonic acid group as side chains and hydrogen sulfate as anion. 1-(4-sulfonic acid) butylpyridinium hydrogensulfate showed the best catalytic performance with a conversion of 92% after 5 hours, at the optimum reaction conditions of a molar ratio of 12:1, catalyst concentration of 5.7 wt%, and 170 ºC.

More recently, Han *et al.* [128] prepared biodiesel from waste oil using acidic [HSO_3-BPyr)[HSO_4] as a catalyst. The testimony yield was found to be 93.6% using 6:1 molar ratio, and 6% catalyst concentration, at 170°C after 4 hours of reaction.

2.4. The mechanism and kinetics of transesterification

The general equation for transesterification reaction of TGs with alcohol in the presence of a catalyst is shown in equation 2.1. The overall process involves three consecutive-reversible reactions with intermediates formation of monoglycerides (MG) and diglycerides (DG) [11, 66, 185].

From the general equation of the chemical reaction, the stoichiometry for this reaction is three moles of alcohol are required to react with one mole of TGs, and one mole of ester is liberated at each step. However the reaction is reversible. Hence, the molar ratio of alcohol to oil is usually increased to 6:1, or more. This is to force the equilibrium to the right in order to obtain higher product yield [2, 15, 102, 111].

2.4.1. Reaction kinetics theory

Although the importance of biodiesel as the best substitute for petroleum fuel has grown in the last few years, the chemical kinetics of the alcoholysis reaction is still contentious. A few studies have discussed the kinetics for both acid and alkali-catalyzed alcoholysis of VOs. Those include the kinetics of transesterification of palm oil [186], soybean oil [132, 187], rapeseed oil [188], sunflower oil [189], and cottonseed oil [190]. To the best of the author's knowledge the kinetic study of IL-catalyzed transesterification of palm oil is a new study and has never been done before.

The transesterification reaction of TGs with alcohol in the presence of a suitable catalyst, to form three molecules of alkyl esters and one molecule of glycerol, is represented by the three equations. From equation 2.2, the first step is the formation of ester and DGs from the reaction of TGs and some excess of alcohol. The second step, shown in equation 2.3, is the conversion of DGs to MGs and ester, and equation 2.4 is the final step of the conversion of MGs to Gl and the third mole of ester [132, 187]. Various researchers have described the kinetics for acid-catalyzed [18, 187] and alkali-catalyzed [13, 132] transesterification reactions.

$$\text{TG} + 3\text{MeOH} \xrightleftharpoons{\text{catalyst}} 3\text{ME} + \text{GL} \tag{2.1}$$

Where R is an alcohol alkyl chain, R' is alkyl or alkenyl chain.

Diasakou *et al.* [191] recommended the overall thermal transesterification reaction to be divided into three consecutive-reversible reactions with intermediate formation of DGs and MGs. The stepwise reactions are:

$$\text{TG} + \text{MeOH} \xrightleftharpoons[k_4]{k_1} \text{DG} + \text{ME} \tag{2.2}$$

$$\text{DG} + \text{MeOH} \xrightleftharpoons[k_5]{k_2} \text{MG} + \text{ME} \tag{2.3}$$

$$\text{MG} + \text{MeOH} \xrightleftharpoons[k_6]{k_3} \text{GL} + \text{ME} \tag{2.4}$$

The general outline of the governing set of equations characterizing the forward and reversible reactions involved in the transesterification, without the shunt reactions, calculated from the TGs and the intermediates differential equations are as follows [192]:

$$\frac{d[\mathrm{TG}]}{dt} = -k_1[\mathrm{TG}][\mathrm{MeOH}] + k_4[\mathrm{DG}][\mathrm{ME}] \tag{2.5a}$$

$$\frac{d[\mathrm{DG}]}{dt} = k_1[\mathrm{TG}][\mathrm{MeOH}] - k_4[\mathrm{DG}][\mathrm{ME}] - k_2[\mathrm{DG}][\mathrm{MeOH}] + k_5[\mathrm{MG}][\mathrm{ME}] \tag{2.5b}$$

$$\frac{d[\mathrm{MG}]}{dt} = k_2[\mathrm{DG}][\mathrm{MeOH}] - k_5[\mathrm{MG}][\mathrm{ME}] - k_3[\mathrm{MG}][\mathrm{MeOH}] + k_6[\mathrm{GL}][\mathrm{ME}] \tag{2.5c}$$

$$\frac{d[\mathrm{Gl}]}{dt} = k_3[\mathrm{MG}][\mathrm{MeOH}] - k_6[\mathrm{Gl}][\mathrm{ME}] \tag{2.5d}$$

Then the overall differential equations of MeOH and ME giving 2.5e and 2.5f, respectively:

$$\frac{d[\mathrm{ME}]}{dt} = k_1[\mathrm{TG}][\mathrm{MeOH}] - k_4[\mathrm{DG}][\mathrm{ME}] + k_5[\mathrm{DG}][\mathrm{MeOH}] - k_5[\mathrm{MG}][\mathrm{ME}] + k_3[\mathrm{MG}][\mathrm{MeOH}] - k_6[\mathrm{Gl}][\mathrm{ME}] \tag{2.5e}$$

$$\frac{d[\mathrm{MeOH}]}{dt} = -k_1[\mathrm{TG}][\mathrm{MeOH}] + k_4[\mathrm{DG}][\mathrm{ME}] - k_5[\mathrm{DG}][\mathrm{MeOH}] + k_5[\mathrm{MG}][\mathrm{ME}] - k_3[\mathrm{MG}][\mathrm{MeOH}] + k_6[\mathrm{GL}][\mathrm{ME}] \tag{2.5f}$$

$$\frac{d[\mathrm{MeOH}]}{dt} = -\frac{d[\mathrm{ME}]}{dt} \tag{2.5g}$$

Where [TG], [DG], [MG], [ME], [GL] and [MeOH] denote the molar concentration of triglycerides, diglycerides, monoglycerides, glycerol, methylesters and methanol, respectively, and k_1, k_2, k_3, k_4, k_5, and k_6 are reaction rate constants.

