CHAPTER 3

RESEARCH METHODOLOGY

This chapter concentrates on the synthesis of several water-stable Brønsted acidic ionic liquids based on imidazolium, ammonium and pyrazolium cations with two different alkyl side chains linked with two different alkane sulfonic acid group chains and a hydrogensulfate anion.

The experimental part is divided into two parts, as summarized in Figure 3.1, the synthesis of ILs for the transesterification reaction of crude palm oil, and the synthesis and characterization of the synthesized biodiesel. Using known transesterification technique, biodiesel was synthesized from crude palm oil in the presence of methanol. For each trial, one of the 24 synthesized ILs was used as catalyst.

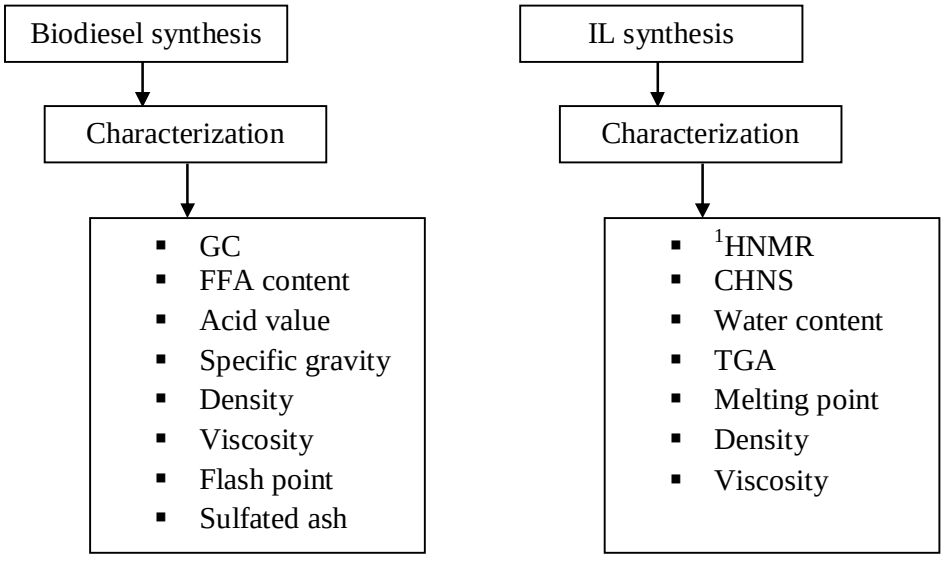


Figure 3.1 Flow diagram of IL synthesis and biodiesel characterization

In order to investigate the capability of the ILs to catalyze the transesterification of CPO, many experiments were carried out. As well as, to determine the process variables that could affect the yield of palm oil methyl ester; such as types of ILs and their concentrations, reaction temperature and molar ratio of methanol to CPO (v/v). The reaction kinetics of the investigated oil and biodiesel were also studied.

3.1. Synthesis of ionic liquids

3.1.1. Materials and chemicals

Table 3.1 lists all the chemicals used in the first part of the experiments, and their physical properties. All chemicals were used without drying or any further purification.

Table 3.1 Chemicals used for synthesizing ILs

Chemical name	Purity	Mw (g/mol)	b.p. (°C)	Brand
1,3-Propanesultone	≥99.0%	123.15	180	Aldrich
1,4-Butanesultone	≥99.0%	136.17	165	Fluka
1-Methylimidazole	≥99.0%	82.11	198	Sigma
1-Butylimidazole	99.0%	124.19	197	Aldrich
1-Methylpyrazole	Synthesis	82.11	126	Merck
Pyrazole	≥98.0%	68.08	-	Fluka
Triethylamine	99.5%	101.19	88.8	Fluka
Diethyl methylamine	≥97.0%	87.17	64	Aldrich
Sulfuric acid	≤98.0%	98.08	290	Sigma
Diethyl ether	99.9%	74.12	34.6	Sigma
2,4,4-trimethyl-1-pentene	99.9%	112.2	101.2	Aldrich
Toluene	99.8%	92.14	110.6	Sigma-Aldrich
Acetone	99.9%	58.08	56.5	Sigma-Aldrich

Figure 3.2. General synthesis procedures.

Figure 3.2. General synthesis procedures.

3.1.2. Synthesis of RTILs

As mentioned earlier, there are many problems appears during using the ILs in catalysis. These problems including that the halide routes ILs remaining halide impurities in the product and the formation of hazardous HF or HCl resulted during from the metathesis reaction of salts commonly used to prepare ionic liquids [37, 232].

In this project, a recent synthetic path of direct combination for preparing ILs was followed without using the metathesis step. The design of functionalized ILs may reveal high conversion and the ILs are not requiring extensive purifications since no byproduct was produced along with the IL. Moreover this method may well able to improve the acidity, and to avoid of the formation of HF or HCl.

