CHAPTER 5

SYNTHESIS OF PALM BIODIESEL

5.1. Characterization of CPO

The CPO was characterized in terms of its physical and chemical properties and the results are presented in Table 5.1. As seen in Table 5.1, the viscosity of CPO is very high at 43.4 mm^2/s. The high viscosity of CPO is due to the presence of high molecular weight triglycerides and large chemical structures [252, 272]. The FFA was calculated in terms of acid value and the value is higher than the specified acid value for alkali catalyzed reaction, as mentioned in chapter 2.

Table 5.1 Physical and chemical properties of Crude palm oil (CPO)

Property	CPO
Density at 15ºC (g/cm^3)	0.9983
Kinematic viscosity at 30ºC (mm^2/s)	43.4
Acid value (mg KOH/g)	6.98
FFA (%)	3.50
Water content (w/w%)	0.02
Mean molecular weight (g/mol)	845.6

5.2. Solubility of $BSBIMHSO_4$ in CPO

Trial experiments were carried out to determine the solubility of 5.0 wt% $BSBIMHSO_4$ in three different solvents of pure CPO, POME and in CPO using methanol as co-solvent.

Experimental results show that the synthesized ILs are not miscible with CPO and POME, even at 170 °C. $BSBIMHSO_4$ remained un-dissolved even when excess solvent, CPO and POME were used, the mixtures remained as separated layers. Since the solubility of IL in CPO requires the presence of a co-solvent to make the IL-catalysis viable and to simplify the contacts between the involved reaction phases, methanol was chosen as the co-solvent.

Since it is presented as one of the reactants for the transesterification, the use of methanol as co-solvent reduces the number of chemicals inside the reactor and the reaction media viscosity too. This enhances the possibility of reaction to occur since the reaction medium is in two-phase instead of three-phase. A two-phase system of CPO-methanol/IL-methanol is able to proceed faster because there is better diffusion between the catalyst, alcohol and oil [273, 274].

The miscibility of $BSBIMHSO_4$ in CPO was studied in the range of 40 – 170 °C and a miscibility curve is plotted as a function of methanol concentration (wt%) against temperature as presented in Figure 5.1. From the curve, a maximum miscibility is observed at 90 °C; as indicated in the graph at this temperature only 2wt% of methanol is required to dissolve the IL in CPO. From 40 to 90 °C, the miscibility increase with temperature as fewer methanol is required to assist the dissolution of IL in CPO.

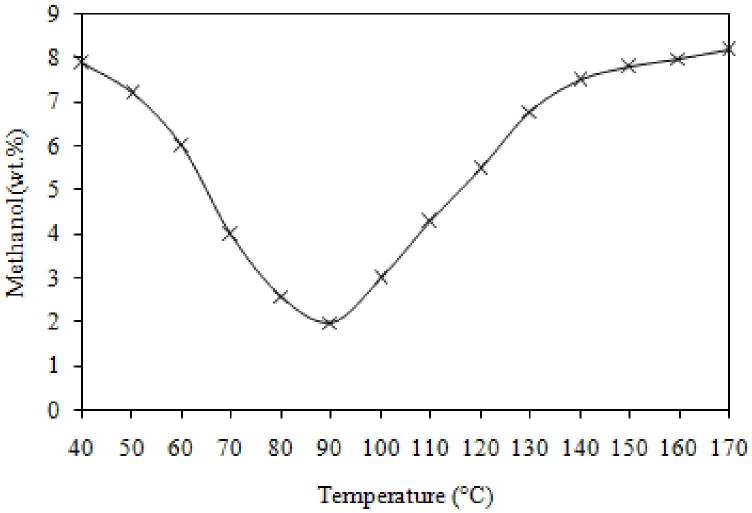


Figure 5.1 Effect of methanol amount on the solubility of IL in CPO. The IL/CPO mass ratio is 0.05:1.

However as the temperature increases above 90 °C, the miscibility decreases as more methanol is required. This observation can be explained by the evaporation of methanol, at temperatures above 90 °C where more methanol evaporates to form vapour leaving only a small amount in solution. These results indicate that the miscibility of IL-CPO depends on the amount of alcohol used and the amount of alcohol depends on the applied reaction temperature.

5.3. Thermal decomposition of CPO

In order to study the transesterification reaction under high temperature, the thermal decomposition of the CPO was investigated. As can be seen in Figure 5.2, the first decomposition step, i.e. drop, begins at 220 and ends at 340 °C.

The first decomposition step starts slowly because at the beginning only the evaporation took place and a few chains are broken and their weight loss is too small to show noticed reduction [275]. The second weight drop starts from 380 to 440 °C. The final drop step showed many weight loses peaks, begins at 460 °C and ends at 530 °C. On the other hand, there are no significant losses after 550 °C. The CPO behavior towards heating was similar to other vegetable oils studied by [276].

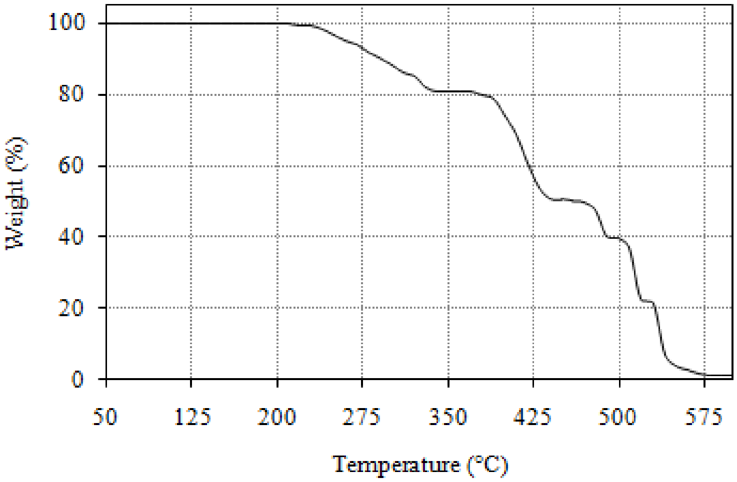


Figure 5.2 TGA result for CPO

5.4. Optimization of H_2SO_4/IL catalyzed-transesterification

The effects of various reaction variables that contribute towards the conversion of CPO into methyl esters were evaluated. Among the parameters were type of catalyst, either H_2SO_4 or any of the 12 acidic ILs, amount of catalyst, molar ratio of methanol to oil, reaction temperature, FFA content and the mixing intensity. The ILs acidities were identified by electron theory method and ILs proceedings. The effect of temperature change on CPO conversion was studied in the range of 100–180 ºC, since several researchers have revealed the positive influence of temperature on the acid-catalyzed reaction [1, 13, 63, 277, 278].

The biodiesel conversion was calculated based on the equation (5.1) below [21], while the ester content from each experimental run was calculated from the contents of methyl esters in the ester phase as determined by GC and the theoretical yield was calculated according to equation 5.2 [120, 279]:

$$\text{Biodiesel yield} = \frac{\text{weight of product}}{\text{weight of oil}} \times 100 \cdots\cdots\cdots\cdots\cdots\cdots (5.1)$$

$$\text{Esters content (\%)} = \frac{\text{Actual esters concentration}}{\text{Theoretical esters concentration}} \times 100 \cdots\cdots\cdots\cdots\cdots (5.2)$$

The actual concentration is from the GC results while the theoretical concentration is calculated from the chemical equation.

5.4.1. Effect of different parameters on H_2SO_4 catalyzed transesterification

5.4.1.1. Effect of reaction temperature

As shown in Figure 5.3, a maximum yield of 95.4 % was obtained at 130 ºC, 5.0 wt% H_2SO_4, methanol to CPO molar ratio of 30:1 and mixing speed of 700 rpm for an 8 hour reaction. At temperatures above 140 ºC, decreases in yield were observed possibly due to that the reversible reaction induced by the high temperature that significantly reduces the overall biodiesel yield. It was also observed that the products obtained at 140 ºC were darker than those synthesized at lower temperatures.

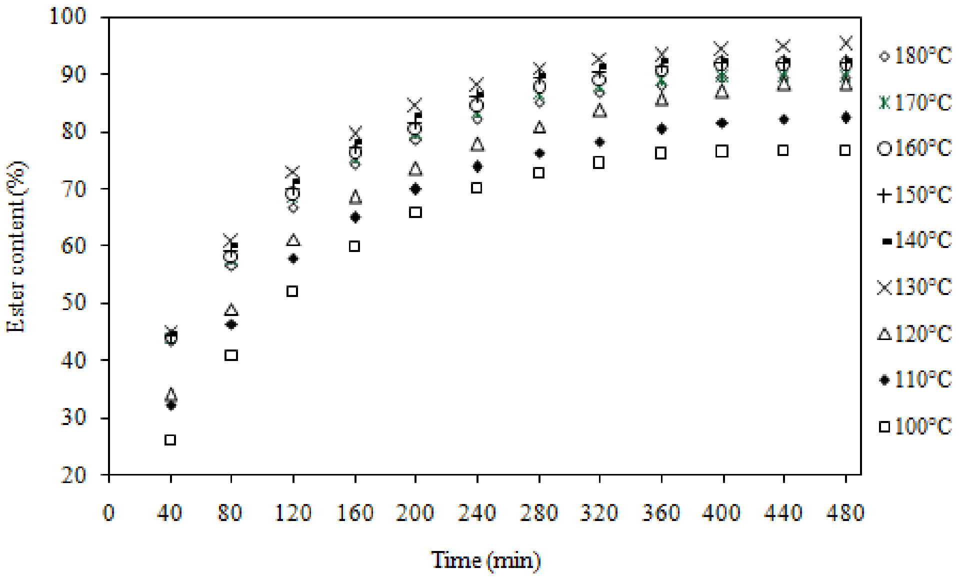


Figure 5.3 Effect of temperature on the yield of palm oil methyl esters (methanol/oil molar ratio 30:1, H_2SO_4 5.0%, stirring rate 700 rpm).

5.4.1.2. Effect of acid concentration

The sulfuric acid mass was varied in the range of 4.4–5.2 wt%. These percentages are based on the CPO weight for the acidic-transesterification reaction. The amount of sulfuric acid affects the yield of the process as shown in Figure 5.4. Biodiesel yield increases as acid concentration increases.

The acid–catalyzed process achieved maximum yield at 5.0 wt% H_2SO_4. Increasing the concentration above 5.0 wt% showed unnoticed increase the product yield. Thus, 5.0 wt% of H_2SO_4 was adopted as the optimal concentration in order to avoid increasing the time required to remove the acid from the valuable biodiesel. Moreover, to avoid the extensive water washing requires. This excess water can complicate its separation and cause reduction in the final product [11, 25].

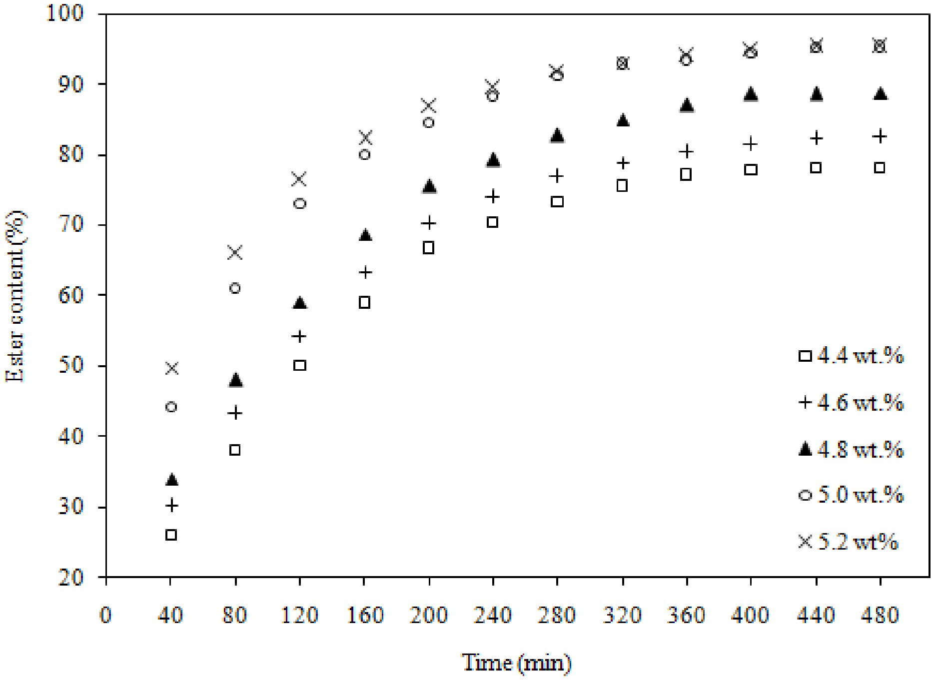


Figure 5.4 Effect of H_2SO_4 concentrations on the yield of palm oil methyl esters (methanol/oil molar ratio 30:1, reaction temperature 130 °C, stirring rate 700 rpm).

5.4.1.3. Effect of molar ratio

The alcohol to oil molar ratio is one of the most important parameters that have significant effect on the yield of esters [102, 111].

In order to study the effect of molar ratio on biodiesel yield, numbers of experiment were conducted by varying the molar ratio of methanol to oil from 10:1 to 40:1, while the reaction conditions of temperature and catalyst concentration were the optimum conditions determined previously. The yield of biodiesel versus time at different molar ratios of methanol/oil, such as, 10:1, 15:1, 20:1, 25:1, 30:1, 35:1, 40:1 are presented in Figure 5.5.