2.4.2. Mechanism of acid catalyzed transesterification reaction

For the reaction process design, the chemical kinetics of transesterification is a very important issue. Biodiesel production using homogeneous acid-catalyzed transesterification is less preferred commercially due to the fact that alkali catalyzed transesterification was found to be faster than the acid catalyzed reaction. It can proceed approximately 4000 times faster than acid catalyzed transesterification for the same amount of catalyst used [15, 18, 187]. However, the use of acidic catalyst is more suitable for lower quality feedstocks that have relatively high quantity of FFA and water [15, 24, 193].

Transesterification can be catalyzed by homogeneous Brønsted acids, preferably sulfuric [194], hydrochloric [146], sulfonic [2], and phosphoric acids [195]. The mechanism of homogeneous acid catalyzed transesterification of VOs, presented in Figure 2.3, is proposed by many researchers [2, 17, 148, 196].

The reaction mechanism is a three step mechanism. The first mechanism involves protonation of the oxygen atom at the carbonyl functional group of the TG by the acid leading to carbocation.

The second mechanism is alcohol attack on the nucleophile, which causes proton migration and finally the breakdown of the tetrahedral intermediate. The same cycle of reactions occur for DG and MG. After repeating this cycle to the DG and MG, the GLYCEROL is eliminated by the intermediates to form new ester and to regenerate the catalyst (H^+A^-) [2].

After transesterification of TG, the product mixture will contain esters (main product), GLYCEROL (byproduct), excess of alcohol, catalyst residue and un-reacted tri-, di-, and mono-glycerides. However, obtaining pure esters is quite difficult, since these impurities are present in the esters [13].

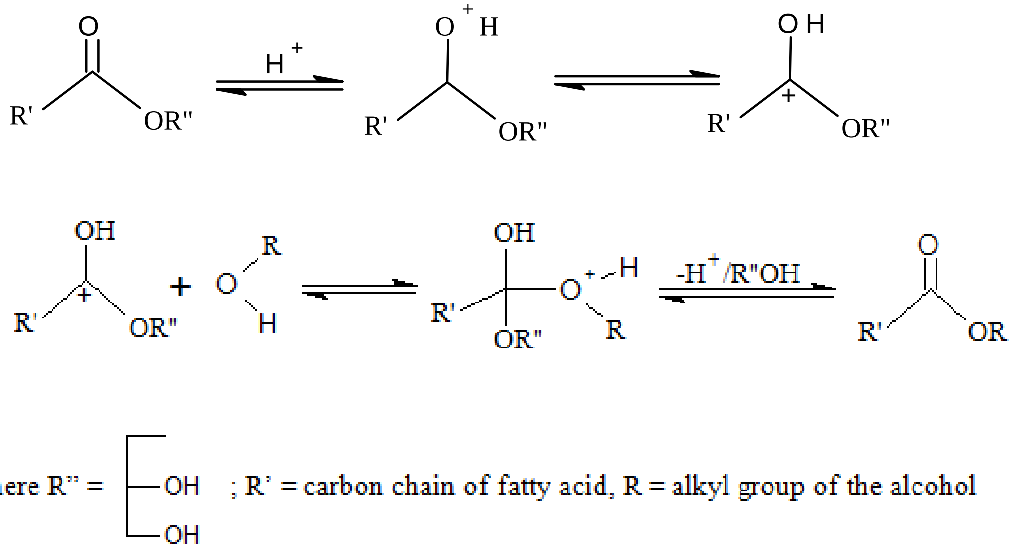


Figure 2.3 Mechanism of acid-catalyze transesterification of VOs. (Redrawn using literature reference [2]).

2.4.3. Mechanism of alkali catalyzed transesterification reaction

Ma and Hanna [13] described that alkali catalyzed transesterification is formulated based on a number of consecutive-reversible reactions.

The kinetic mechanism for alkali catalyzed transesterification reaction has been reported by several researchers [2, 18, 197]. The mechanism is formulated in four steps, as illustrated in Figure 2.4 [2, 14].

The pre-step involves the dissociation of alcohol to an alkoxide ion, when the catalyst is dissolved in alcohol. Then the nucleophile (RO$^-$) attacks the carbonyl carbon atom in the TG to form the tetrahedral intermediate in the first step. In the second step, the alkoxide ion is regenerated from the reaction between this tetrahedral intermediate with alcohol.

The last step involves the rearrangement of tetrahedral intermediate forming the fatty acid ester and DGs. The processes are repeated to yield MGs and production of Glycerol with concomitant release of biodiesel [2].

Pre-step

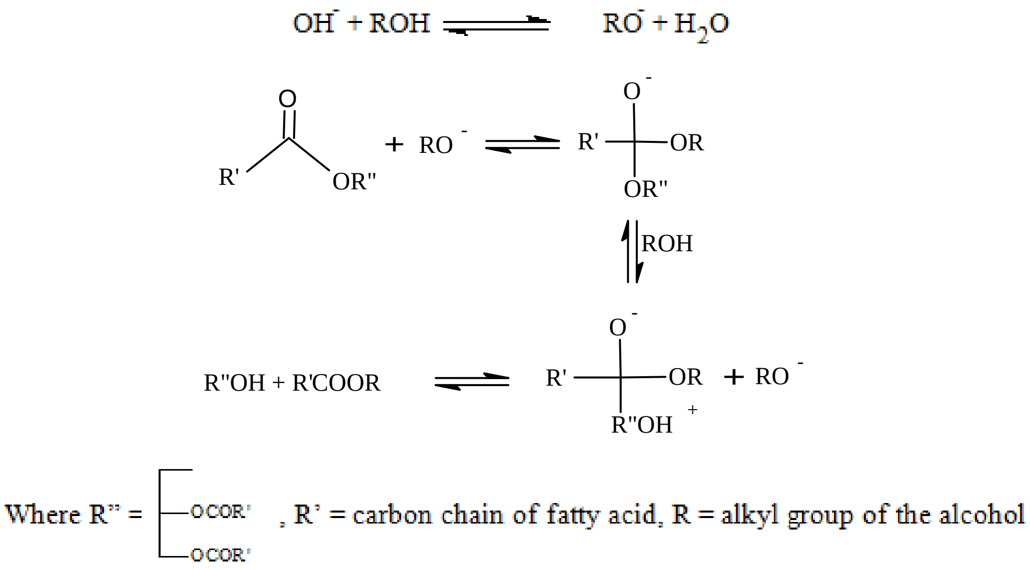


Figure 2.4 Mechanism of base-catalyze transesterification of VOs [2].