In order to study the cation behavior towards the acidity behavior of the IL, imidazole, pyrazole and ammonium were used. Since the anion was considered as it's playing a major rule of acid/base behavior, alkane sulfonate side chain and hydrogen sulfate were applied as two different anions.

Figure 3.2 presents typical synthesis routes of Brønsted ILs of imidazolium, pyrazolium and ammonium, at different conditions. The synthesis routes for each RTILs are given separately in Appendix A.

The reactions were conducted in a three neck round-bottom flask fitted with a reflux condenser, magnetic stirrer under N_2 gas blanket. All materials were taken by syringe and the injections were done under gentle stirring and degassing.

All the ILs were synthesized in a two step reaction; first forming zwitterionic intermediate ILs, and the second step combining with sulfuric acid. The product yield was calculated quantitatively and the purity was assessed by ^{1}H NMR spectroscopy.

3.1.2.1. Synthesis of 1-Methyl-3-(3-sulfopropyl) imidazolium hydrogensulfate

1-Methyl-3-(3-sulfopropyl) imidazolium hydrogensulfate ($MSPIMHSO_4$) was synthesized according to the two step reaction as shown in Figure 3.3.

In a typical procedure, 2.7 ml or 0.03 mole of 1,3-propanesultone was dissolved in 15 ml anhydrous toluene in a dried round-bottom flask under vigorous stirring followed by dropwise addition of equal molar amounts of N-

methylimidazole, i.e. 2.4 ml, under cold condition. The mixture was slowly heated up to 60 ºC for a period of 2 hours.

Then, a biphase was formed and the white solid zwitterion was filtrated from the upper phase containing toluene and unreacted reactants. The filtrated white solid was washed thoroughly with toluene (4×10 ml) and vacuum dried at 0.01 mmHg and 80 ºC for 12 h, giving 1-methyl-3-(propyl-3-sulfonate) imidazolium (MPSIM) (6.06 g).

Under vigorous stirring, 4.1 g or 0.02 mole of MPSIM was firstly dissolved in 11 ml of deionized water and then stoichiometric amount of concentrated sulfuric acid (1.1 ml) was added dropwise, slowly at room temperature. The reactant mixture was then slowly heated up to 80 ºC for a period of 3 hours.

After removing water, followed by washing with diethyl ether and trimethylpentene and then vacuum dried at 0.01 mmHg and 80 ºC for 12 h, a viscous yellow liquid of $MSPIMHSO_4$ (5.81 g) was obtained.

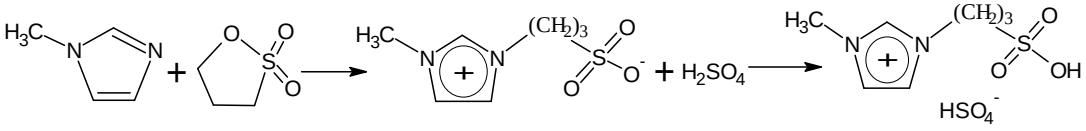


Figure 3.3 Typical path for the preparation of $MSPIMHSO_4$.

3.1.2.2. Synthesis of $MSBIMHSO_4$

A Brønsted $MSBIMHSO_4$ was synthesized according to the scheme given in Appendix A-1. Under vigorous stirring, 3.6 ml or 0.035 mole of 1,4-butanesultone and 10 ml of anhydrous toluene were charged into a 100 ml round-bottom flask in an ice bath. Equal molar of 2.8 ml of N-methylimidazole was added slowly over a period of 20 min. After that, the mixture was slowly heated up to 70 ºC for a period of 3 hours. The precipitate formed was collected by filtration.

The white precipitate was washed thoroughly with toluene (4×10 ml) and vacuum dried at 0.01 mmHg and 80 ºC for 12 h, resulting in 7.3 g of MBSIM. The zwitterionic white solid, required to give the desired $MSBIMHSO_4$, was dissolved in

DI and reacted with equal-mole H_2SO_4 using a procedure similar to the second step used for the $MSPIMHSO_4$. A viscous yellow liquid of 95.4 % yield was obtained.

3.1.2.3. Synthesis of $BSPIMHSO_4$

$BSPIMHSO_4$ was synthesized according to the two step reactions given in Appendix A.2. Under vigorous stirring, 3.6 ml of 0.04 mole of 1,3-propanesultone and 15 ml anhydrous toluene were charged into a 100 ml round-bottomed flask in an ice bath. Equal molar of 5.4 ml of N-butylimidazole was dropped slowly over a period of 30 min.

Then, the mixture was slowly heated up to 70 ºC. After 6 h a biphase was formed; the upper phase containing toluene and unreacted reactants was decanted. The lower heavy viscous oil phase was washed thoroughly with 10 ml toluene for three times. Then, the yellow wax/semi-solid was re-crystallized from acetone to yield a zwitterion white solid which was dried under vacuum at 0.01 mmHg and 40 ºC for 3 h, resulting in BPSIM.