When the ratio was increased from 10:1 to 30:1, the biodiesel yield increased from 49.5% to 95.4%. At molar ratios above 30:1, no further yield increase was noticed. Same trend was observed by Berrios *et al*. [122] in their study for the transesterification of sunflower oil. From these results the molar ratio 30:1 was identified as the optimal ratio and was used in subsequent experimental works in this study.

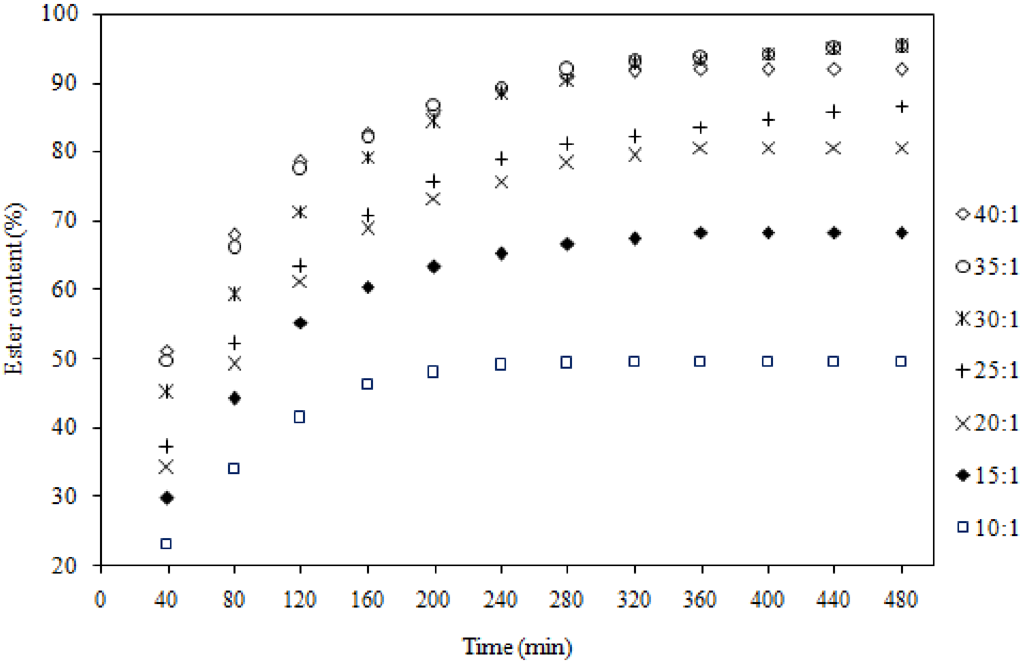


Figure 5.5 Effect of methanol/oil molar ratio on the yield of palm oil methyl esters (H_2SO_4 5.0 % , reaction temperature 130 °C, stirring rate 700 rpm).

5.4.1.4. Effect of mixing intensity

The mixing intensity appears to have a significant effect in the transesterification reaction. The reaction can take place without mixing but only at the interface of the oil and alcohol/catalyst mixture [114]. The stirring mechanism increases the contact area between the oils and catalyst methanol solution, and assists in the initiation of the reaction.

The mixing speed was varied in the range of 300 – 900 revolution per min (rpm). The yield of biodiesel versus time at different rates of mixing is shown in Figure 5.6. At stirring rates of 300, 400 and 500 rpm, the biodiesel yield was 68.5%, 77.8% and 88.8 %, respectively. The low yield could be because of the high viscosity of the CPO-acid mixture that requires higher stirring speed to induce better homogenization of the reactants.

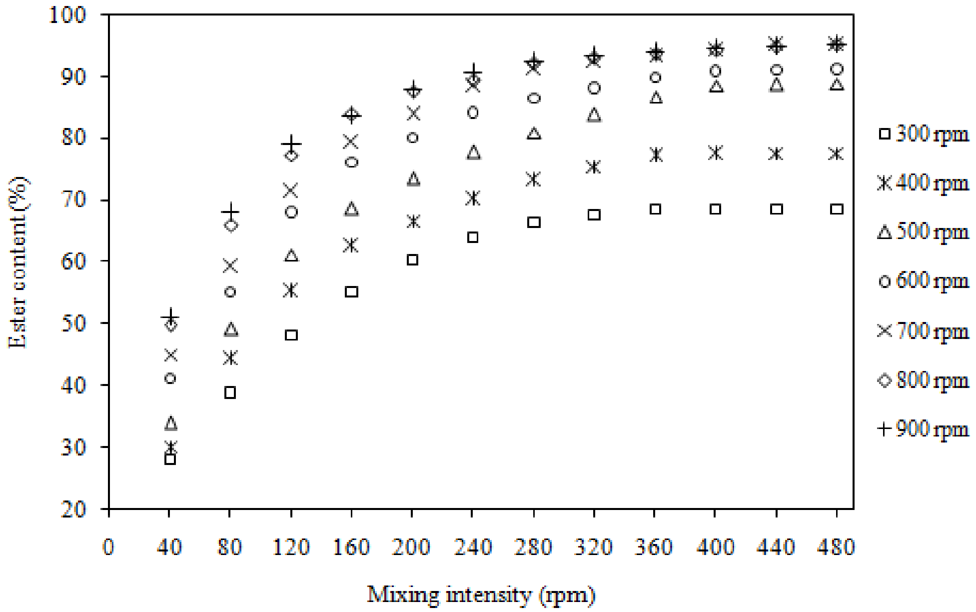
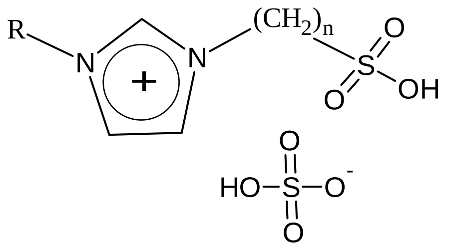


Figure 5.6 Effect of mixing intensity on the yield of palm oil methyl esters (methanol/oil molar ratio 30:1, reaction temperature 130 °C, H_2SO_4 5.0 %).

Although mixing speed of 600 rpm was recommended by Berrios *et al.* [122] for the acid-catalyzed transesterification of sunflower oil reaction system, in this work however, a higher conversion of the oil was observed at 700 rpm. This result may be due to those different oils having different viscosities.

5.4.2. Mechanism of imidazolium functionalized acidic IL catalyzed-transesterification

Figure 5.7 shows the SO_3H-functional imidazolium Brønsted acidic ILs in four different structures. Their acidities were evaluated when applied as catalysts for the transesterification of CPO with methanol in order to produce biodiesel.



IL1a: R = CH$_3$, n=3

IL1b: R = CH$_3$, n=4

IL2a: R = C$_4$H$_9$, n=3

IL2b: R = C$_4$H$_9$, n=4

Figure 5.7 Structures of four imidazolium functionalized Brønsted ILs.

5.4.2.1. Effects of catalyst type and concentration

The effects of catalyst type and concentration on palm biodiesel yield were investigated on four IL catalysts; MSPIMHSO$_4$, BSPIMHSO$_4$, MSBIMHSO$_4$ and BSBIMHSO$_4$ by varying their concentrations from 4.4 to 5.8 wt% (based on the weight of raw oil).

To evaluate the performance of each catalyst, the four catalysts were subjected to the same reaction conditions fixed at: reaction time of 8 h, molar ratio of methanol to oil at 12:1, reaction temperature of 170 °C and mixing rate of 800 rpm. The results presented in terms of biodiesel yield and esters conversion against catalyst concentration are as in Figures 5.8 and 5.9.

As can be observed from Figures 5.8a and 5.8b, as the ILs concentrations increase, the conversion of triglyceride, as well as the ester content also increases. The four catalysts exhibit similar trends on the conversion of triglycerides to esters; however different amount of catalyst was required to achieve the maximum conversion.

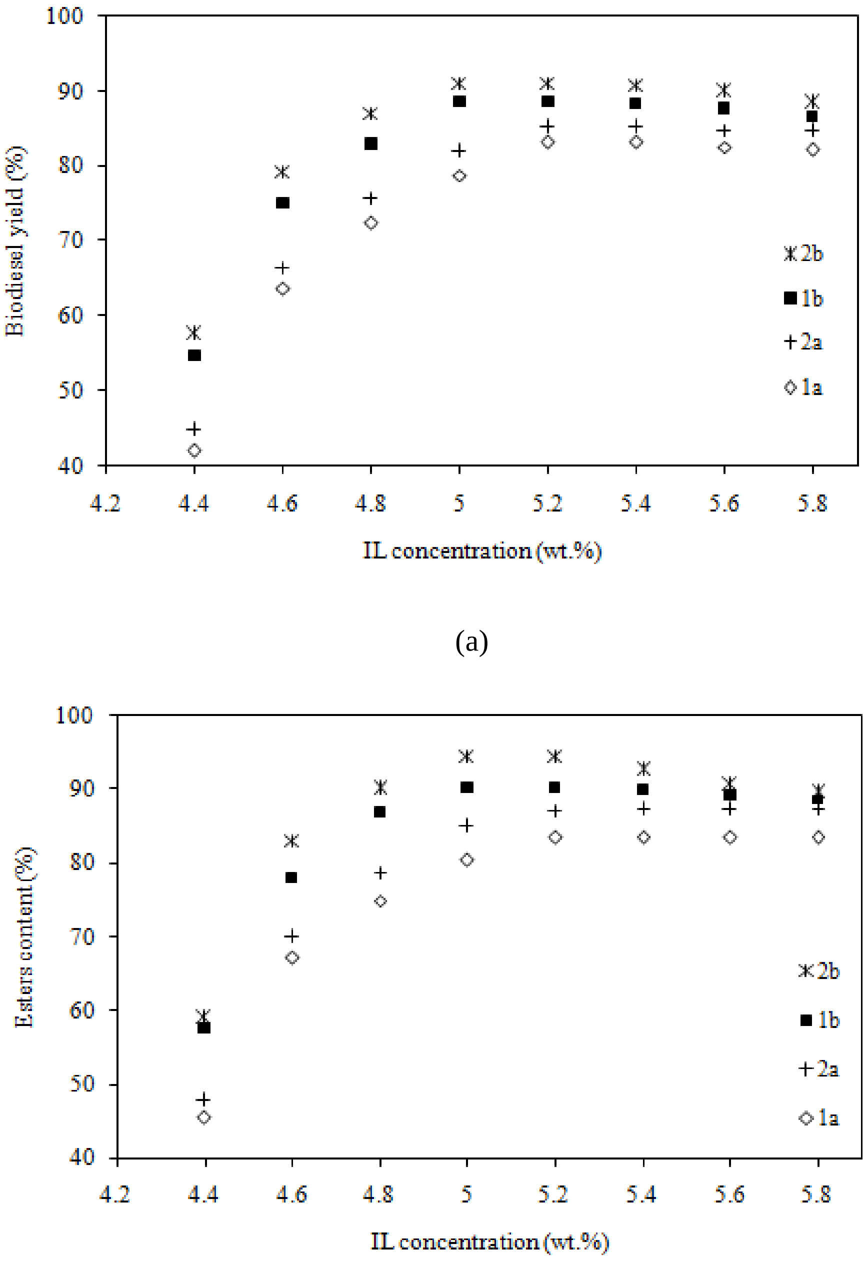
The lowest catalysts concentration i.e., 4.4 wt.% was insufficient to produce high ester conversions. High biodiesel yield of 80.3%, 85%, 88.6% and 93.1% was obtained at 5.2 wt.% MSPIMHSO$_4$, 5.2 wt.% BSPIMHSO$_4$, 5.0 wt.% MSBIMHSO$_4$and 5.0 wt.% BSBIMHSO$_4$, respectively.

Further increase in catalyst concentration neither enhances further biodiesel conversion nor raises the ester content. In fact, increasing the MSBIMHSO$_4$ and/or BSBIMHSO$_4$, concentrations more than 5.2 wt.% caused a dramatic decrease in the biodiesel yields and esters contents. Both $MSBIMHSO_4$ and $BSBIMHSO_4$ are highly viscous with viscosities of 1427 and 1592 cP, respectively.

Therefore, increasing the amount of this catalyst increases the viscosity of the reaction media and as a results decreases the contact between the two phases during the reaction. Another explanation offered by Kawashima *et al*., [279] is due to the formation of a complex from the interaction of the IL catalyst with glycerol since glycerol is a trihydric alcohol. This IL-glycerol complex may acts as a deactivator for the transesterification reaction.

Maximum esters contents were also obtained for 5.0 wt.% of $MSBIMHSO_4$ and $BSBIMHSO_4$ and 5.2 wt.% of $MSPIMHSO_4$ and $BSPIMHSO_4$. As observed in Figure 5.8b, $BSBIMHSO_4$ and $MSBIMHSO_4$ catalysts exhibit the best activities, but $BSBIMHSO_4$ is more active than $MSBIMHSO_4$. These results reveal that increasing the chain length of both sides of the chain, i.e. linked with N1 and N3 in the imidazole, increases the catalytic activity of IL.