Freedman *et al.* [187] studied the kinetic order and rate constant of soybean oil transesterification, examining the effect of different alcohols, molar ratios, the effect two different types and concentrations of catalysts: acidic and basic, and different temperature range. They concluded that:

(i) With the two catalysts, the reaction followed pseudo-first-order kinetics with highest molar ratio. However, for alkali catalyst with the lowest ratio, the reaction followed consecutive second order reaction.
(ii) The reaction rate for alkali is much higher than acid catalyzed transesterification.
(iii) The rate constant increased with increasing catalyst concentration.
(iv) For all forward and reverse reactions, the activation energy can be determined from the plot of log k vs. 1/T (where k is the rate constant and T (K) is the temperature)**.**

Later, in a separate work, Noureddini and Zhu [132] and Darnoko and Cheryan [186] reported that base catalyzed transesterification is a second order reaction. Characteristically, the rate equation is dependent on the concentration of reactants. The complexity of feedstocks is one of the major difficulties associated with obtaining reliable kinetic parameters, and also poor miscibility of TGs and alcohol at the beginning of the reaction [132, 187, 189].

2.5. Biodiesel fuel from palm oil

Oil palm (*Elaeis guianensis*) originates from Africa. It grows well in humid places like Malaysia [198, 199]. In Southeast Asia, Malaysia have a rich oil palm industry and a huge quantity of palm oil trees, enough to supply for the domestic edible oil consumption and probably it to cater for its fuel consumption in the future. Palm oil production in Malaysia has increased from 2.57 million metric tons in the year 1980 to 14.96 million metric tons in 2005, and more than 3.79 million hectares of land are cultivated by oil palm [199, 200].

Palm oil, unlike other oils, is composed mainly of palmitic acid. Palmitic acid (C16:0) is a saturated (no double bond) fatty acid and contains equivalent amounts of saturated and unsaturated fatty acids. It is ready to be used for any research (laboratory tests or large scale continuous research) since it is available in stores all over Malaysia. According to their commercial brands, palm oils are available with different types of fatty acids content such as refined palm oil, crude, bleached and deodorized palm olein [96].

Palm oil is considered as one of the four leading VOs traded in the world oil market and it is cheapest in price compared to canola, rapeseed and soybean; making palm oil as the cheapest raw material for biodiesel production and as good ready substitution or blend for diesel fuel [145, 201]. Developing renewable energy resource is one of the Malaysian government strategies. The Malaysian government began a palm oil biodiesel project in 1982, where around 10% of total palm oil production has been allocated for the biodiesel research [202, 203]. Likewise, European Union is going to replace 20% of the total motor fuel consumption with biofuels by 2020; and currently, the fossil diesel blended with 20% of soybean biodiesel is available in the US market [24, 154].

In the area of biodiesel production technology, few works that uses crude palm oil as feedstock are found in the literature, while uncountable researches have been done for the well refined palm oil [192, 204, 205].

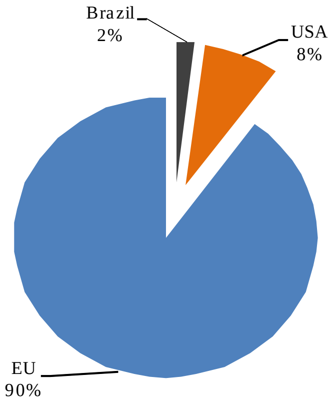


Figure 2.5 Overall biodiesel productions in the World in 2005 [203]

However, lower price feedstock is required, since biodiesel from food-grade oils is not economically competitive compared with petroleum based fuel [109]. As mentioned earlier, alkali catalyzed transesterification is faster than acidic ones, but the type of feed oil used controls the manner of the chemical process. This shows that alkali catalysts favors refined oil having low acid value, while crude oil having high acid value favors acidic catalysts. Crabbe *et al.* [206] transesterified crude palm oil (6.9 mg KOH/g) using concentrated H_2SO_4. Using a 5.0 % catalyst concentration, 95 °C and 23:1 ratio of methanol to oil, the ester yield was 82.0 %. At this concentration and temperature, the yield increased to 96.7 % when the ratio was increased to 40:1. When the catalyst amount was increased from 1.0 % to 5.0 %, the yield increased gradually from 52.0% to more than 80.0%. The effect of temperature was investigated too, at 75, 80 and 95°C using 5.0 % catalyst concentration and molar ratio of 40:1 for a period of 24 hours. Their results showed increasing rate of reaction as the temperature increased.

Prateepchaikul *et al.* [207] reduced the CPO-FFA level to less than 2 wt% in 60 min at 70 ºC, using 3-5 wt% of H_2SO_4. Similarly, Jansri *et al.* [208] reduced the FFA level in CPO to less than 1.0 wt% within 30 s by using the stoichiometric molar ratio of methanol to oil (3:1), temperature of 60 ºC and catalyst concentration of 0.8 wt%.

More recently, Prateepchaikul *et al.* [123] designed a continuous esterification reactor to reduce the FFA content of CPO. In order to optimize the four important reaction variables, a 5-level, 4-factor, central composite design was employed to overcome the removal of acidic waste water formed during the esterification using H_2SO_4 as catalyst. Their technique showed ease of waste separation in a simple continuous separator. Since the FFA content is less than 1.0%, this could make the acidified CPO suitable to be used in subsequent transesterification reactions.