$BSPIMHSO_4$ with yield of 95.0 wt% was obtained as a light yellow viscous liquid using the procedure similar to the second step used in section 3.2.1.1.

3.1.2.4. Synthesis of $BSBIMHSO_4$

$BSBIMHSO_4$ was synthesized according to the two step reaction given in Appendix A.3. To a vigorously stirred mixture of 5.1 ml of 0.05 mole of 1,4-butanesultone and 10 ml anhydrous toluene at 0 – 5 ºC, equal molar of 6.6 ml N-butylimidazole was added dropwise, over a period of 30 min. After the dropping was completed, the mixture was slowly heated up to 80 ºC for 10 h.

Then, the toluene layer was decanted and the remained heavy viscous oil was washed with 10 ml toluene for three times. Then, the yellow wax/semi-solid was re-crystallized from acetone to yield a zwitterion white solid which was dried under vacuum at 0.01 mmHg and 40 ºC for 3 h, resulting in BBSIM with 92 wt% yield. The synthesis of 94.9 wt% of a yellow viscous $BSBIMHSO_4$ was carried out from the combination of BBSIM and H_2SO_4 according to the second stage procedure described in section 3.2.1.1.

3.1.2.5. Synthesis of $SPPHSO_4$

A 5.3 ml/ 0.06 mole of 1,3-propanesultone and 18 ml anhydrous toluene were charged into a 100 ml round-bottomed flask in an ice bath. Equimolar of 4.168 g of pyrazole, after it has been dissolved in 8 ml anhydrous toluene, was dropped slowly to a stirred propanesultone solution over a period of 35 min.

Then, the mixture was slowly heated up to 80 ºC for 12 h. The white precipitate, collected by filtration, was washed thoroughly with 15 ml of toluene and vacuum dried (0.01 mmHg and 80 ºC) for 12 h, resulting in 10.4 g of PSP. The synthesis of a heavy yellow viscous $SPPHSO_4$ of 94.5 wt% yield was carried out from the combination of PSP and H_2SO_4 according to the second stage procedure described in section 3.2.1.1. The reaction scheme is given in Appendix A.4.

3.1.2.6. Synthesis of $SBPHSO_4$

The respective zwitterionic white solid of BSP was synthesized following the steps for synthesizing SPP, by reacting stoichiometric amounts of 1,4-butanesultone and pyrazole. However, the reaction took longer time (16 h) to achieve an 88.9 wt% yield. The heavy yellow viscous liquid of $SBPHSO_4$, with 95 wt% yield, was obtained by combining BSP and H_2SO_4 (see Appendix A.5) according to the second stage procedure described in section 3.2.1.1.

3.1.2.7. Synthesis of $MSPPHSO_4$

A 4.4 ml of 0.05 mole of 1,3-propanesultone and 15 ml of anhydrous acetone were charged into a 100 ml round-bottomed flask in an ice bath. Equal molar of 4.2 ml of 1-methylpyrazole was dropped slowly over 30 min to a vigorously stirred

propanesultone solution. Then, the mixture was slowly heated up to 80 ºC for 16 h. The white precipitate, collected by filtration, was washed several times with acetone and vacuum dried at 0.01 mmHg and 40 ºC for 3 h, resulting 89.1 wt% of MPSP. The synthesis of a colourless viscous liquid of $MSPPHSO_4$, in 91.9 wt% yield, was carried out from the combination of MPSP and H_2SO_4 (see Appendix A.6) according to the second stage procedure described in section 3.2.1.1.

3.1.2.8. Synthesis of $MSBPHSO_4$

A yield of 90.5 wt% of $MSBPHSO_4$ was obtained in the same manner as the procedure described in section 3.2.1.7 by two direct combination steps (see Appendix A.7).

3.1.2.9. Synthesis of $DEMSPAMHSO_4$

Under vigorous stirring, 5.3 ml of 0.06 mole of 1,3-propanesultone and 10 ml anhydrous acetone were placed into a 100 ml round-bottomed flask in an ice bath. Equal molar of 7.6 ml of diethyl methylamine was dropped in slowly. Then, the mixture was heated up to 40 ºC for a period of 48 hours. Upon completion, the toluene was decanted and the remained white solid was washed with toluene for several times, and then mixed with acetone. The flask was frozen in the refrigerator for 24 h. After filtering the zwitterion crystals, they were air dried to evaporate off the acetone and then were further dried under vacuum at 760 mm Hg and 40 ºC for 3 h. A yield of 90 wt% of DEMPSAM was obtained.

$DEMSPAMHSO_4$, a yellow viscous liquid, was synthesized by combining DEMPSAM and H_2SO_4 according to the second stage procedure described in section 3.2.1.1. A yield of 94.1 wt% was obtained. The chemical reaction is as shown in Appendix A.8.