The activity is found to be in the order of $MSPIMHSO_4 < BSPIMHSO_4 < MSBIMHSO_4 < BSBIMHSO_4$. It was observed that increasing the sulfonate chain has a greater effect on increasing the catalytic activity compared to increasing the alkyl chain. This behavior possibly be due the tendency to dissociate H^+ ion more easily by longer carbon chain in Brønsted acidic ILs belonging to the same nitrogen group, i.e. imidazolium, thus gives rise to a stronger Brønsted acidity.



(a)

(b)

Figure 5.8 Effect of catalyst concentration on conversion of CPO to (a) palm biodiesel, (b) POME; under fixed reaction conditions: methanol/CPO molar ratio 12:1, 170 °C, and mixing intensity of 800 rpm for 4 catalysts: 1a = $MSPIMHSO_4$; 1b = $MSBIMHSO_4$; 2a = $BSPIMHSO_4$; 2b = $BSBIMHSO_4$.

Figure 5.9, from left to right, shows the GC chromatogram of solvent and esters peaks of *n*-heptane, methyl laurate, methyl myristate, methyl palmitate, methyl stearate, methyl oleate and methyl linoleate, at different percentages depending on the catalytic activity of the 4 imidazolium route ILs. The highest peak areas indicates the high ester content obtained after the reaction being catalyzed with $BSBIMHSO_4$, followed by the peaks of $MSBIMHSO_4$, $BSPIMHSO_4$, and $MSPIMHSO_4$, respectively. This chromatogram approved the catalytic activities of the investigated functionalized imidazolium ILs.

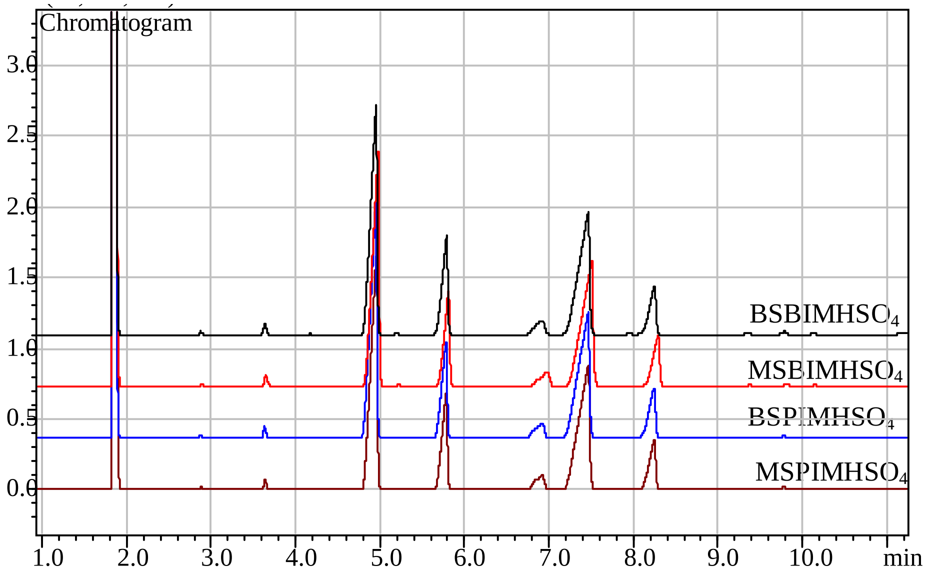


Figure 5.9 GC Chromatogram of biodiesel from CPO for 4 imidazolium catalysts. The peaks from up to down indicating biodiesel sample catalyzed with $BSBIMHSO_4$ catalyst, $MSBIMHSO_4$, $BSPIMHSO_4$, and $MSPIMHSO_4$.

5.4.2.2. Effect of reaction temperature

The effect of reaction temperature was investigated by varying the reaction temperature from 100 to 180 °C using the four imidazolium ILs. Other reaction parameters such as molar ratio of methanol to oil (12:1), reaction time of 8 h, mixing speed of 800 rpm, and catalyst concentrations 5.2 wt.%, 5.2 wt.%, 5.0 wt.% and 5.0 wt.% were kept constant. The results are presented in Figure 5.10.

The experimental results shown in the figure presented that when the temperature was increased the esters conversions were enhanced. This is because, conducting a reaction at a higher temperature delivers more energy into the system and increases the reaction rate by causing more collisions between particles, as explained by collision theory.

The experimental results show that when transesterification reactions were carried out at temperatures less than 140 °C and atmospheric pressure, the conversions were less than 80 % with even the superior IL (BSBIMHSO$_4$).

When the temperature was increased from 130 °C to 170 °C, with MSPIMHSO$_4$, BSPIMHSO$_4$, MSBIMHSO$_4$ and BSBIMHSO$_4$ catalysts, the esters content increased. Optimum conversions occurred at 170 ^{o}C for all four catalysts and the yield was 83.4%, 87.2%, 90.2% and 94.6%, respectively.

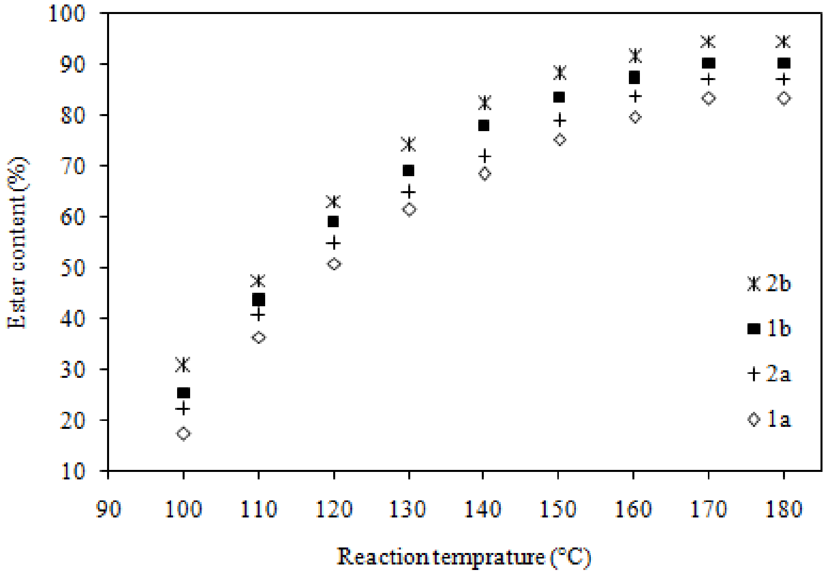


Figure 5.10 Effect of reaction temperature on ester content – a comparison among four types of catalysts. 1a – mixing 5.2 wt.% MSPIMHSO$_4$; 1b - 5.0 wt.% MSBIMHSO$_4$; 2a - 5.2 wt.% BSPIMHSO$_4$; 2b - 5.0 wt.% BSBIMHSO$_4$. Other reaction parameters: molar ratio - 12:1 and stirring speed - 800 rpm and reaction time - 8 hours.

No further yield increase was observed for all four catalysts when the reaction temperature was increased above 170 °C. A similar observation was reported by other researcher, Han *et al.* [128], who found that the best temperature, for transesterification of waste cocking oil using HSO$_3$-BPyrHSO$_4$ as a catalyst, is 170 °C.

For the alkali transesterification reaction, many researchers concluded that higher temperatures have to be avoided due to that the side saponification reaction will take place which produces a negative effect on the product yield [15, 21, 111, 114, 129]. However, with the ILs as catalyst, applying higher temperatures accelerated the transesterification reaction of triglycerides [62, 128, 181] since no soap was seen in the product media. Moreover, applying higher temperatures may lead to excessive decrease in CPO and IL viscosities and thus, improves the contact between the reactants, thereby getting higher conversions.

5.4.2.3. Effect of methanol/CPO molar ratio

The molar ratio of alcohol to TG is considered as the most effective variables affecting the yield of esters [263]. Hence, it has to be explored for increasing the biodiesel yield as well as to reduce the purification cost and steps. However, catalyst type has a significant effect on the molar ratio [63].

In this work, the methanol/oil molar ratio was varied (3:1, 6:1, 9:1, 12:1, 15:1 and 18:1) in order to determine the effect of methanol amount on POME production using the four types of SO_3H-functionalized imidazolium ILs. The same reaction conditions used to investigate the effect of catalyst type and concentration were applied in all of these experiments. The results in terms of ester yield and methanol/CPO molar ratio are presented in Figure 5.11.

Based on the chemical equation, the stoichiometry for this reaction is three moles of alcohol to one mole of TG. However, the stoichiometric ratio of 3:1 methanol/CPO gave the lowest ester conversions of less than 24% for all four types of imidazolium ILs. Among the four catalysts, the ester yield using $BSBIMHSO_4$ catalyst was the lowest. This low yield could be due to the high viscosity of $BSBIMHSO_4$, which is the highest of all four catalysts.

A large amount of alcohol is required to reduce the viscosity of the reaction media and to facilitate the contact between the two phases. In practice, the molar ratio 6:1 of alcohol to oil is usually used to force the equilibrium to favour product formation, since the reaction is reversible.

The ester content increased from 23% to 58%, when the molar ratio was increased from 3:1–6:1, under the same reaction conditions using $MSBIMHSO_4$ as catalyst. Although, several researchers reported 6:1 as the optimal ratio for alkali catalyzed transesterification [13, 21, 112], however, in this work, 12:1 was found to be the optimum ratio for the ILs used except for $BSPIMHSO_4$; the optimum molar ratio for $BSPIMHSO_4$ was 9:1.

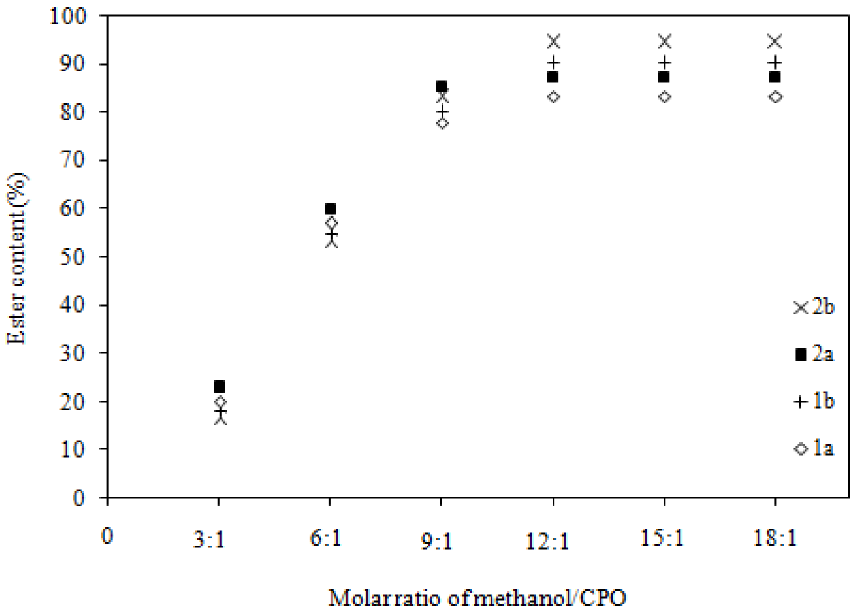


Figure 5.11 Effect of methanol/CPO molar ratio on palm biodiesel yield – a comparison of four catalysts. 1a - 5.2 wt.% $MSPIMHSO_4$; 1b - 5.0 wt.% $MSBIMHSO_4$; 2a - 5.2 wt.% $BSPIMHSO_4$; 2b - 5.0 wt.% $BSBIMHSO_4$. Other reaction parameters: reaction temperature - 170 °C, stirring speed - 800 rpm, reaction time - 8 hours.

This is because of its low viscosity. In IL-catalyzed transesterification, at low alcohol concentrations it is possible that methanol behaves as a reactant and reacts with the raw oil and does not act as a co-solvent, thus increasing the viscosity of the reaction media and causes mixing difficulty. Therefore sufficiently excess amount of alcohol is required to reduce the viscosity of the reaction media and subsequently aids homogenization and improves the contact between the CPO and IL-methanolic solution to initiate the reaction. As observed from the behaviour of $BSPIMHSO_4$, the optimum alcohol/oil molar ratio is affected by the viscosity of the IL catalyst itself.

Further increases in the ratio beyond 12:1 even up to 18:1 did not lead to neither higher POME yield nor noticeable effect on the esters content. In fact, higher quantities of methanol had a negative effect of complicated the ester recovery process and raised the cost for methanol recovery and longer time will be required for the separation stage as separation of the ester layer from the other layers becomes more difficult with the addition of a large amount of methanol. This result is due to the fact of that methanol is acting as an emulsifier, since it is having one polar hydroxyl group [21].

5.4.2.4. *Effect of mixing intensity*

Reactants stirring can facilitate the initiation of transesterification reaction. In this study, the effect of mixing intensity on methanolysis was investigated at different rates ranging from 300–900 rpm using the four imidazolium catalysts and same reaction conditions as before. The yield of methyl esters at different mixing rates is shown in Figure 5.12.

The results show that mixing intensity is another variable that affects the transesterification reaction using ILs as catalysts. As observed in Figure 5.12, the ester content increases with increasing mixing intensity. For all four catalysts, increasing the stirring speed above 900 rpm did not produce any increase in POME content. It was observed that for BSBIMHSO$_4$, the ester content at 300 rpm is the lowest due to its high viscosity. At 900 rpm and 800 rpm were almost the same. Hence, for all the ILs, 800 rpm was identified as the optimal mixing intensity.