The heterogeneous catalyst was studied for palm oil transesterification and found to be effective, giving high palm oil biodiesel yield [83, 209]. Krisnangkura and Simamaharnnop [204], during the transesterification of palm oil at 70°C with sodium methoxide, observed that the conversion yield increased with the alcohol ratio.

Most studies of palm oil transesterification have looked into conversion rate, homo and heterogeneous catalytic activity, changes in product composition during reaction, reaction kinetics and quality of the produced palm biodiesel. However, none has dealt with using ILs for biodiesel production from crude palm oil.

As such other related aspects of IL catalyzed transesterification such as biodiesel and esters yields and the influence of reaction parameters such as molar ratio of alcohol to oil, IL concentration, reaction temperature, reaction time and the agitation speed are not presented anywhere.

2.6. Chromatographic methods for determination of biodiesel composition

Gas chromatographic method is usually used to analyze the compositions of the starting materials [21, 120] and the transesterification products of GL, MG, DG, TG, as well as calculating the yield and quantity of esters [2]. While other analytical methods such as HPLC [210], enzymatic method [211], and TLC/FID [212] are used to determine the biodiesel constituents.

HPLC has the advantages of small sample volume, does not require sample derivatization, and less analysis time is required [23]. Although HPLC method is found to be operationally superior to GC technique, it has been found to be less accurate and sensitive to the FFA content, than the GC method [210].

Enzymatic method is another method used for analyzing the Glycerol content in biodiesel and to test for completeness of the transesterification reaction. This method is quite complex and does not have good reproducibility. It is no longer available commercially [213, 214].

A combination of TLC with FID is also a known chromatographic method for the analysis of biodiesel, and the first analysis was reported by Freedman *et al.* [63]. In spite of the ease of application of the TLC-FID technique, it has a lower accuracy and sensitive to humidity. In addition, the instrument is expensive [23].

Several researchers reported the use of GC with flame ionization detectors (FID), to determine the specific class of contaminants in biodiesel in order to study the kinetics of transesterification and the variables affecting ester yield [215, 216, 217]. To achieve useful GC results (of biodiesel contents); a sample needs to be derivatized with specific reagent because the Gl, MG and DG contain free hydroxyl group and these materials are not detectable by FID [2].

Theoretically, the biodiesel contents can be analyzed on highly inert columns coated with polar stationary phases without derivatization. However, the MG, DG, and Gl having free hydroxyl groups can cause some difficulties in the GC performance and progress. Accordingly, derivatization by trimethylsilylation of free hydroxyl groups in the biodiesel can improve their performance significantly, and offers a better resolution with comparable properties, gets better ruggedness of the procedure, and obtains excellent peak shapes with acceptable recovery and low detection limits [2, 23].

Most reports on the silylation of partial glycerides demonstrated that silylation can be achieved by using N-methyl-N-trimethylsilyl-trifluoroacetamide (MSTFA) [218] or bis-trimethylsilyl trifluoroacetamide (BSTFA) [2] under different conditions.

2.7. Biodiesel standards

Table 2.4 European standards for pure (100%) biodiesel for vehicle use [23, 161]

Property	Limit	Units	Test method
Density; 15º C	860–900	kg/m^3	EN ISO 3675, EN ISO
Kinematic viscosity; 40º	3.5–5.0	mm^2/s	EN ISO 3104, ISO 3105
Flash point	120 min	ºC	EN ISO 3679
Sulfur content	10.0 max	mg/kg	EN ISO 20884
Carbon residue (10%	0.30 max	%(mol/mol)	EN ISO 10370
Cetane number	51 min	–	EN ISO 5165
Sulfated ash	0.02 max	%(mol/mol)	ISO 3987
Water content	500 max	mg/kg	EN ISO 12937
Total contamination	24 max	mg/kg	EN ISO 12662
Oxidative stability, 110ºC	6.0 min	h	EN 14112
Acid value	0.5 max	mg KOH/g	EN 14104
Iodine value	120 max	g I_2/100 g	EN 14111
Linolenic acid content	12.0 max	%(mol/mol)	EN 14103
Methanol content	0.20 max	%(mol/mol)	EN 14110
MAG content	0.8 max	%(mol/mol)	EN 14105
DAG content	0.8 max	%(mol/mol)	EN 14105
TAG content	0.2 max	%(mol/mol)	EN 14105
Free glycerine	0.02 max	%(mol/mol)	EN 14105, EN14106
Total glycerine	0.25 max	%(mol/mol)	EN 14105
Group I metals (Na + K)	5.0 max	mg/kg	EN 14108, EN14109
Group II metals (Ca +	5.0 max	mg/kg	prEN 14538
Phosphorus content	10.0 max	mg/kg	EN 14107
Pour point	–	ºC	ISO 3016
Heating value	–	MJ/kg	DIN 51900-2

With the increasing interest and use, the development of reliable standards of biodiesel properties and quality has become of paramount interest to facilitate its commercialization and market acceptance.

The pure biodiesel (100%) properties must be satisfied and generally conformed to the international standards for alternative fuels, shown in Table 2.4 and 2.5, without compromising on the durability of engine parts [4, 15]. Accordingly, the European biodiesel standards, DIN EN 14214 has been established and developed in 2003. In 2002, ASTM D6751-02 was adopted in the United States (US).

In the year 2006, the ASTM standard was finalized and updated to ASTM D6751-03, in which the acid value standard, which measures the free fatty acid content, was reduced from 0.8 to 0.5 mg KOH/g (see Table 2.5). Following that, the standard was adopted in other regions around the world including South Africa, Australia, Brazil, and elsewhere [23, 219].