3.1.2.10. Synthesis of $DEMSPAMHSO_4$

DEMSBAMHSO$_4$ was synthesized as the same manner as DEMSPAMHSO$_4$ (see Appendix A-9), giving an intermediate zwitterion white solid of DEMBSAM in the first step and a yellow viscous of DEMSBAMHSO$_4$ in the second step.

3.1.2.11. Synthesis of TESPAMHSO$_4$

TESPAMHSO$_4$ was synthesized in the same manner as DEMSPAMHSO$_4$, giving an intermediate zwitterion white solid TEPSAM in the first step and a yellow viscous of TESPAMHSO$_4$ in the second step (see Appendix A-10).

3.1.2.12. Synthesis of TESBAMHSO$_4$

TESBAMHSO$_4$ was synthesized as the same manner as DEMSPAMHSO$_4$, giving an intermediate zwitterion white solid TEBSAM in the first step and a yellow viscous of TESBAMHSO$_4$ in the second step (see Appendix A-11).

3.1.3. CHNS analysis

The carbon, hydrogen, nitrogen and sulfur percentages in ILs were analyzed according to the approved method ASTM D-5291 by employing Leco-CHNS-932 analyzer. The solid samples of less than 2 mg each were covered in silver capsule and then analyzed while the liquid ones were analyzed in silver capsules containing sorbit pad.

The equipment settings were as follows; Oxygen Dose: 20 cc, oxidation furnace temperature: 1000 °C, reduction furnace temperature 650 °C, and helium was used as the carrier gas for the measurement.

3.1.4. Compounds decomposition and melting point measurements

The most efficient method for melting point determination is the differential scanning calorimetry (DSC). Though, the realization of thermal behaviors of many known ILs is relatively complicated [26].

A Perkin Elmer Pyris II differential scanning calorimetry (DSC) instrument was used to detect the thermal behavior of the prepared ILs following the procedure described by Song *et al*. [249], in a sealed aluminum pan. The sample of ≤ 10 mg was firstly cooled to -60 °C from ambient temperature, and then the sample was scanned from -60 ^{o}C to 150 ^{o}C at heating rate of 10 °C/min, under a flow of nitrogen. The results obtained are presented in Table 4.2.

Thermogravimetric measurements were conducted using Perkin Elmer TGA, Pyris I to investigate the thermal stability of the prepared ILs and the CPO. A sample of ≤ 10 mg held in a capped Al pan was heated at a heating rate of 10 ºC/min from 50 ºC to 600 ºC at a heating rate of 10 ºC/min under nitrogen flow [222]. The experimental decomposition temperatures are presented in terms of weight loss (%) and TG (ºC) in Figures 4.4, 4.5 and 4.6.

3.1.5. ILs density, viscosity and water content measurements

Other important properties of ILs such as water content, density and viscosity were determined due to their direct effect on the reactivity of IL catalyst during the transesterification reaction. Both the absolute viscosity and kinematic viscosity were analyzed by SVM 3000 Anton Paar viscometer. As shown in Equation 3.1 below, the sample density (ρ) was calculated according to the relationship between the absolute viscosity (η) normalized by the kinematic viscosity (υ) of the same sample [26]. The water content of ILs was determined by coulometric Karl-Fisher titration technique [250]. Triplicate measurements were performed for all samples.

$$\upsilon = \frac{\eta}{\rho} \quad \text{(3.1)}$$

3.2. Biodiesel synthesis and characterization

3.2.1. Materials and Chemicals

The raw material used in this work is CPO and was collected from Felcra Nassaruddin Factory in Perak, Malaysia. The chemicals used in this part were: the reference standards; lauric acid methyl ester (C12:0), myristic acid methyl ester (C14:0, 99%), palmitic acid methyl ester (C16:0, capillary GC grade), stearic acid methyl ester (C18:0, 99%), oleic acid methyl ester (cis-C18:1, capillary GC grade), linoleic acid methyl ester (C18:2, 99%), methyl heptadecanoate (esters internal standard), 1,2,4-butanetriol (ISTD1), tricaprin [(1,2,3-tricaproylglycerol], (ISTD2) (8 mg/ml)]; were purchased from Supelco, USA.

Other chemicals including MSTFA, 1-monopalmitin (99%) (5 mg/ml), 1,3-dipalmitin (99%) (5 mg/ml), 1,2,3-tripalmitin (99%) (5 mg/ml), anhydrous methanol (≥99.8%), n-hexane (GC grade, >99.0%), and n-heptane (GC grade, >99.0%) were purchased from Sigma-Aldrich Company (Malaysia). All chemicals were used without drying or any further purification.

3.2.2. Pre-treatment of CPO

The CPO found to be contaminated with water and solid particles. Since water creates a problem during transesterification, CPO was pre-treated before the reaction by heating to above 100 ºC for 1 h [251].