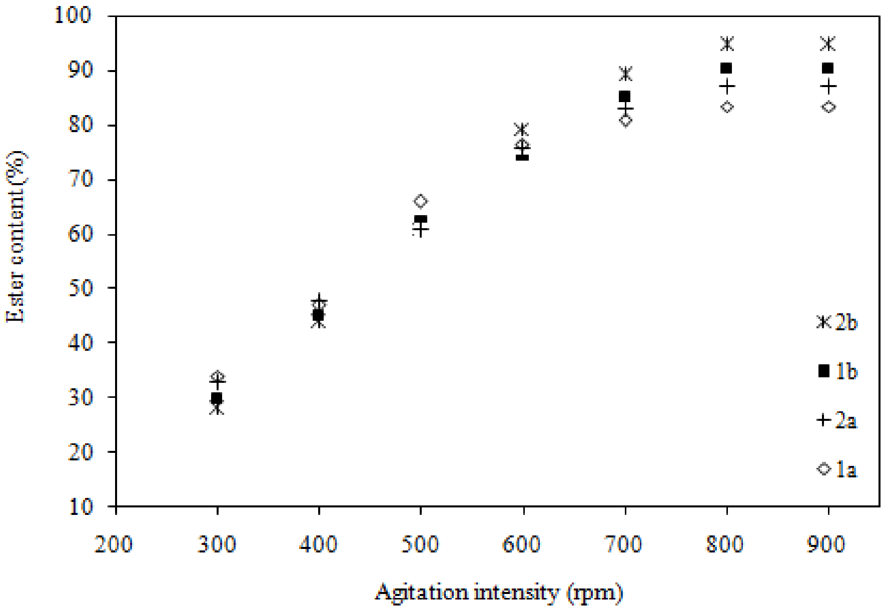


Figure 5.12 Effect of mixing intensity on the yield of POME – a comparison of four catalysts. 1a - 5.2 wt.% MSPIMHSO$_4$; 1b - 5.0 wt.% MSBIMHSO$_4$; 2a - 5.2 wt.% BSPIMHSO$_4$; 2b - 5.0 wt.% BSBIMHSO$_4$. Other reaction parameters: temperature - 170 °C, methanol/CPO molar ratio - 12:1, reaction time - 8 hours.

5.4.2.5. *Effect of reaction time on esters formation*

Figure 5.13 represents the gas chromatographic evaluation of POME produced over the course of reaction time. The main methyl ester was palmitate with a percentage of 45.503%, followed by oleate (35.41%), linoleate (8.231%), stearate (4.105%) and myristate (1.01%).

The maximum POME concentration (94.6%) was achieved after almost 8 hours using 5.0 wt.% of $BSBIMHSO_4$, methanol/CPO molar ratio at 12:1, reaction temperature of 170 °C and mixing intensity of 800 rpm. No significant change in the methyl esters concentrations was seen after 5 h of starting the reaction. The curve shows an asymptotic tendency in the first 5 hours of reaction and starts to stabilize after 6 hours.

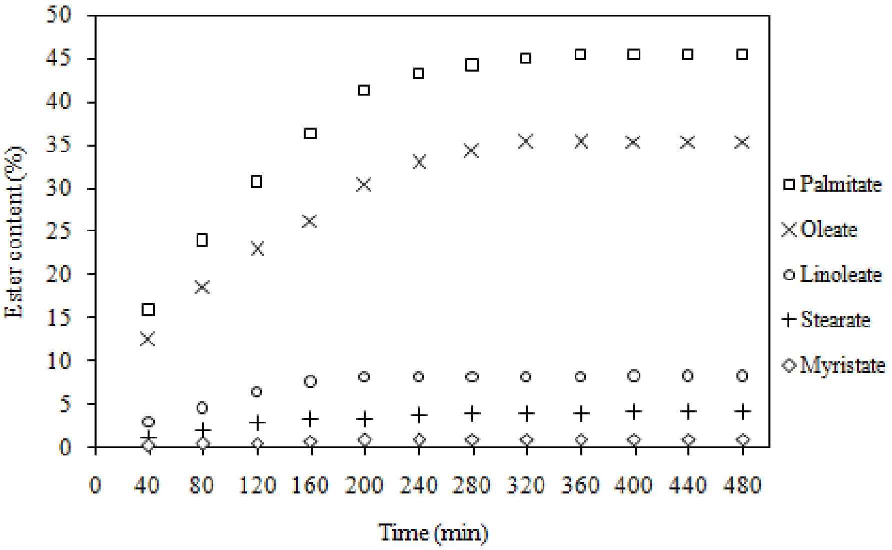
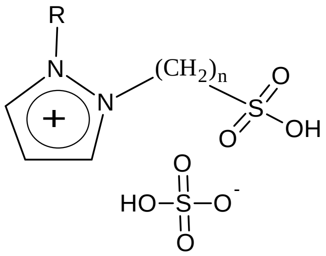


Figure 5.13 Evaluation of POME concentration with time using 5.0 wt.% $BSBIMHSO_4$, methanol/CPO molar ratio of 12:1, 170 °C, mixing intensity of 800 rpm.

5.4.3. Mechanism of pyrazolium functionalized acidic IL catalyzed-transesterification

Figure 5.14 presents the SO_3H-functional pyrazolium Brønsted acidic ILs in four forms. Those ILs were used as catalysts for the synthesis of palm biodiesel by transesterification of CPO with methanol.



IL3a: R = H, n=3

IL3b: R = H, n=4

IL4a: R = CH_3, n=3

IL4b: R = CH_3, n=4

Figure 5.14 Structures of four pyrazolium functionalized Brønsted ILs.

5.4.3.1. Effects of catalyst type and concentration

The effect of catalyst type on POME production has been established experimentally using $SPPHSO_4$, $SBPHSO_4$, $MSPPHSO_4$ and $MSBPHSO_4$ at concentrations range of 4.4–5.4 wt.%. The reaction conditions for all of the experiments were fixed at: reaction temperature of 170 °C, methanol/CPO molar ratio of 15:1, reaction time for 8 hours and stirring speed of 800 rpm.

From Figure 5.15, the optimum yields of POME were achieved with catalyst concentrations of 5.2 wt.% of $SBPHSO_4$, 5.2 wt.% of $SPPHSO_4$, 5.2 wt.% of $MSBPHSO_4$, and 5.4 wt.% of $MSPPHSO_4$. The catalysts in the order of catalytic activity are $SBPHSO_4 > SPPHSO_4 > MSBPHSO_4 > MSPPHSO_4$.

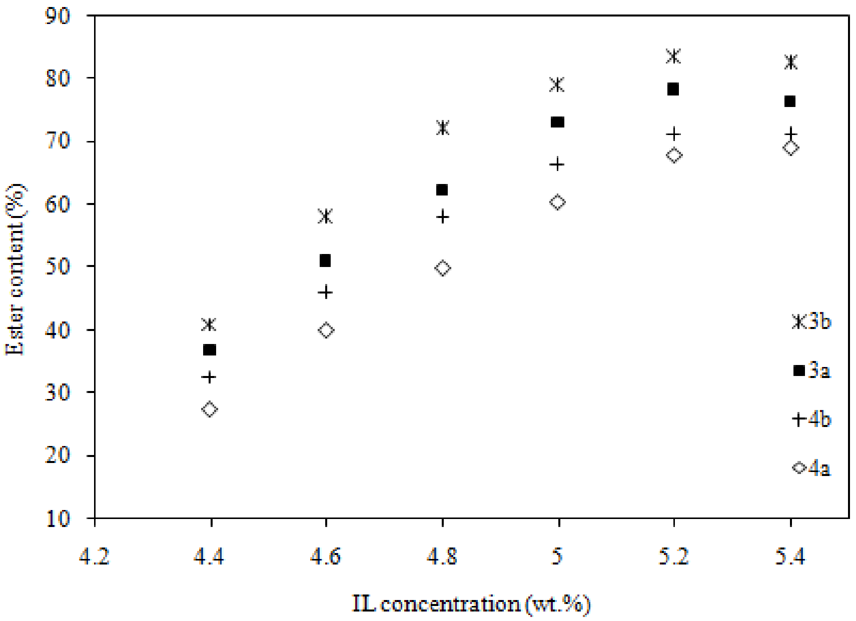


Figure 5.15 Effect of functionalized pyrazolium type and concentration on the yield of POME – a comparison of four catalysts. 3a - $SPPHSO_4$; 3b - $SBPHSO_4$; 4a - $MSPPHSO_4$; 4b - $MSBPHSO_4$. Reaction conditions: methanol/CPO molar ratio 15:1, 170 °C, mixing intensity 800 rpm and reaction time 8 hours.

Further increase in the IL amount did not show any noticeable increase in the esters content except for $MSBPHSO_4$; when the concentration was increased from 5.2 to 5.4 wt.% the POME content increased slightly from 67.8 to 69%. Therefore, 5.2 wt.% was identified as the optimal concentration for the 4 functionalized pyrazoliums.

When N1 was occupied by a proton and N2 occupied by butane sulfonate, the IL $SBPHSO_4$ showed higher catalytic activity producing 83.4% POME. However, replacing the butane sulfonate, at N2 by propane sulfonate, lowered the activity of $SPPHSO_{4,}$ producing 78.2% of POME, for the same concentrations.

Replacing the H at N1 in $SBPHSO_4$ by a methyl group, produces $MSBPHSO_4$, but the ester yield dropped from 83.4% to 71.2%. This result indicates that the H bonding with N1 contributes to the high activity and acidity of pyrazole. This is may be accounted by the ability of $SBPHSO_4$ to dissociate positive charge quivering between N1 and its H bond.

5.4.3.2. Effect of reaction temperature

As can be observed from Figure 5.16, evaluation of the effect of reaction temperature on transesterification of CPO was carried out at 100°C and from 110 – 180 °C. The same reaction conditions as before were applied and the catalyst concentration used was 5.2 wt.% for all 4 types of ILs.

The experimental results show that the reaction rate was slow at low temperatures. For example, for all four types of catalysts yields of less than 40% were produced at 110 °C compared to 65.8%, 71.2%, 78% and 83.4% of POME produced at 170 °C. This temperature, 170 °C is identified as the optimum temperature since increasing the temperature to 180 °C did not show any further increase in the POME yield.

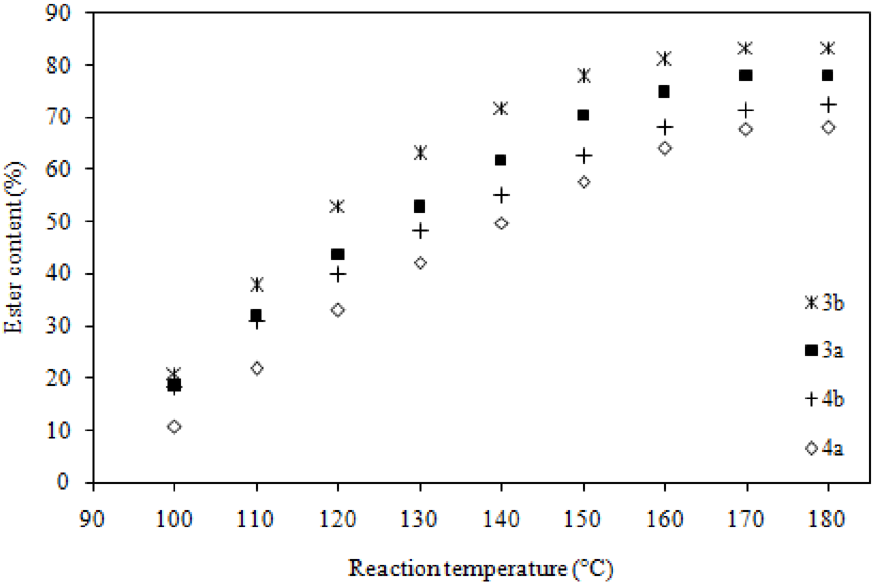


Figure 5.16 Effect of reaction temperature on POME yield – a comparison of four pyrazolium ILs catalysts under fixed conditions: molar ratio - 15:1, mixing intensity - 800 rpm, reaction time - 8 hours, and catalyst concentration - 5.2 wt.%. 3a - SPPHSO$_4$; 3b - SBPHSO$_4$; 4a - MSPPHSO$_4$; 4b - MSBPHSO$_4$.

5.4.3.3. Effect of methanol/CPO molar ratio

The methanol/CPO molar ratio was varied (3:1, 6:1, 9:1, 12:1, 15:1 and 18:1) to determine the effect of methanol amount on POME production using 4 -SO$_3$H functionalized pyrazolium ILs. The transesterification reaction was carried at fixed operational conditions of 5.2 wt.% catalyst concentration, 170ºC, 800 rpm mixing intensity for 8 hours. Figure 5.17 shows the effect of methanol amount on the reaction rate.

For all four catalysts, the percentage of ester conversion increased when the molar ratio was increased from 3:1 to 15:1. The conversion increased from 7%, 10.7%, 4% and 6% at 3:1 ratio to 65.8%, 71.2%, 78% and 83.4% at 15:1, using $MSPPHSO_4$, $MSBPHSO_4$, $SPPHSO_4$ and $SBPHSO_4$, respectively. At the stoichiometric ratio 3:1, $SPPHSO_4$ and $SBPHSO_4$ showed lowest catalytic activity; however at the highest ratio 15:1 they showed the highest activity.