Table 2.5 ASTM standard for pure biodiesel [23, 219]

Property	Limit	Units	Test method
Flash point	130 min	ºC	D 93
Water and sediment	0.05 max	% volume	D 2709
Kinematic viscosity, 40 ºC	1.9–6.0	mm^2/s	D 445
Sulfated ash	0.02 max	% mass	D 874
Sulfur(S15)	0.0015 max	% mass (ppm)	D 5453
Copper strip corrosion	No. 3 max	–	D 130
Cetane number	47 min	–	D 613
Cloud point	Report	ºC	D 2500
Carbon residue	0.05 max	% mass	D 4530
Acid number	0.5 max	mg KOH/g	D 664
Free glycerin	0.02	% mass	D 6584
Total glycerin	0.24	% mass	D 6584
Phosphorus content	0.001 max	% mass	D 4951
Distillation temperature, atmospheric equivalent temperature, 90% recovered	360 max	ºC	D 1160

Table 2.4 presented the specifications in the EN standards, and Table 2.5 listed the corresponding information for the ASTM standards, both for pure alternative diesel fuel. Some biodiesel specifications are carried over from petrodiesel standard tests. However, not all of these tests are well suited for biodiesel analysis [23].

2.8. Selection of ionic liquids for this research

Developments in the field of reaction catalysis are being reported continually, in the form of preparation of novel catalytic reactions and alternative methodologies to synthesize materials that are commercially accepted. Many efforts have been given to develop promising catalytic systems in which easy separation of products and reusability of catalyst is possible, along with high reactivity and selectivity.

Ionic liquids (ILs) are new, important class of organic salts that are gaining great amount of interest as the media for performing many types of chemical reactions with some notable results [220, 221]. These liquids can be obtained by coupling a great number of different organic cations and anions. The combinations of these cations and anions allow tailoring of the physicochemical properties of ILs to adapt to specific chemical reactions. The most widely used cations are quaternary ammonium cations [29], heterocyclic aromatic compounds [222], phosphonium [223] and pyrrolidinium cations [224], with a variety of inorganic anions [183]. Figure 2.6 shows the most common classes of ILs.

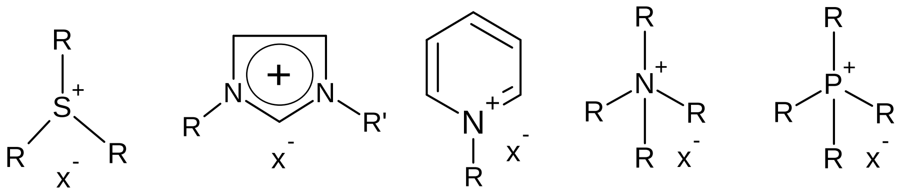


Figure 2.6 Structure of typical ionic liquids. R, R’ = e.g., methyl, propyl, butyl, octyl. x = e.g., Cl, Br, HSO_4, H_2PO_4, PF_6, BF_4.

There are two different classifications for the IL anions: those which give polynuclear anions, e.g. $AlCl_4$ and Al_2Cl_7, and fluorous anions, e.g. BF_4 and PF_6. Even though BF_4 and PF_6 are the two types of anion commonly used in most IL applications, their disadvantage is that they decompose to HF in the presence of water [29]. Moreover, the fluorinated anions have a tendency to be expensive. In the response to cost and safety concerns, new ILs with non-fluorous ions have been developed. In the preparation of these ILs, anions are derived from economical bulk chemicals. Alkylsulfate anions are considered as the most popular non-fluorous anions for their nontoxic and biodegradable properties [29].

Generally, IL is a salt where one of the anion or cation, or both are large, while the cation having low degree of symmetry. This factor contributes to their lower melting point. ILs are recognized as designer solvents since the design and choice of ionic liquids is commonly focused on their physical properties, which can be customized to suit the exact process needs. Properties such as viscosity, thermal stability, conductivity, melting point, density and hydrophobicity are always verified by the anion type and structure [30, 225]. ILs are often referred to as environmental friendly since they have essentially no vapour pressure at normal temperatures and they have high thermal stability. The overall properties of ILs result from the composite properties of the cations and anions; including superacidity, basicity, hydrophilicity, water miscibility and hydrophobicity. However, the effects of chemical structure of ILs on various characteristics are still poorly understood [54].

Several methods of ionic liquid synthesis have been described by a number of researchers using a simple setup of round-bottom flask equipped with a reflux condenser and, in order to prevent water and air from entering the reaction processes, the reaction should be protected by a blanket of nitrogen or any other inert gases [26]. However, according to Ohno [226], there is no particular method for the synthesis of any kinds of salt from a mixture, especially in preparing new ILs.

The usual methodologies used in the synthesis of ILs are three basic techniques: a two-step quaternization-metathesis reaction, acid-base neutralization (protonation), and direct combination [29]. Some typical preparation techniques for ILs are given in Figure 2.7 [26]. Alkylammonium, pyridinium and imidazolium halides can be easily prepared through quaternization reaction by mixing amine, pyridine and imidazole, respectively, under heating and stirring with the appropriate halogenoalkane and solvent. The solvent and reaction conditions applied are very dependent on the nature of the reactants [226]. Also, the reaction temperature and time are dependent on the halogenoalkane and length of alkane used. The reactivity of alkyl iodide is greater than alkyl bromide, which is more reactive than alkyl chloride. The reactivity of halogenoalkane decreases with increasing alkane chain length [26].

Referring to the reaction scheme in Figure 2.7, after the quaternization of a halide salt, the metathesis reaction of a halide salt of the organic cation (b) with group I elements in the periodic table or ammonium salt would offer desired anion of the same ionic liquid. Metathesis of cations is still the easiest way to synthesize such materials and it is considered an efficient method to synthesize water-miscible ILs. However, besides the large quantities of solid by-product produced, it can only be used for limited range of valuable salts [26, 183].