Solid particles of CPO were removed by a centrifuge. Water was removed by mixing CPO with 10 wt% silica gel followed by stirring the mixture and vacuum filtration using Whatman filter paper for the removal of silica gel [252]. This step was performed three times to ensure complete removal of the water present in the CPO.

3.2.3. Determination of CPO properties

The physicochemical properties of the feedstock oil were determined. The CPO density was measured with an Anton Paar DMA5000 instrument, kinematic

viscosity was determined using an Ubbelohde glass viscometer while the FFA content in terms of acid value of the raw oil was determined by titration.

The fatty acid composition was determined according to the test methods of AOCS Ce 1-62 and Ce 2-66 [253] using Agilent Hewlett-Packard 6890 series gas chromatograph with flame ionization detector. SP-2340 capillary column (60 m in length, 25 mm of internal diameter, and 0.2 μm film thickness) and split ratio of 100:1 was used. Before injection, the samples were diluted 100 times in n-hexane. The oven temperature programming was: initial temperature 150 ºC held for 1.5 min, then increased to 210 ºC at 3 ºC/min and maintained for 0.5 min, finally increased to 240 ºC at the same rate and maintained for 8 mins. The detector and injector were maintained at 240 ºC. The carrier gas was high-purity helium (>99.95 mol%) with a flow rate of 0.8 ml/min. Each sample was analyzed three times.

3.2.4. Transesterification reactions

Figure 3.4 shows the apparatus used for the transesterification reaction. It consists of a 250 mL dry 2-necked round bottom flask batch reactor, assembled with a double reflux condenser, an oil bath, and a hot plate with stirrer. The reactor was immersed in a constant-temperature silicon oil bath, which is capable of maintaining the reaction temperature within ±1.0 ºC. Each experiment was carried out in triplicate in order to determine the variability of the results and to evaluate the experimental errors. The arithmetical averages and all experimental data are reported as the mean value ± standard deviation.

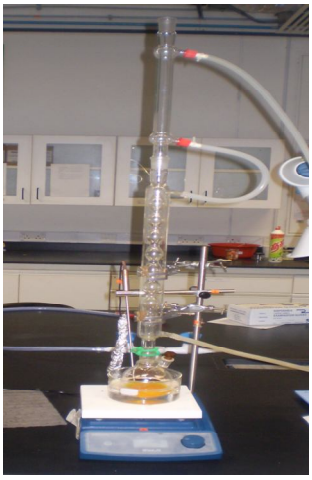


Figure 3.4 Transesterification reactor setup

The reactor was initially charged with fixed mixture of the catalyst and methanol. Under agitation, the methanolic solution was heated up to a predetermined temperature. Then, the desired amount of oil (25 g), at the same reactor temperature was added.

The reaction was timed as soon as CPO was added into the catalyst-methanol solution. When the reaction had reached the pre-set time, heating and stirring were stopped and the mixture was transferred to a separatory funnel. The mixture was left to stand for 6 hours to allow the products to separate by gravity. With traditional acidic catalyst, usually two distinct liquid phases will be observed: glycerol in the upper layer and esters in the lower layer. However with IL catalyst, it was observed that as soon as the reaction stopped, dissimilar layers appeared: esters in the upper layer, and glycerol in the lower layer, indicating that the viscous IL might be mixed with glycerol. This is the cases with the ammonium and imidazolium catalysts. However with heavy viscous pyrazolium salts, the product was separated into clear three layers: esters in the upper, glycerol in the middle, and IL in the lowest layer. In all cases, the product was separated into three phases after cooling down.

In all experiments, after removing the glycerol layer, the methanol was recovered by BÜCHI rotary evaporator under reduced pressure. The general procedure for preparation of palm biodiesel using IL as catalyst is shown in Figure 3.5. The final stage of the transesterification reaction is the purification step, which involves purification of the remaining homo-catalysts and IL-catalysts.

3.2.4.1. Removal of homo-acidic catalyst

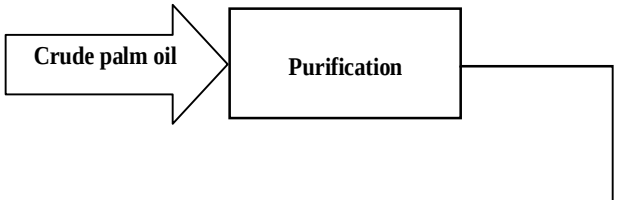
The separated crude ester phase was quenched with cold deionized water several times to remove glycerol, methanol residuals and the catalyst (H_2SO_4) until the washed water became clear [21, 63]. Then the excess water in the ester phase was removed by evaporation at atmospheric conditions.

3.2.4.2. IL catalyst recovery

The whole procedure for the transesterification of CPO with ILs is shown in Figure 3.5. After the transesterification of triglycerides, traces of IL was removed from the separation funnel and the esters upper layer was isolated by phase separation from the water, glycerol and methanol.