Similar to this behaviour could be attributed to their high viscosity compared to the other two catalysts. A slight increased in the conversion was observed at the ratio 18:1, less than 1.0 %, making the ratio 15:1 as the best ratio.

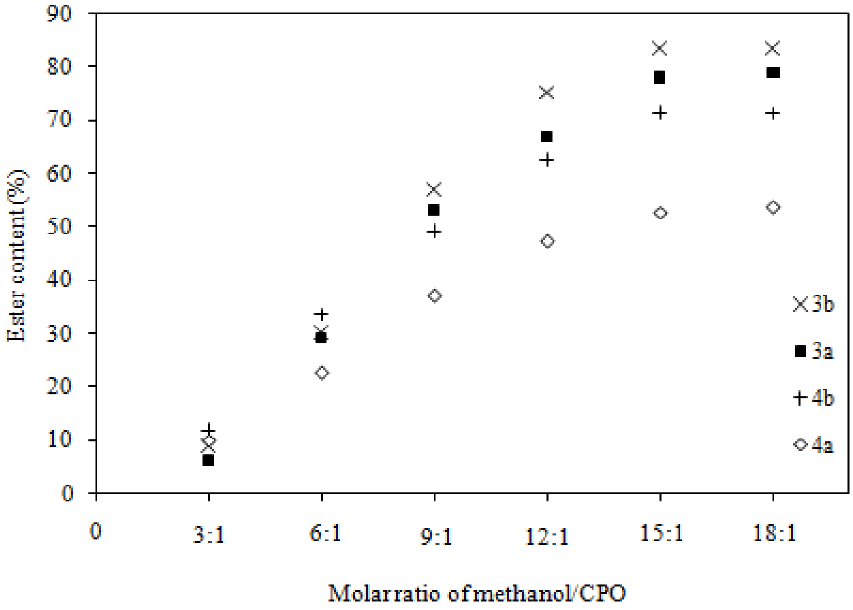


Figure 5.17 Effect of methanol/CPO molar ratio on ester content catalyzed – a comparison of four pyrazolium ILs catalysts under fixed reaction conditions: temperature -170 °C, mixing intensity - 800 rpm, reaction time - 8 hours , and catalyst concentration - 5.2 wt.%. 3a - $SPPHSO_4$; 3b - $SBPHSO_4$; 4a - $MSPPHSO_4$; 4b - $MSBPHSO_4$.

5.4.3.4. Effect of mixing intensity

The mixing intensity can be considered as a particularly significant parameter for the transesterification process since the pyrazolium ILs are highly viscous.

Figure 5.18 presents the experimental data for transesterification of CPO using the 4 catalysts under fixed experimental conditions of 170 °C, 15:1, 8 hours and catalyst concentration of 5.2 wt.%. As observed in the figure, the ester content increases with increasing mixing speed. The results show that the optimum intensity is 800 rpm for all the catalysts.

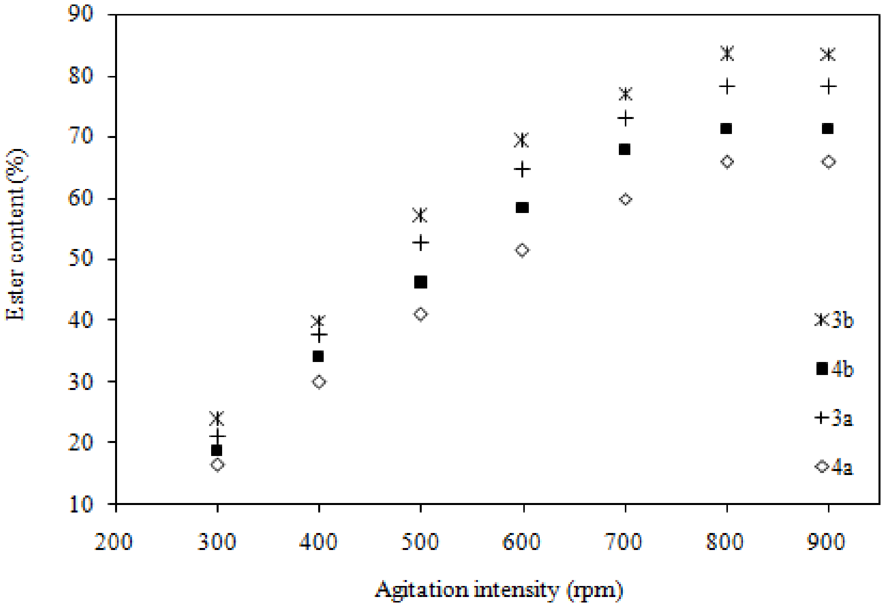


Figure 5.18 Effect of mixing intensity on ester content catalyzed with pyrazolium ILs under fixed reaction conditions: temperature - 170 °C, methanol/CPO molar ratio - 15:1 reaction time - 8 hours , and catalyst concentration - 5.2 wt.%. 3a - $SPPHSO_4$; 3b – $SBPHSO_4$; 4a - $MSPPHSO_4$; 4b - $MSBPHSO_4$.

5.4.3.5. Effect of reaction time on esters formation

Figure 5.19 shows the concentration of POME produced over the course of the reaction time, using $SBPHSO_4$ as catalyst. The reaction conditions were 170 °C, stirring rate 800 rpm, methanol/CPO molar ratio 15:1 and 5.2 wt.% of catalyst the final yield of POME mixing was 83.42%.

The produced esters contained 40.9% of palmitate, 29.9% of oleate, 8.05% of linoleate, 3.39% of stearate, 0.87% of myristate and a minor quantity of laurate, 0.31%. After 320 minutes of starting the reaction, inconsiderable change in POME concentrations was observed. The curve shows an asymptotic tendency with respect to time and becomes stable after 6 hours.

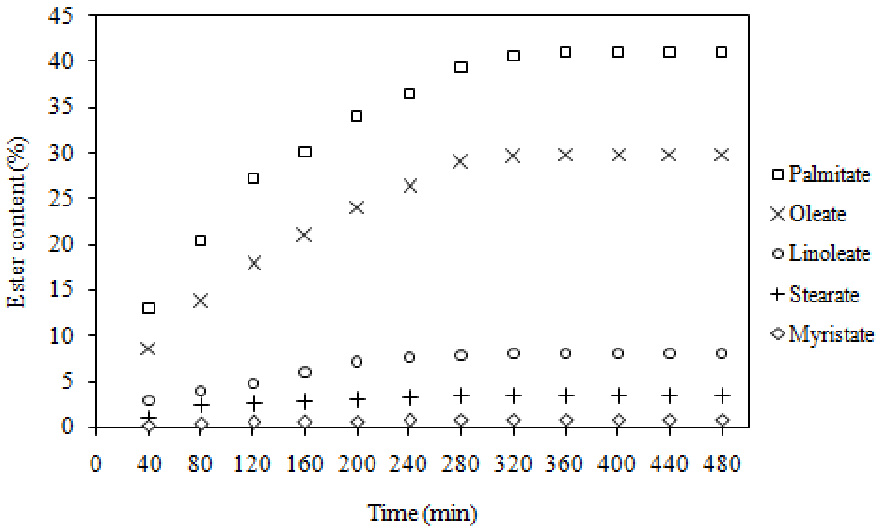
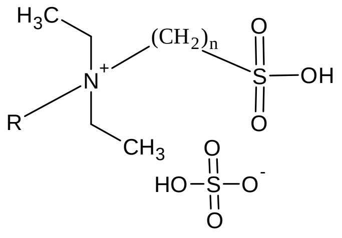


Figure 5.19 POME concentrations over the course of reaction time. Reaction conditions: 170°C, mixing intensity 800 rpm, methanol/CPO molar ratio 15:1, and 5.2 wt.% of $SBPHSO_4$ mixing intensity.

5.4.4. Mechanism of ammonium functionalized acidic IL catalyzed transesterification



IL5a: R = CH_3, n=3

IL5b: R = CH_3, n=4

IL6a: R = C_2H_5, n=3

IL6b: R = C_2H_5, n=4

Figure 5.20 Structures of four ammonium functionalized Brønsted ILs.

Figure 5.20 shows the four different structures of SO_3H-functional pyrazolium Brønsted acidic ILs. Their acidities were evaluated for the transesterification of CPO with methanol to produce biodiesel.

5.4.4.1. Effect of reaction parameters on ammonium-catalyzed transesterification

Table 5.2 POME content for each type of functionalized ammonium catalyst after 8 hours of reaction time

Catalyst type	Catalyst Conc. (wt.%)	Reaction temp. (°C)	MeOH:CPO molar ratio	Mixing intensity (rpm)	POME content (%)
$TESPAMHSO_4$	5.2	170	15:1	800	55.1 ± 1.3
$TESPAMHSO_4$	5.6	170	15:1	800	53.3 ± 0.9
$DEMSPAMHSO_4$	5.2	170	15:1	800	64.8 ± 0.4
$DEMSPAMHSO_4$	5.6	170	15:1	800	64.2 ± 1.1
$TESBAMHSO_4$	5.2	170	15:1	800	70.0 ± 1.0
$TESBAMHSO_4$	5.2	170	15:1	800	63.6 ± 0.4
$DEMSBAMHSO_4$	4.8	170	15:1	800	60.2 ± 0.8
$DEMSBAMHSO_4$	5.0	170	15:1	800	69.0 ± 1.4
$DEMSBAMHSO_4$	5.2	170	15:1	800	75.1 ± 0.5
$DEMSBAMHSO_4$	5.2	170	6:1	800	28.1 ± 0.4
$DEMSBAMHSO_4$	5.2	170	9:1	800	51.9 ± 0.7
$DEMSBAMHSO_4$	5.2	170	18:1	800	75.0 ± 1.1
$DEMSBAMHSO_4$	5.2	150	15:1	800	67.8 ± 1.3
$DEMSBAMHSO_4$	5.2	160	15:1	800	72.3 ± 0.6
$DEMSBAMHSO_4$	5.2	180	15:1	800	75.1 ± 0.8
$DEMSBAMHSO_4$	5.2	170	15:1	600	52.2 ± 1.2
$DEMSBAMHSO_4$	5.2	170	15:1	700	68.9 ± 0.9
$DEMSBAMHSO_4$	5.4	170	15:1	800	75.0 ± 1.2

The results of the study on the influence of catalyst type and concentration are summarized in Table 5.2. The influence of catalyst type and concentration were investigated using the same reaction parameters. When $TESPAMHSO_4$ was used, low yields were obtained even for 5.6 wt.% catalyst concentration.

The catalyst $DEMSPAMHSO_4$ showed higher activity when one of the ethyl group in $TESPAMHSO_4$ was replaced with methyl group. Also, when the sulfonate chain in $TESPAMHSO_4$ was increased from propyl to butyl to form $TESBAMHSO_4$, higher activity was observed in $TESBAMHSO_4$ than $TESPAMHSO_4$ and $DEMSPAMHSO_4$.

Changing the ethyl chain in $TESBAMHSO_4$ to methyl, giving $DEMSBAMHSO_4$ produced the most acidic one and superior IL among the tested ammonium SO_3H-

functionalized ILs. This behavior may be attributed to a more dense positive charge on the ethyl chain than the methyl chain, which resulted from the alkyl group donation of an electron. Therefore, the basicity of the amine cation was increased. The effects of other reaction parameters were also investigated and the optimum values obtained for reaction temperature is 170^{o}C, optimum molar ratio of methanol/CPO is 15:1 and optimum mixing intensity is 800 rpm.

5.4.5. Determination of the ILs acidity

Acidity determination of ILs is a relatively new subject, and it is even rarer to find work on the development of acidity relationship based on the acidity nature of ILs [280].

The 12 ILs used in this work have shown different catalytic activity for palm biodiesel synthesis. Their initial ILs, i.e., with sulfonate chain as anion and before combining with H_2SO_4, as shown in Appendices A1-A11, showed no catalytic activity for the transesterification reaction even at higher parameters. This may be because the imidazolium is acting as an unstable base cation, while the pyrazolium and ammonium cations are considered as base cations [62]. Once those cations were combined with -SO_3H acidic functional chain, they act as neutral ILs and offer both hydrogen donor and acceptor sites. However, when combined with the greater Brønsted acidity hydrogen sulfate (HSO_4^-) anion, this perhaps produced a stronger proton donor ILs [54]. This could also be attributed to the ILs with HSO_4^- as anion, which are highly immiscible with the produced FAME and supports the shifting of the reaction equilibrium to the product side [281]. Thus, offering great enhancement in the transesterification reactions. The acidity of the 12 ILs was also investigated by comparing POME generation by each catalyst over the whole period of reaction, while all other reaction parameters were fixed. The plot of ester conversion against time over the 8 hours reaction time for each catalyst is presented in Figure 5.21.

The experimental results show that the Brønsted acidity of the ionic liquids with different nitrogen groups is in the sequence imidazole > pyrazole > amine. However, the quantity of the 4 functionalized-Brønsted imidazolium ILs required for the transesterification reactions is less (5.0 wt.%) than the other ILs (5.2 wt.%).