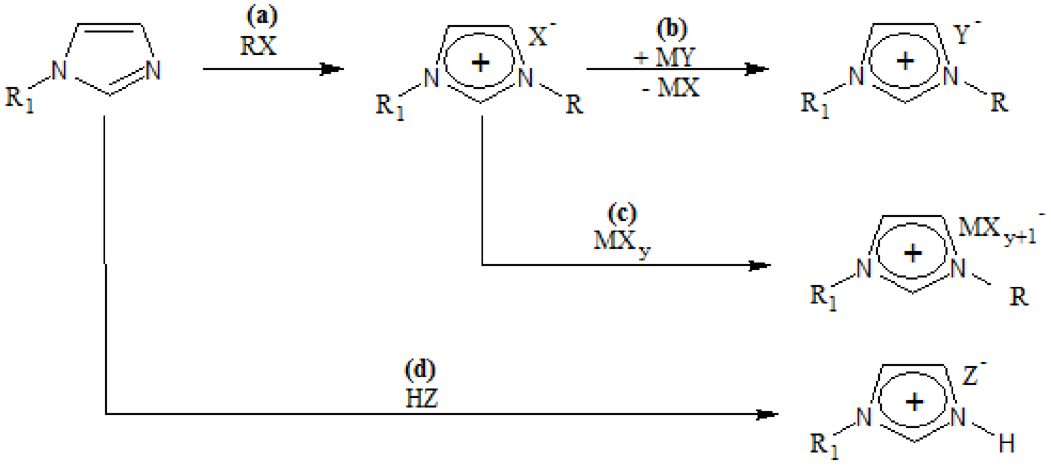


Figure 2.7 Typical preparation routes for ILs [26, 226].

The halide salt bonded with organic cation (c) may react with a Lewis acid [183], as shown in Figure 2.7. The first Lewis acid based ILs was obtained in 1951, by treating halide salt with Lewis acid [26].

The protonation reaction (d) illustrates the first method applied in 1914 by Walden to synthesize ethylammonium nitrate by the neutralization of aqueous ethylamine with nitric acid [26]. Those neutral ILs were found to be excellent solvents for the Diels-Alder reaction and showed considerable rate improvement over molecular solvents [30].

New synthetic paths for preparing ILs, sometimes called second generation ionic liquids, by direct combination of cation and halide-free anion have recently emerged [227, 228]. Bonhote *et al.* [229] synthesized 1-ethyl-3-methylimidazolium triflate and 1-ethyl-3-methylimidazolium trifluoroacetate by alkylating N-methylimidazole with ethyl triflate and ethyl trifluoroacetate, respectively. Arce *et al.* [230] synthesized 1-ethyl-3-methylimidazolium ethyl sulfate by reacting equimolar of 1-methylimidazole and diethyl sulfate in toluene under helium blanket. A colourless oil of 1,2-diethyl-3-methylpyrazolium tetrafluoroborate was prepared by AbuLebdeh *et al.* [231] by reacting N-ethyl-3-methylpyrazole with triethyloxonium tetrafluoroborate.

The application of ionic liquids in catalysis is not without problems, one being remaining halide impurities in the product. Halide contamination results from the metathesis reaction of salts commonly used to prepare ionic liquids. Despite this, the designing of highly pure ionic liquids that exhibit specific properties to enhance catalytic activity is gaining increasing attention [232].

The design of task-specific ionic liquids (TSILs) containing functional groups is going to push the limitations of ionic liquid in the field of catalysis [232]. As an example, Liu *et al.* [233] designed new ionic liquids of functionalized alkane sulfonic acid group based dialkylimidazolium containing an alkyl sulfate as anion, to improve the melting point, viscosity, acidity, and to avoid of the formation of HF or HCl. Figure 2.8 shows some functionalized ionic liquid cations that has been developed for many catalyzed applications [37, 232, 233].

Most of the published articles in the field of ILs purity reported that standard spectroscopic measurements is sufficient to ensure that the ILs are free of any unreacted starting materials, residual, solvents or any other impurities [26].

Figure 2.8

2.9. Economic overview of ionic liquid-catalyzed transesterification

2.9.1. Current problem in biodiesel production

Any material that contains fatty acids can easily produce biodiesel, even though the qualities might be different. Various vegetable oils and fats, animal fats, waste greases and edible oils can be used as feedstocks for biodiesel production. However, the feedstock selection is based on many factors, such as local availability, economic considerations and government support [234].

The biodiesel market is considered especially well-established in the United States and the European Union. Between 2000 and 2005, the worldwide production of biodiesel increased by 295% (see Figure 2.9), indicating that there is more interest in the production of this fuel.

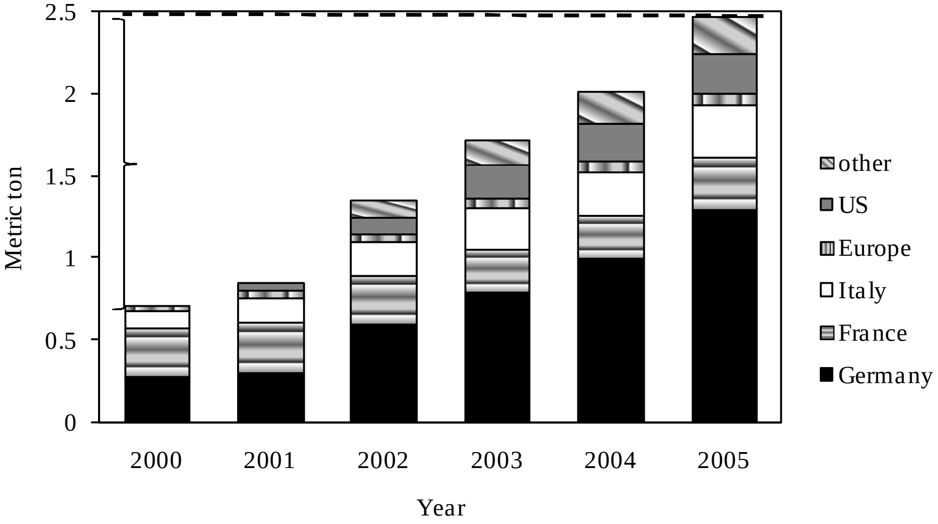


Figure 2.9 Biodiesel production during the years 2000 – 2005 in biodiesel producing countries [203].

In Malaysia, biodiesel production reached 2.6 million tons in the year 2007, and currently there are three operating biodiesel plants and ten more under construction. The Malaysian Government took more steps to enhance future production capacity by granting another 32 licenses for biodiesel plants, with a prospective capacity of 5.0 million ton/year [203].