Then it washed off with 5 ml of cold deionized water, three times to ensure that the IL was completely separated from the POME. Also, ethyl acetate and ethanol, in the same volume ratio, were used as washing solvents in comparison with deionized water. The reaction would stop completely when the IL residue in the product mixture has been removed during this process. Subsequently the washing solvent (deionized water, acetate or ethanol) was removed by evaporation and the remaining IL was collected for reuse.

The purification process is shown in detailed in Figure 3.6. The lower layer possibly consisted of IL residue, methanol and unreacted oil mixed with glycerol. The glycerol, IL, and methanol are extremely soluble in water, whereas biodiesel is not [13]. After evaporation of the produced water and recovering the methanol, the remaining glycerol and IL showed two immiscible layers, therefore, the separation of lower layer IL from glycerol was easy.



To ensure total IL recovery, the glycerol layer was washed repeatedly with ethyl acetate and the IL was separated by decantation. Then, the recovered IL catalyst was washed with acetone several times, and then vacuum dried (0.01 mmHg

and 40 ºC) for 3 h before reuse it. The washed esters, after drying under vacuum in a rotary evaporator, were stored at 5 ºC for further analyses [254, 255]. The same conditions were applied for all experimental runs except for the variables being investigated.

The product yield was calculated after purification of the product mixture. The esters after distilled from the final product, was analyzed by GC to calculate the esters content and to determine the quality of biodiesel.

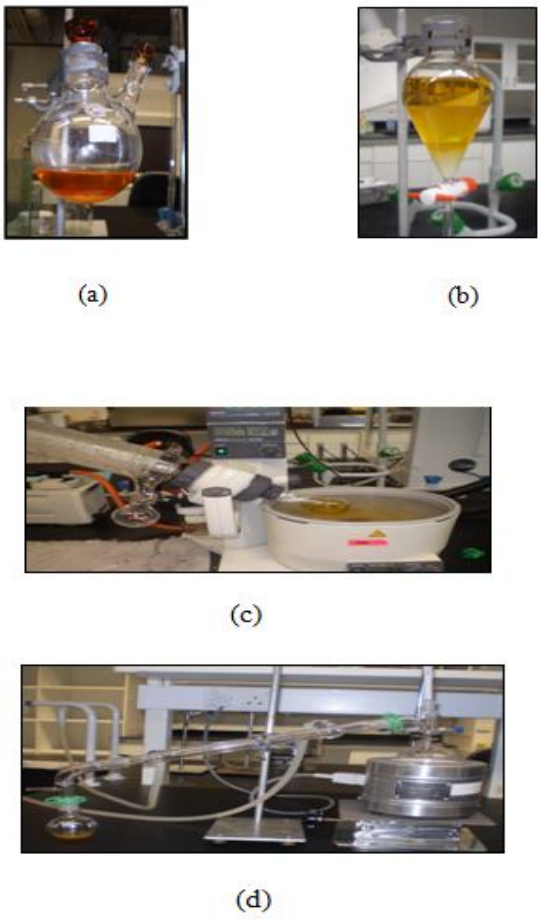


Figure 3.6 Separation processes (a) Precipitation of IL; (b) Settling; (c) Evaporation; (d) POME distilation

The parameters affecting product yield, as mentioned earlier, molar ratio of alcohol to oil, mass ratio of catalyst to oil, reaction temperature, time, and agitation speed were varied. The effect of each parameter was investigated individually, each time only one parameter was changed while keeping the others constant. The best

value of the investigated parameter was determined, and this optimal value was used for the optimization of the next parameter.

3.2.4.3. POME distillation

The distillation process was carried out in order to purify the esters from the residue produced during the reaction or present in the oil. It was performed in a 500 mL one-neck round-bottom flask, equipped with a thermometer, a receiver flask, and condenser connected to a vacuum pump. The vacuum was adjusted to 40 ± 5 mmHg [154]. The POME collection started at 187 ºC, and the distillation was terminated when no more distillate was seen in the receiver flask.

3.2.5. IL solubility tests

The solubility of 5.0 wt% of $BSBIMHSO_4$ in CPO, POME and CPO/methanol mixtures was measured analytically at a temperature range of 40 to 170 °C. The experiments were carried out in capped sample tubes.

3.2.6. Determination of Methyl ester and glycerides composition

3.2.6.1. Calibration

The four component types (ME, MG, DG, and TG) were calibrated using stock solutions of 1-monopalmitin, 1,3-dipalmitin, and tripalmitin in pyridine. A stock solution of tricaprin was used as internal standard. Relevant amounts of solutions were quantified according to the reference method described by BS EN 2003 [256]. The four standard solutions were added in a 20 mL separate sampling vials, and then, using a microsyringe, 100 µl of MSTFA was added to each of the four calibrated solutions.