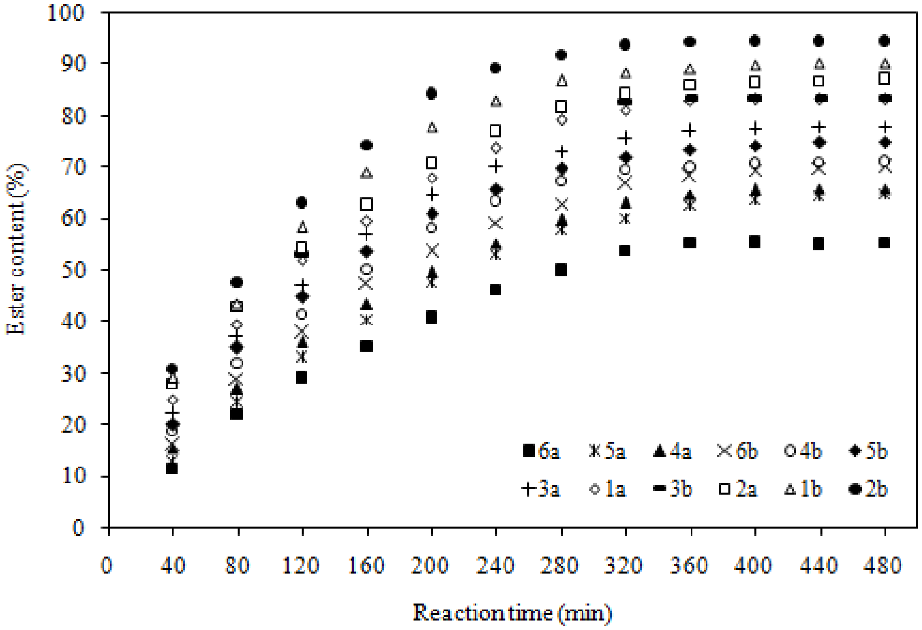


Figure 5.21 The effect of ILs types on POME yield at optimum reaction conditions. 1a = $MSPIMHSO_4$; 2a = $MSBIMHSO_4$; 1b = $BSPIMHSO_4$; 2b = $BSBIMHSO_4$, 3a = $SPPHSO_4$; 4a = $MSPPHSO_4$; 3b = $SBPHSO_4$; 4b = $MSBPHSO_4$, 5a = $DEMSPAMHSO_4$, 5b = $DEMSBAMHSO_4$, 6a = $TESPAMHSO_4$, 6b = $TESBAMHSO_4$.

The reason for that is the density of positive charge on the nitrogens of the imidazoles and pyrazoles is larger than that of the amines [181]. Therefore, it is easier for the imidazolium-based and pyrazolium-based ionic liquids to dissociate H^+ compared to the alkylammonium-based ionic liquid; making them stronger Brønsted acids.

The comparison between the functionalized imidazolium and ammonium ones were in agree with those results obtained by Wu *et al.* [181] in the transesterification of cottonseed oil with alcohol.

Compared with the pyrazolium-based ionic liquids, the presence of an acidic proton at the C-2 position in the imidazolium ring improved its stability and made the cation behaved as an acidic cation besides the side chain length, which also contributed to the increase in acidity of these ILs [39].

5.4.6. Acidity reduction, monitoring of reactants’ concentration and water formation

The effect of FFA content on transesterification reaction of oils and fats has been investigated by several previous researchers, who noted that the FFA content in the starting material should be kept as low as 0.5% [13, 20, 24, 67, 68].

In order to confirm the conversion of FFA during the process, samples from the reaction media were taken manually and the FFA content was analyzed by AOCS cd 3d-63 titration method [253]. The conversion of FFA was calculated from the acidity reduction using the following equation [107]:

$$\text{FFA conversion (\%)} = \left(\frac{\text{AVi - AVt}}{\text{AVi}}\right) \times 100 \cdots\cdots\cdots\cdots\cdots (5.3)$$

Where AV_i is initial acid value of the mixture and AV_t is the acid value at t time. The rate of change of FFA started from 6.98 mg KOH/g (equivalent to 3.49 % FFA content) without catalysts. Figure 5.22 illustrates the experimental results of acidity reduction (FFA conversion) during the transesterification reactions using ILs and $H_2SO_4^-$ catalysts at the optimum conditions. For the H_2SO_4 catalyzed transesterification, the figure shows that the acidity drops drastically and reaches to almost zero (0.0026 mgKOH/g CPO) after 120 minutes of reaction.

On the other hand for the ILs catalyzed transesterifications, the FFA conversion started very late, i.e., after 160 minutes of reaction. Among the 12 ILs, $SPPHSO_4$, $MSBPHSO_4$, $DEMSBAMHSO_4$, $TESBAMHSO_4$, $TESPAMHSO_4$, $DEMSPAMHSO_4$, and $MSPPHSO_4$ showed very small FFA conversion of <10%. Their results mentioned in Appendix D. The ammoniums and pyrazoliums showed the lowest activity to catalyze the FFA esterification reaction and these results may approve that they are having less acidity than the other investigated ILs. Among the pyrazoliums, only $SBPHSO_4$ showed higher activity to catalyze the esterification reaction. All the imidazoliums, beside $SBPHSO_4$, showed good catalytic activity and they are in the order of $MSPIMHSO_4 < SBPHSO_4 < MSBIMHSO_4 < BSPIMHSO_4 < BSBIMHSO_4$. The FFA conversion by these ILs up to 480 minutes are 14%, 14.1%, 47.3%, 55.9%, and 75.3%, respectively.

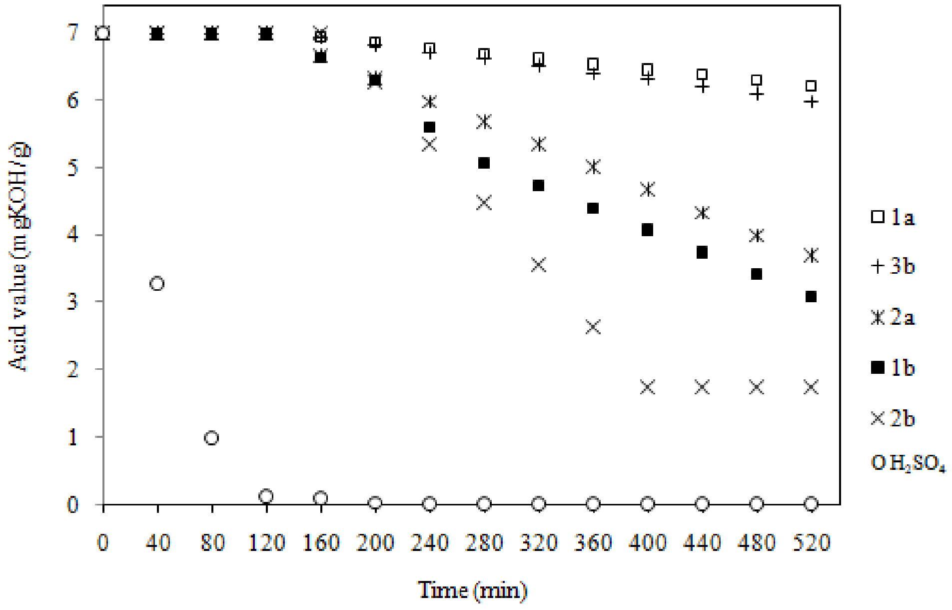


Figure 5.22 CPO acidity reductions during transesterification reaction. 1a - $MSPIMHSO_4$; 1b - $BSPIMHSO_4$; 2a - $MSBIMHSO_4$; 2b - $BSBIMHSO_4$; 3b - $SBPHSO_4$.

The FFA conversion time by these ILs is much longer than those reported by some researchers for acidic catalysts. A complete FFA esterification reduction has been reported to occur within 15 minutes for Brønsted homogenous H_2SO_4 [282], 40 minutes for acidic ion-exchange resins [283], and 100 minutes for acidic ion exchange polymeric resin [284]. Their results indicate that acidic catalysts prefer FFA esterification reaction prior to the transesterification. However, the ILs catalysts used in this work have been found to favour transesterification of TG than the esterification of FFA.

The concentrations of the reactants and POME were monitored over the whole duration of the experiment and the experimental results are plotted as shown in Figure 5.23. From the figure, it is observed that the TG concentration drops by 16% after 40 minutes of reaction. At 160 minutes, the TG concentration drops by 63%, while no drop was seen in the FFA content. These results show that the IL, i.e., $BSBIMHSO_4$, favours the transesterification reaction of TG. At 200 minutes slight drop of 10 % was observed in the FFA. Then the $BSBIMHSO_4$ catalyzed the FFA esterification and TG transesterification simultaneously. However, the FFA drop is higher than the TG. This is because the production of water may reduce the reaction rate as it is considered as one of the TG transesterification reaction problems [15, 140].

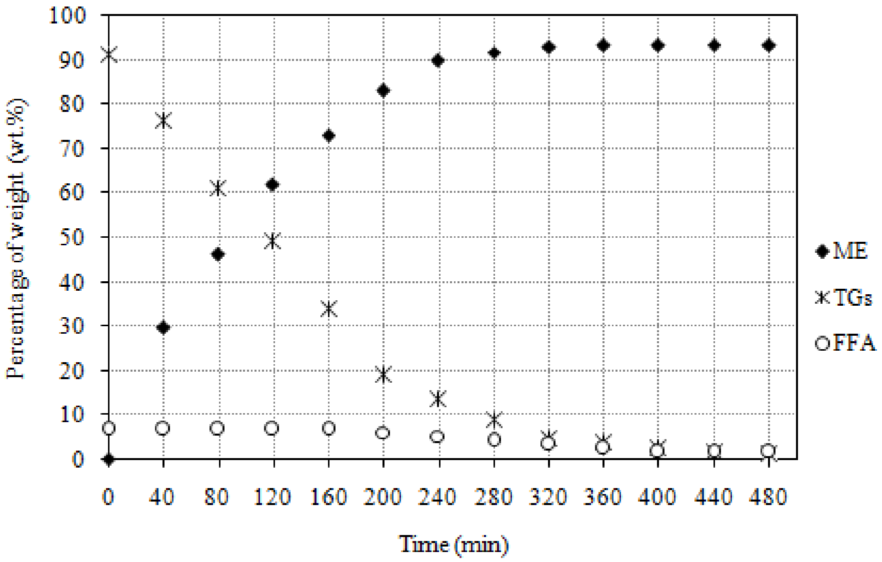


Figure 5.23 The effect of $BSBIMHSO_4$ catalyst on the TG and FFA conversion to ME.

As well, the other imidazolium functionalized ILs; i.e. $MSPIMHSO_4$, $MSBIMHSO_4$ and $BSPIMHSO_4$; primarily performed the transesterification as $BSBIMHSO_4$ (see Appendix F).

The water byproduct, which associated with the esterification reaction, as observed in Figure 5.24, was started forming after 160 min. Water, which is produced as a byproduct during the traditional alkali/acid catalyzed transesterification and esterification reactions, is one of the variables affecting the transesterification of VOs [2]. Therefore, it is important to determine the effect of water formation during the IL-catalyzed transesterification too. This was investigated by monitoring the biodiesel product and water byproduct formed during the time of reaction. The concentration of produced biodiesel (wt%) and water content (wt%) were plotted as a function of time and the results are as shown in Figure 5.24.

As discussed above, the IL favours the transesterification than the esterification reaction. It started to form the esters while no water byproduct was observed up to 160 minutes.

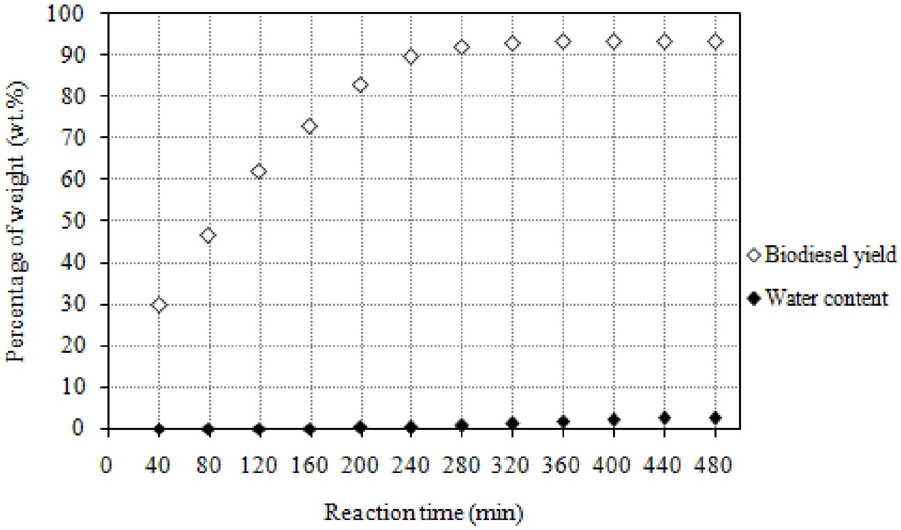


Figure 5.24 Water formation during the BSBIMHSO$_4$-catalyzed transesterification of CPO.

After 200 minutes, a water content of 0.16 wt% was formed simultaneously with the formation of glycerol. When the reaction time reached 240 minutes, the water content reached 0.33 wt%, the IL-catalyzed transesterification progress seems to be quenched. This is in agreement with the observations by other researchers, [13, 15, 140, 169], who reported that water content should be kept as low as possible.