Despite several advantages of using biodiesel, the high production cost mainly due to expensive feedstock is the major obstacle preventing its commercialization [7, 18, 235]. Thus economic considerations are the key driving force behind the development of cheap feedstocks for biodiesel production. The factors associated with the high production cost of biodiesel are discussed following this.

2.9.2. Factors affecting the production cost

2.9.2.1. The feedstock cost

From the viewpoint of transesterification reaction, highly refined vegetable oil is the best starting material to produce biodiesel because the conversion of pure TG to FAME is high and the reaction time is relatively low [24].

Nowadays, beside the technical aspects, the economic possibility is becoming more and more important due to the possibility of future biodiesel production plants [9]. However, all projects to date have shown that biodiesel produced from refined vegetable oil is more expensive, about 10 to 50% more than petroleum-based diesel fuel. Zhang *et al*. [121], and Leung and Guo [21] reported that the cost of raw materials accounted approximately between 70 to 95% of the total cost of biodiesel production. Haas *et al*. [234] estimated the cost of feedstock to be 88% of total biodiesel production cost for soybean oil. Thus other feedstocks options are being evaluated by several researchers, instead of the highly refined oil. Among others include crude vegetable oil and recycled waste feedstock as the acceptable ways to lower the biodiesel production cost [19, 20].

In fact, to date no plants have been designed to produce commercial biodiesel from oils containing high FFA by acid-catalyzed process [22]. Marchetti and Errazu [236] projected a technical and economic outlook on acid catalyzed process for high FFA feedstock. They assessed the costs involved in producing 36,036 ton/year of biodiesel involving spent oil with 5% of free fatty acid with an alkaline process with acid pre-esterification of FFA, a homogeneous acid-catalyzed process, and a continuous heterogeneous process using solid resins as catalyst.

Their processes described the economical analyses and covered all cost details with consideration of all additional costs for producing biodiesel using conventional catalytic technology. Similarly, Sakai *et al.*, [237] assessed the economic feasibility of producing biodiesel from waste cooking oil for the capacity range from 1452 to 14,520 ton/year using four processes.

The four processes assessed were KOH catalyzed and hot water purification process, KOH catalyzed and vacuum FAME distillation process, CaO catalyzed and hot water purification process, and CaO catalyzed and vacuum FAME distillation process. Among these four processes, continuous heterogeneous acid-catalyzed process had the lowest manufacturing costs.

2.9.2.2. Byproduct benefits

As the production cost can be developed by the type of feedstock employed, it can be developed by the value of glycerol produced and by changing the process chemical technology. The process chemistry and technology are believed that there are other considerations for reducing the production cost of biodiesel, such as the viability of a continuous transesterification process and high recovery of valuable glycerol [234, 238, 239]. Canakci and Gerpen [67] estimated a production cost of $1.58/gal from refined soybean feedstock, without including the profits can be gained from the sale of glycerol.

2.9.2.3. Catalyst removal cost

For applicable fuel in the market, the produced biodiesel must be purified to meet international specifications. Both alkali and acidic homogeneous catalyzed processes require water to neutralize the catalyst and to purify the biodiesel as well as the glycerol [236]. This waste water affects the biodiesel recovery and creates some soap during the purification step [21]. In order to decrease waste water, several types of catalysts have been investigated, such as the, supercritical process [167, 240], enzymatic process [241, 242], and heterogeneous catalyst process [155, 156]. The literature review illustrates the drawbacks in using those catalyst systems.

The optimized cost should include not only ester formation rate, but also separation efficiency and recovery cost [148, 196].

2.9.2.4. Biodiesel production units design

Traditional acid catalysts are difficult to recycle and they also give rise to serious environmental and corrosion problems. According to Freedman *et al.* [187], alkali catalysts are less corrosive than the acidic ones; therefore carbon steel can be used when the NaOH concentration is less than 50 wt% with temperature up to 95 °C. However, Zhang *et al*. [121] used stainless steel reactor for KOH catalyzed transesterification reaction.

As for H_2SO_4, many researchers recommended the use of stainless steel for H_2SO_4 concentration of below 5 wt% and temperature below the acid boiling point. Stainless steel type 316 has been recommended as an acceptable corrosion material for 5.0 wt% H_2SO_4 and temperatures below 100 °C, while for temperatures between 50-100 °C and H_2SO_4 concentrations less than 60 wt%, stainless steel type alloy 20 was found to have good corrosion resistance [22].

2.9.3. Economic viability of IL catalyzed transesterification of crude palm oil

2.9.3.1. Crude palm oil price

Figure 2.10 shows price comparison of diesel fuel against biodiesel produced from refined palm oil and other vegetable oils. The Figure shows that the prices of biodiesel either from palm oil or other vegetable oils are still expensive compared to the diesel price.

Comparing the prices of biodiesel from the three different sources, palm biodiesel shows the cheapest price; this indicates that palm biodiesel has better economic potential than the other indicated oils. Among the four leading vegetable oils traded on the world market, CPO is much cheaper than canola, rapeseed or soybean [206]. In October 2008, the price of CPO was approximately half (55%) of the price of crude soybean oil [243].

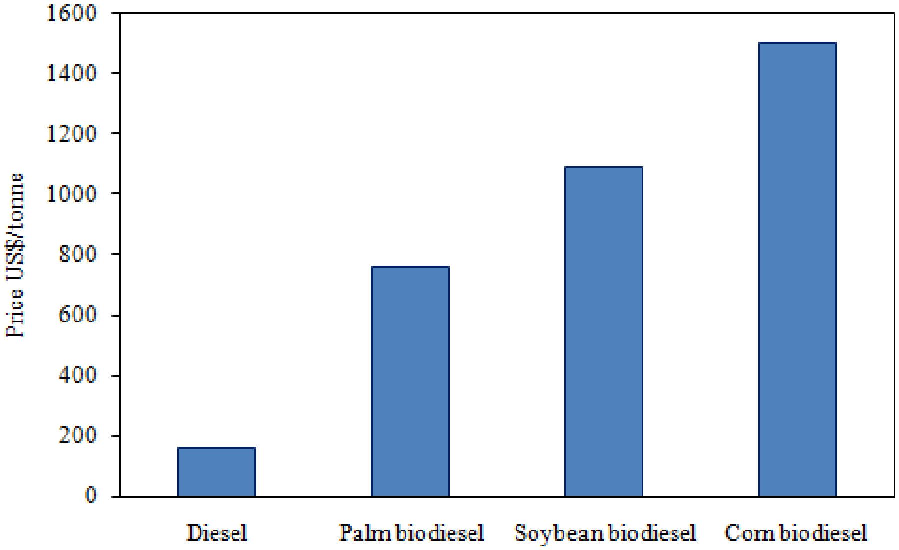


Figure 2.10 Prices of diesel fuel and biodiesel from different sources [201].