The vials were closed hermetically to avoid moisture contact, shaken vigorously, and allowed to stand for 20 mins at room temperature. Before injection

into the gas chromatograph, the samples were diluted with 8 ml n-heptane, according to the BS EN method [256].

3.2.6.2. Sample preparation

In a 10 ml vial, 0.1 g of homogenized sample was added. Then, 80 µl of ISTD1, 100 µl ISTD2 and 100 µl of MSTFA stock solutions were mixed with the sample in the same vial. The vial was capped, shaken vigorously and stored at room temperature for 15 mins. The concentrated stock mixture was diluted in 8 ml of *n*-heptane before injecting 1.0 µl of the reaction mixture.

3.2.6.3. Thin Layer Chromatography (TLC)

As a supplement to GC analysis, thin layer chromatography was used for qualitative analysis to detect the presence of ester, free fatty acid, mono-, di- and triglyceride in the product samples, which indicates the changes in product compositions during the transesterification reaction, and the distribution extent of various components in the reaction system [21]. Fractionation was achieved using hexane and diethyl ether as developing solvent with ratio of 90:10 (v/v) [257]. The samples were diluted in ethyl acetate, and then it was spotted on the TLC silica plate. Iodine chamber was used for visualization.

Figure 3.7 shows a TLC plate with several spots indicating the presence of methyl ester, triglyceride, free fatty acid, diglyceride and monoglycerides in the biodiesel sample.

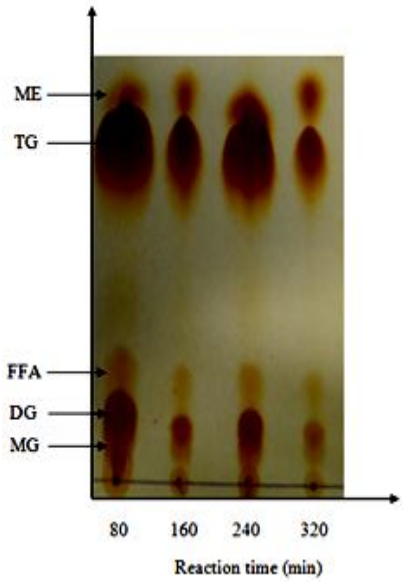


Figure 3.7 TLC result for biodiesel produced using $BSBIMHSO_4$ as catalyst

3.2.6.4. Gas Chromatography (GC)

Internal standard, tricaprin (ISTD2) was used to determine the response factor (RF) of glycerides (MG, DG and TG) for the reference standards of monopalmitin, dipalmitin and tripalmitin. The MSTFA was used as silylating reagent to make the MG and DG volatile enough for GC analysis [168]. All reference retention times and relative retention times corresponding to their peaks are given in Table 3.2.

The derivatized samples were analyzed in duplicate to determine the concentration of palm oil methyl esters, monoglycerides, diglycerides, and triglycerides by gas chromatography.

Table 3.2 The retention times of glycerol and glycerides standards for GC

Standard	Retention Time (min)	Relative Retention Time (RRT)
Glycerol	4.698	0.75
ISTD 1	5.841	1.00
Monopalmitin (MG)	17.234	0.68
ISTD 2	19.995	1.00
Dipalmitin (DG)	21.365	1.21
Tripalmitin (TG)	25.474	1.61

The analysis was performed on a Shimadzu Gas Chromatograph (GC-2010) equipped with AOC-20i automatic injector and flame ionization detector (FID), using SUPELCO SGE HT-5 capillary column with length of 10 m, internal diameter of 0.32 mm and coated with 0.1 μm film thickness of 100% dimethylpolysiloxane. The temperature programming for the analysis was: initially 50 ^{o}C stabilized for 1 min, increased to 180^{o}C at 15 °C/min, then increased to 230 °C at 7 °C /min, next increase to 370 °C at 10 °C/min and was held at 370 °C for 5 mins.

The total analysis time was about 30 mins to ensure complete elution of glycerides. The carrier gas was high-purity helium (≥99.95 mol%) set at a flow rate of 3 ml/min and a split ratio of 100:1 was used. The detector temperature was 380 °C. 1.0 μL of the sample was injected automatically into the GC.