Other researcher specified the water content to be less than 0.3 wt% ([144]). This is due to that the water can easily reacts with the alkali catalyst to form soap and this soap complicated the transesterification progress [21]. However, the catalysts studied in this work are totally different than the alkali catalysts. These results indicated that the behavior of IL is still unknown and requires an extensive research in order to understand their basicity/acidity performance. As shown in Figure 5.24, when the water content reach 1.7 wt.%, the reaction seems to be totally halted as indicated by a small increment of 0.62 wt.% in the biodiesel yield. Since IL has an affinity to absorb water, it is possible that the water absorbed could inhibit the catalytic activity of ILs. In compare to alkali-catalyzed transesterification the water consumes the catalyst itself.

5.4.7. The effect of IL-moisture on biodiesel yield

For conventional catalyst such as H_2SO_4 and alkaline, the effect of water on transesterification reaction has been investigated by several previous researchers, who noted that the water level in the starting material should be kept as low as possible [15, 140, 169]. Ma and Hanna [13] reported that water content is a more critical variable affecting the progress of transesterification reaction than the FFA. Yang *et al.*, [144] proposed that the oil should have water content of less than 0.3 wt.%. This is because water will react with alkaline catalyst to produce soap, due to saponification side reaction [169], thus consume the conventional catalyst [21].

Since the CPO was well treated and dried, and anhydrous grade methanol was used, the effect of water content in IL catalyzed transesterification reaction was studied separately using $BSBIMHSO_4$ as catalyst. The synthesized $BSBIMHSO_4$ was used with different ways of drying and storage keeping. Fifteen samples (1.25 g each) were taken from the well dried $BSBIMHSO_4$ (81 ppm water content), the first sample was kept in a dry dessicator before using it and the other 14 samples were exposed to air for various length of time ranging from 0 to 145 mins. Figure 5.25 shows the increase of water content versus the contact time of IL with air.

The water content of the exposed ILs was measured by coulometric Karl-Fisher titration. The increasing water content in $BSBIMHSO_4$ after longer exposure to the atmosphere indicates that it is miscible with water. After 145 minutes of exposure, the water content in the IL increased to about 0.04% of the IL weight. The selectivity of the anion has been described as one of the primary factors determining the solubility of IL in water and the cation has a secondary effect [250]. All 24 ILs, containing HSO_4^- as an anion, exhibit high water solubility. This indicated the influence of anion on the water solubility properties of the ILs.

The 15 moisturized samples of $BSBIMHSO_4$ were used as catalysts in the transesterification reaction at the optimum reaction conditions of temperature, methanol/CPO molar ratio, mixing intensity, and the concentration of catalyst used was 5 wt.%.

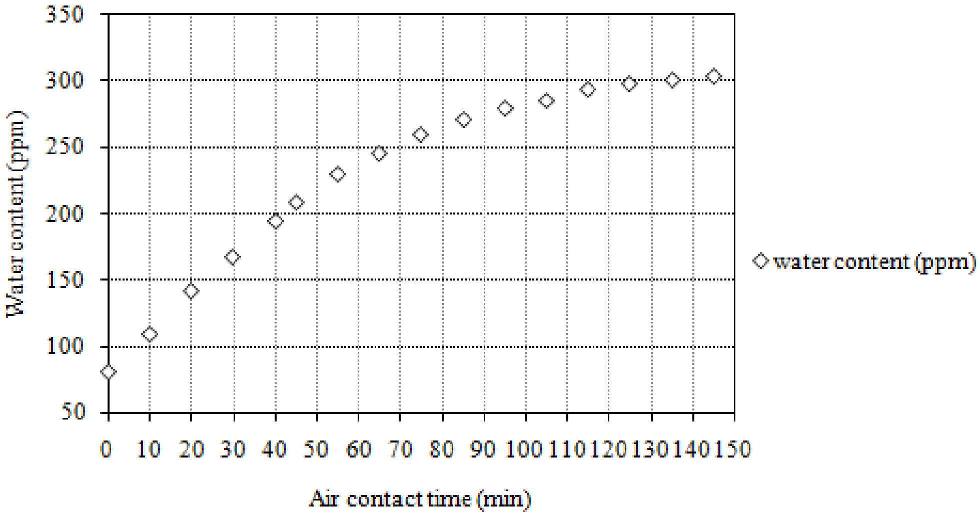


Figure 5.25 BSBIMHSO$_4$ water absorption from atmospheric air at different period of exposure at ambient temperature.

The experimental results of biodiesel yield versus the IL moisture content are presented in Figure 5.26. The figure shows that when the IL water content increases from 81 ppm to 142 ppm, the biodiesel yield drops from ~93 % to ~83.3 %, a reduction of 10 %. When the moisture content is 215 ppm, the yield reduces to ~40 %.

When the moisture content reaches 303 ppm, the yield is reduced to 2.5%. This low yield indicates that the catalytic activity of BSBIMHSO$_4$ was quenched by this amount of moisture. According to Seddon *et al.* [250], for any efficient application of IL, the moisture content should be maintained at about 100 ppm. This effect was observed in our work, where maximum biodiesel yield was obtained at moisture content of approximately 100 ppm.

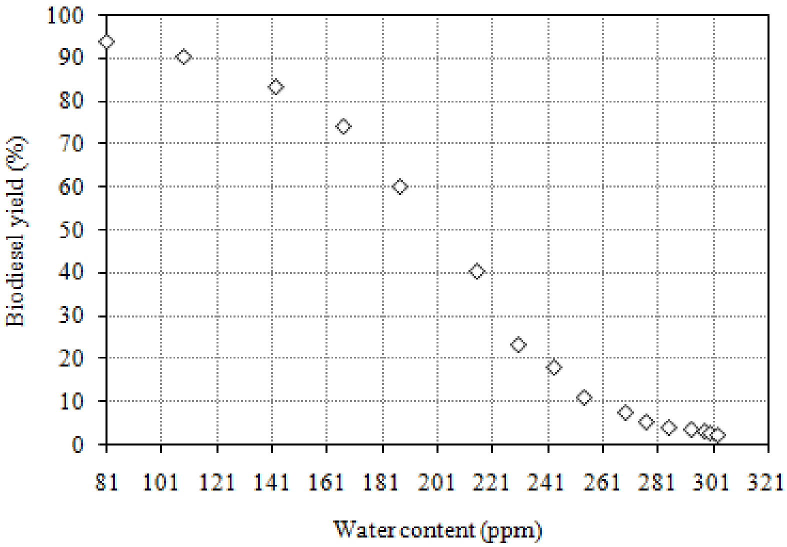


Figure 5.26 The effect of BSBIMHSO$_4$ water content on biodiesel yield.

5.4.8. Reusability of SO$_3$H-functional imidazolium Brønsted ILs

Upon completion of the transesterification reaction and the IL has been recovered by separation, the IL was dried under vacuum at 0.01 mmHg and 80 ºC for 4 hours to remove any traces of water before being re-used. The experimental results in Figure 5.27 revealed that 100% recovery of IL is possible. This is because the ILs showed no miscibility with the produced POME. In these set of experiments, the SO$_3$H-functional imidazolium Brønsted ILs was re-used eight times, or occasionally more, and the POME content retained at each run was 99.99 %. This high percentage indicates that the activity of the catalyst was retained after recycling. The high catalytic activity after recycling was also observed in pyrazolium and ammonium functionalized ILs (see Appendix G). This property indicates high potential of the selected ILs to be considered as replacement for conventional catalyst in transesterification reaction, possibly even for large scale production of biodiesel.

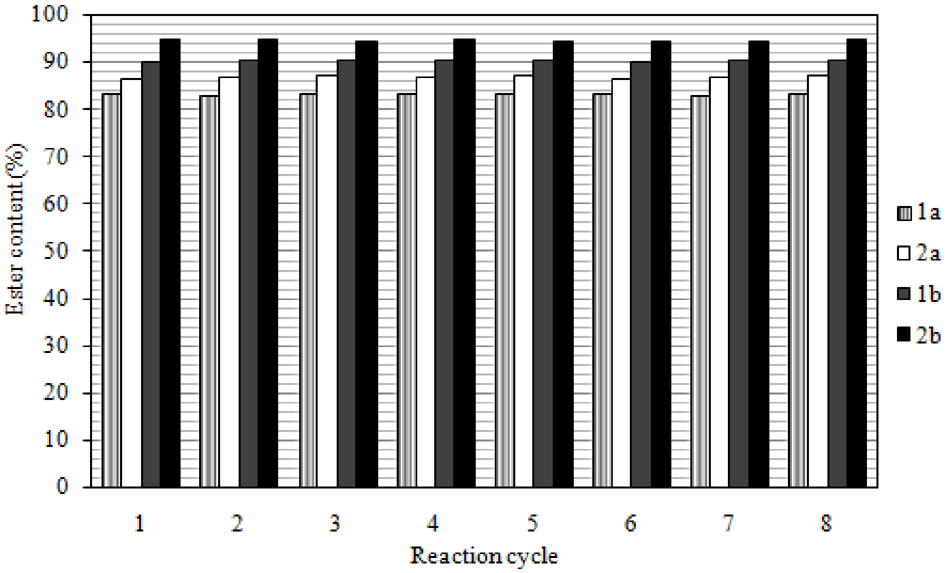
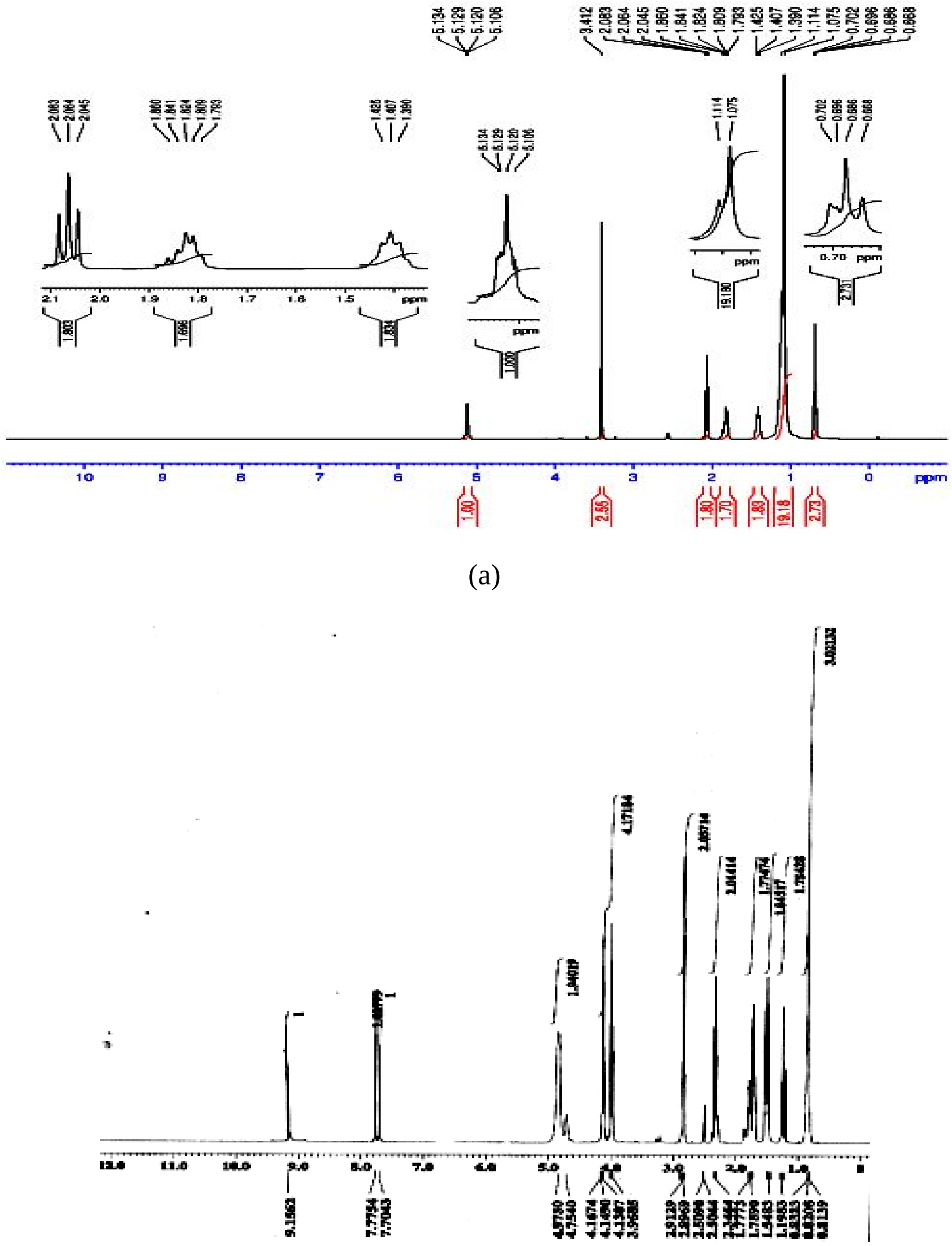


Figure 5.27 Comparison of biodiesel yield after recycling of the functionalized imidazolium acidic ILs. 1a - $MSPIMHSO_4$; 1b - $BSPIMHSO_4$; 2a - $MSBIMHSO_4$; 2b - $BSBIMHSO_4$.