2.9.3.2. Benefits of IL catalyzed transesterification

Although the overall economics of biodiesel production depend on feedstock costs [21], there are other considerations that must be taken into account, such as the process cost, i.e. purification, and chemical used.

As mentioned, low cost feedstock requires special chemicals such as mineral homogeneous catalysts to treat the presence of high FFA, and to lead direct catalysis for the transesterification.

H_2SO_4 is a typical example of a "non-green" process because of many problems, such as safety aspects [183]. Besides, the high operating costs, which includes the removal of acid catalyst and waste water from the esters reactor [78]. These will add extra costs to the production cost and become another important factor affecting the biodiesel price.

The replacement of problematic mineral homogeneous acidic catalysts with ILs catalysts, which are non-corrosive, separatable, recyclable, leading to continuous processing, less waste water formation [30], along with environmental benefits would greatly solve many problems, and these problems have significant effects in the production cost:

(i) The IL catalyzed system will reduce the number of reaction (i.e., performing simultaneous FFA esterification and TG transesterification).

(ii) Would solve problems such as expensive separation and purification steps of traditional acid catalyzed transesterification.

(iii) No neutralization steps needed for stopping the reaction progress.

(iv) No pre-esterification step required with the ILs, allowing for more economical continuous processing.

(v) Along with the biodiesel, the IL-catalyzed transesterification may offer a higher purity glycerol due to ease of glycerol recovery and its immiscibility with IL, allowing it to be sold at a more competitive price. The valuable glycerol would reduce the production cost by ~6% [234].

(vi) Although ILs are expensive compared to conventional catalysts as much as 15 times approximately than the price of KOH [128], however, another advantage lies in the reusability of the catalyst. Experimental works conducted in this research indicate that the ILs can be recycled more than 8 times with similar catalytic activity. This recyclability can reduce its production cost to 1/8 (or more), which makes it competitive.

(vii) ILs are generally much less corrosive than their relative traditional ones [244]. So the materials used for designing the transesterification reactors and the other units will not be affected by the contact with ILs, even at high temperatures. This will reduce the capital cost of equipment, as well as reducing the environmental problems associated with traditional processes [45, 172].

(viii) Today, RTILs are a growing market that will drive domination of imidazoles in the coming years. As the use of RTILs becomes more common, more industries will demand bulk quantities at lower prices. The common usage of RTILs will seek improvements in the cost of imidazole RTIL products and will make the industry more willing to adopt RTILs as replacements for organic solvents, and for applications in catalytic systems.

2.10. Summary

In recent years, RTILs have attracted great interest as promising catalyst. However, not many works have been done in the synthesis of biodiesel using those catalysts.

Chris [62] in his patent, transesterified refined oil with 1-ethyl-3-methylimidazolium hydrogensulfate, assisted by microwave irradiation to increase the rate of reaction as well to the increase product yield. In the process, microwave irradiation was also used to ensure completion of reaction. However, the content of free fatty acids increased in vegetable oil during heating in microwave oven [245], which complicated the reaction process. Azcan and Danisman [246] considered the use of microwave irradiation as uneconomical for biodiesel production due to its impracticality for commercial scale production and safety concerns.

Another study was conducted by Wu *et al.* [181] using Brønsted acidic ILs. Their published work discussed three based cations of pyridinium, imidazolium and ammonium with functionalized SO_3H chain and HSO_4^- as anion. Although they studied the catalytic activity change by changing the sulfonated side chain, however, they did not study the effect of changing the alkyl chain linked to the cation, which is able to affect the acidity behavior of ILs that is still missing from the literature. Their work was done mainly with refined cottonseed oil.

Recently, only Han and his co-workers [128] studied the waste oil transesterification using commercial ILs with alkane sulfonic side chain. They have discussed well the reaction parameters that effect transesterification. They tested the catalytic activity of pyridinium with functionalized SO_3H chain and HSO_4^- as anion. Although, their biodiesel preparation steps were analyzed by an HPLC, the method was founded to be less accurate and sensitive to the FFA content compared to GC method [210].

More recently, Liang *et al.* [247] reported a yield of 98.5 % from transesterification of refined soybean oil using triethylammonium chloroaluminate $[Et_3NHCl][AlCl_3]$. Unfortunately, chloroaluminate ILs are considered to have low solubility, corrosive, and difficult to be separated from the ester product [30, 248].

From the review of the various available techniques of biodiesel synthesis using ILs, there are many ideas were followed:

1. Transesterification method is found to be the popular suitable technique. For this reason it was applied in this research.

2. The acid-catalyzed transesterification, using traditional or IL, was always associated with high reaction temperature, high amount of alcohol, and longer reaction time, while the agitation intensity depends on the contact between the oil in alcohol, which depends on the miscibility between the alcohol/catalyst mixture and the feedstock. However, in using the IL, a high viscosity factor has to be considered.
3. Triethylammonium and methylimidazolium based cations have been studied for biodiesel production. However, to the best of the author’s knowledge, pyrazolium ILs and ammonium and imidazolium with different side chains are absent from the literature.
4. As the feedstock used in this project having high FFA For biodiesel analysis, GC technique with derivatization was proven to be less sensitive to the FFA content and more accurate than the other techniques.