3.2.6.5. Glycerides percentages calculation

The percentages of individual glycerides, MG, DG and TG in the sample were expressed from the corresponding calibration plot using its slope and y-intercept, can be calculated, using the following expressions, (3.2a), (3.2b), and (3.2c), respectively, [257, 258]:

$$M = \left[a_m\left(\sum A_{mi}/A_{ei2}\right) + b_m\right] \times \left(M_{ie2}/M_s\right) \times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(3.2a)}$$

$$D = \left[a_d\left(\sum A_{di}/A_{ei2}\right) + b_d\right] \times \left(M_{ie2}/M_s\right) \times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(3.2b)}$$

$$T = \left[a_t\left(\sum A_{ti}/A_{ei2}\right) + b_t\right] \times \left(M_{ie2}/M_s\right) \times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(3.2c)}$$

Where:

M, D, T = the MG, DG and TG percentage (m/m) of in the sample;

$\sum A_{mi}$, $\sum A_{di}$, $\sum A_{ti}$ = the sums of the peak area of the MG, DG and TG;

A_{ei2} = peak area of internal standard 2;

M_{ei2} = mass of internal standard 2 (mg);

M_s = mass of sample (mg);

a_m and b_m are constants coming from regression method for monoglycerides;

a_d and b_d are constants coming from regression method for diglycerides; and

a_t and b_t are constants coming from regression method for triglycerides.

Referring to BS EN 14105, 2003 method [256], the content of free glycerol was calculated using the following expression:

$$G = \left[a_g(A_g/A_{ei1}) + b_g\right] \times (M_{ei1}/M_s) \times 100 \quad \ldots\ldots (3.3)$$

Where:

G = the percentage (m/m) of free glycerol in the sample;

A_g = peak area of glycerol;

A_{eil} = peak area of internal standard 1 (mg);

M_{ei1} = mass of internal standard 1 (mg);

M_s = mass of sample (mg); and

a_g and b_g are constants from the regression method for glycerol.

And, the percentage of total glycerol was calculated using the method prescribes by EN 14214, as follows:

$$G_T = G + 0.255\,M + 0.146\,D + 0.103\,T \quad \ldots\ldots (3.4)$$

Where:

G_T = the percentage (m/m) of total glycerol in the sample;

G = the percentage (m/m) of free glycerol in the sample;

M = the percentage (m/m) of MG in the sample;

D = the percentage (m/m) of DG in the sample; and

T = the percentage (m/m) of TG in the sample.

The basis of the standard test methods of EN 14106/ EN14105 and EN14105, limited the amount of free glycerol and total glycerol in the form of glycerides in biodiesel sample to be $\leq$ 0.02 wt% and $\leq$ 0.25wt%, respectively [23]; for the reason that the combustion of glycerol in biodiesel could lead to acrolein formation [259]. The average of measured free glycerol and total glycerol percentages of the distilled biodiesel samples are provided in Chapter 5.

3.2.7. Palm Biodiesel quality

3.2.7.1. FFA content

The FFA content was determined by titration using the approved AOCS Official Method Cd 3d-63 [253] in terms of acid value of the samples.

The samplings were done manually. The samples taken from the reaction mixture were washed with distilled water to stop the reaction, and to separate the IL and methanol from the mixture. Then, according to the method detailed in the literature [236], the samples were centrifuged for 30 mins to develop the phase separation.

A weighted amount of the sample was dissolved in a mixture of isopropyl alcohol and toluene. Phenolphthalein (1.0 % in isopropyl alcohol) was used as indicator. The mixture was then titrated with suitable increment of 0.02 N alkaline solution of KOH. The amount of consumed KOH in the titration, after equilibrium, was used to calculate the acidity using the following equation:

$$Acid\ value, mg\ KOH/g\ of\ sample = \frac{(A - B) \times (N \times 56.1)}{W} \quad \cdots\cdots\cdots\cdots (3.5)$$

Where:

A = volume of alkali solution employed for titrating the sample (mL),

B = volume of alkali solution employed for titrating the blank (mL),

N = KOH solution normality, and W = weight of sample (g).

3.2.7.2. Viscosity

Viscosity is one of the most significant properties of any fuel as it indicates the ability of the oil to flow and its effect can be seen in the quality of atomization and combustion as well as engine wears [260]. The kinematic viscosity of CPO was measured at 40^{o}C by Cannon Ubbelohde capillary viscometer, according to ASTM D445 method [261].

3.2.7.3. Density and Specific gravity

The testing procedures were based on ASTM 287 [261], where the density was measured at 15.6°C using Bingham Pycnometer, while CPO density was determined with an Anton Paar DMA5000 instrument. The fuel specific gravity (SG) is used as

a predecessor to other fuel properties such as heating value, viscosity, density and cetane number (Yuan *et al*., 2004). The SG was determined according to ASTM D 4052 [261], using Bingham Pycnometer. The SG value was calculated as in equation 3.6:

$$SG = \frac{\text{Sample density}}{\text{Water density}} \qquad (3.6)$$

3.2.7.4. Flash point

The flash point is an important parameter for the handling, storage, and safety of fuels and flammable materials and limits of alcohol content [262, 263]. It is known as a temperature of which the fuel becomes a mixture that will ignite when exposed to a spark or flame, as described in ASTM D 93 [261].

3.2.7.5. Sulfated ash

The sulfated ash for POME was determined using the test method ASTM D 874 [23, 261].