After completing the last run of the transesterification reactions the biodiesel samples and recovered ILs were analyzed by ^1H NMR to check for the purity of biodiesel and the efficiency of the purification method, and to compare the biodiesel conversion calculated from the NMR result with that from the GC result. Figures 5.28a and 5.28b show the proton NMR results for the biodiesel obtained after the 8th run and for the $BSBIMHSO_4$ after it has been recovered.



(a)

(b)

Figure 5.28 Proton NMR spectrum for (a) POME (94.44% obtained after 8 hours at 170 °C, 5.0 wt% of recycled BSBIMHSO$_4$, 12:1 molar ratio of methanol/CPO and 800 rpm); (b) Recycled BSBIMHSO$_4$ spectra after 8 runs of transesterification reaction.

As can be seen from the POME spectrum, the biodiesel is pure, even traces of IL could not be detected. The peaks in Figure 5.28a were identified based on the works of Jin *et al.*, [285, 286]. Peaks 1-7 are identified as C$\underline{H_3}$-C-, -C-C$\underline{H_2}$-C-, -O-CO-C-$\underline{CH_2}$-, -C-C$\underline{H_2}$-

C=, O-CO-C$\underline{H_2}$-, =C-C$\underline{H_2}$-C=. A large signal observed at 3.412 ppm indicates the presence of methyl oleate [62].

Although, the nonappearance of peaks between 4.0 to 4.3 ppm suggests that no traces glycerol was present in the biodiesel sample, however, minor traces of glycerol was detected by GC (see Figure 5.29b). This result may suggest that GC is more sensitive to detect trace amount of glycerol compared to ^{1}H-NMR. The absence of esters peaks in Figure 5.28b indicates no traces of POME remained in the IL.

From the GC results given in Table 5.3, 94.6 % of ester was obtained at the end of the reaction using recycled BSBIMHSO$_4$. Using the area per proton from the NMR spectra and the simple equation below [287], given by Meher *et al.* [2] and da Silva *et al.* [288], the ester content was calculated to be 94.44%. The calculated yield based on ^{1}H NMR results is in good agreement with the GC results.

$$C = 100 \times \left(\frac{2A_{ME}}{3A_{CH_2}} \right) \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (5.4)$$

Where, C is methyl ester percentage; A_{ME} integration value of the protons of the methyl esters; and A_{CH_2} integration value of the methylene protons.

Table 5.3 GC results for FAME[a] content of CPO catalyzed with BSBIMHSO$_4$

FAME	Methyl Laurate	Methyl Myristate	Methyl Palmitate	Methyl Stearate	Methyl Oleate	Methyl Linoleate	Total content
%	0.348	1.02	45.507	4.101	35.408	8.233	94.608

[a] Product obtained at fixed operation conditions of 5.0 wt% recycled BSBIMHSO$_4$, reaction temperature 170ºC, Methanol/CPO molar ratio 12:1, mixing intensity 800 rpm and reaction time 8 hours.

5.4.9. Comparison of BSBIMHSO$_4$ and H$_2$SO$_4$ catalytic systems

The best performance catalyst among the 12 synthesized RTILs, i.e. BSBIMHSO$_4$ was selected for catalytic performance comparison against H$_2$SO$_4$.

In the H$_2$SO$_4$ catalyzed transesterification, maximum yield of 95.3% was obtained at the optimum reaction conditions of 130 °C, molar ratio of no less than 30:1 after approximately 7 hours of reaction. When the same reaction conditions were employed for the $BSBIMHSO_4$ catalyzed transesterification, the maximum yield achieved after 7 hours of reaction was 74 %. However, by increasing the temperature to 170 °C and even reducing the methanol to CPO ratio to 12:1, a higher yield was obtained (94.6 %). This seems to suggest that it is possible to achieve high biodiesel at low methanol concentration by IL catalyzed transesterification, even though the reaction needs to be carried out at a higher temperature.

Table 5.4 Comparison between $BSBIMHSO_4$ and H_2SO_4 catalysts for palm biodiesel production

	$BSBIMHSO_4$	H_2SO_4
Reaction temperature (°C)	170	130
Required molar ratio of MeOH:CPO	12:1	30:1
Catalyst concentration (wt.%)	5.0	5.0
Mixing intensity (rpm)	800	700
Reaction time required (h)	7	7
Yield of POME	94.6	95.3
Purification of POME	Washing	Repeated washing
Removal of methanol	Normal	Requires more time
Recovery of glycerol	Easy	Difficult
Catalyst recovery	Easy	Difficult
Reusability	Reusable	Not reusable

The ratio indicates that less than half the amount of methanol used in acid catalyzed transesterification is sufficient to produce POME of almost the same yield with IL catalyst. This gives the extra advantage of reducing the time and energy for removal of excess methanol.

Compared to H_2SO_4 catalyzed transesterification, the recovery of glycerol in IL catalyzed system, is easier since the HSO_4^- – SO_3H functionalized IL is immiscible in the byproduct. In the laboratory, the IL can be recovered by simple decantation while the H_2SO_4 can be recovered by distillation at a very high temperature since the boiling point of H_2SO_4 equal to 290 °C [13]. However, some oils showed degradations near to 200 °C [275, 276].

Hence, the recoverability indicates that the ILs can be reused for transesterification of CPO and the results shown in Figure 5.28 confirm that.

Even though the experimental results show that at low temperature, the catalytic activity of H_2SO_4 is higher than that of $BSBIMHSO_4$, however the concentrated H_2SO_4 is corrosive and is not easily recovered. Besides, its recovery process is associated with the release of some environmentally unfriendly effluents such as acidic wastewater and presents a series of serious environmental problems. On the other hand, ILs are noncorrosive, recyclable without losing its catalytic activity and much easier to be separated from the esters. In addition, their properties such as negligible vapor pressure, high catalytic activity, good chemical and thermal stability, potential recoverability, and ease of separation of the products from reactants present additional advantages over H_2SO_4. Therefore, in consideration of the catalytic activity and environmental benefits, the $BSBIMHSO_4$ IL catalyst is more superior than concentrated H_2SO_4.

5.4.10. Comparison between IL and other recent catalysts used for transesterification reaction

In most cases, the factors that affect transesterification reactions are the nature of raw materials, types of catalyst and other experimental conditions such as temperature, methanol to oil molar ratio and catalyst concentration.

Table 5.5 Comparison of product yield and reaction conditions of several new heterogeneous catalysts used recently to produce biodiesel

Feedstock	Catalyst	MeOH:oil ratio	Time (h)	Temp (°C)	Yield (%)	Reference
Soybean oil	Al_2O_3	15:1	8	500	96	[289]
Sunflower oil	NaOH/ γ -Al_2O_3	12:1	24	120	86	[290]
Soybean oil	La/zeolite beta	14.5:1	4	160	48.9	[291]
Blended VO	Mesoporous silica/MgO	8:1	5	220	96	[292]
Sunflower oil	CaO/SBA-14	12:1	5	160	95	[293]

Sunflower oil	WO_3/ZrO_2	15:1	5	200	92	[294]
High FFA Feedstock	$SO_4^{2-}/TiO_2–SiO_2$	9:1	6	200	92	[295]
Cottonseed oil	Mg-Al-CO_3 HT	6:1	12	210	87	[80]
Palm oil	Mg-Al-CO_3	30:1	6	100	86.6	[83]
Soybean oil	MgO, ZnO, Al_2O_3	55:1	7	130	82	[296]
VO	ZrO_2/WO_3	15:1	5	200	97	[274]
Palm oil	Montmorillonite KSF	8:1	3	190	79.6	[297]
Sunflower oil	K_2CO_3/Al–O–Si	15:1	> 8	120	95	[298]
Rapeseed oil	ZnL_2	12:1	2	195	54	[299]
Feedstock	Catalyst	MeOH:oil ratio	Time (h)	Temp (°C)	Yield (%)	Reference
Soybean oil	Al/(Mg+Al)	13:1	1	230	90	[300]
Cottonseed oil	S-MWCNTs*	9:1	3	260	89.93	[301]
Canola oil	$AlCl_3$	24:1	18	110	98	[302]
VO	WO_3/ZrO_2	9:1	8	200	98	[303]

*Sulfonated multi-walled carbon nanotubes

In the last two years, numerous efforts have been made to discover new catalyst for low-grade materials and even for well refined oils due to the problems associated with conventional catalysts. However, compared to transesterification by homogenous catalysts, transesterification reaction with solid heterogeneous catalyst requires more extreme reaction conditions, i.e., higher temperatures and pressures, examples given in Table 5.5. This could be due to the existence of a three phase immiscible system of oil, methanol and catalyst [304].

As can be seen from the data presented in the table, different catalysts, molar ratios, and reaction times were used by several researchers at different temperatures to get different yields. The highest ester yield of 98%, using heterogeneous catalysts, was produced by Soriano *et al.*, [302] and Park *et al.*, [303] at temperatures of 110 °C and 200 °C, respectively. Most of the tabulated researchers used very high, i.e. ≥ 200 °C. However, as mentioned above, they did not notice the feedstock degradation temperatures since some of the oils starts to degrade at temperatures above 190 °C, which affecting their yields.

In terms of product yield, IL catalyzed transesterification does not differ much from the conventional processes. However, the significant difference is the advantageous offered by ILs, which lie in their unique properties of being non-corrosive, recyclable, easily recovered, able to catalyze both transesterification and esterification reactions simultaneously in a continuous reaction within an acceptable reaction time (< 8 h) and using less alcohol.

5.5. Palm biodiesel characterization and kinetics

5.5.1. Proposed mechanism of IL-catalyzed transesterification reaction

A reaction mechanism for the transesterification of CPO with methanol using IL catalyst is proposed as in Scheme 5.1. The mechanism involves four steps.

It is proposed that after the mixing of methanol and IL, at high temperatures, i.e. ≥ 100 °C, the HSO_4^- anion extracts H^+ from methanol to create methoxide anion. Since the IL-catalyzed transesterification required higher reaction temperature and it did not show high conversion at <170 °C, these interactions may require extensive heating since the direct catalysis with methoxide base requires low temperatures [259, 263]. This assumption may answers the inquiry of why the IL-catalyzed transesterification requiring high temperature. As discussed in Figure 5.23, the drop of TG was observed before the FFA, and this indicates that the methoxide started directly to react with the TG.

The reaction scheme proposes that in excess of methanol, the methoxide anion is attached to the carbonyl group of the TG in three positions. At the first step, the methoxide anion reacts with TG to form methylester and diglyceride molecule. At the second step, methoxide anion reacts with the diglyceride molecule forming methylester and monoglyceride molecule. Finally at the third step, the monoglyceride molecule reacts with the methoxide anion to form methylester and glycerol. The remained methanol (n–3) and IL are shown in the last step.

5.5.2. Quantification of glycerides

The effects of intermediates concentrations, i.e. formation of DG and MG, on the reaction rate were explored for four functionalized imidazoliums. The rate constants, reaction rates and activation energies were studied at the temperature range of 120–170 °C, while all parameters were kept to the optimal conditions determined previously.

Scheme 5.1

5.5.2.1. Response factor

A calibration curve for glycerides standards was established using four reference materials to simulate the composition of the sample mixtures. The biodiesel composition was determined based on the EN 14214 standard method. However, the contents of free glycerol, monopalmitin (MG), dipalmitin (DG) and tripalmitin (TG) in samples were calculated from the peak area.

The calibration curves for TG, DG, MG and GL are given in Appendix H. The y-intercepts and correlation coefficients indicate good linearity of 0.999, 0.999, 0.997, and 1.0 of the respective calibration curve.

5.5.2.2. Crude palm oil fatty acid composition

The palm oil fatty acid profile shown in Table 5.6 was determined from the GC analysis using the official AOCS method and practice method Ce 1–62 [253].

The results show that CPO contains primarily eleven fatty acids identified as palmitic acid, oleic acid, linoleic acid, stearic acid, myristic acid, lauric acid, palmitoleic acid, margaric acid, linolenic acid, arachidic acid and gadoleic acid. Of these, palmitic (Hexadecanoic) acid, oleic (Octadec-9-enoic) acid, linoleic (9,12-octadecadienoic) acid, stearic (Octadecanoic) acid, and myristic (Tetradecanoic) acid are present in large amount in CPO. They are also frequently found in most of oils [305]. While the other fatty acids; lauric, palmitoleic, margaric, linolenic, arachidic and gadoleic, are present in minor amount.

The amount of linoleic acid in materials for transesterification is important because linoleic acid has a high tendency to oxidize [23]. According to the standard method EN 14214, the maximum allowable linoleic content in oils for transesterification is 12%. This is not a concern with CPO since the quantity of linoleic acid is small of 0.2 wt.% as presented Table 5.6.

Table 5.6 Crude palm oil fatty acid composition

Fatty acid	CPO (wt.%)
Lauric acid (C12:0)	0.40
Myristic acid (C14:0)	1.26
Palmitic acid (C16:0)	46.90
Palmitoleic acid (C16:1)	0.07
Margaric acid (C17:0)	0.10
Stearic acid (C18:0)	4.59
Oleic acid (C18:1)	36.85
Linoleic acid (C18:2)	9.09
Linolenic acid (C18:3)	0.20
Arachidic acid (C20:0)	0.39
Gadoleic acid (C20:1)	0.15

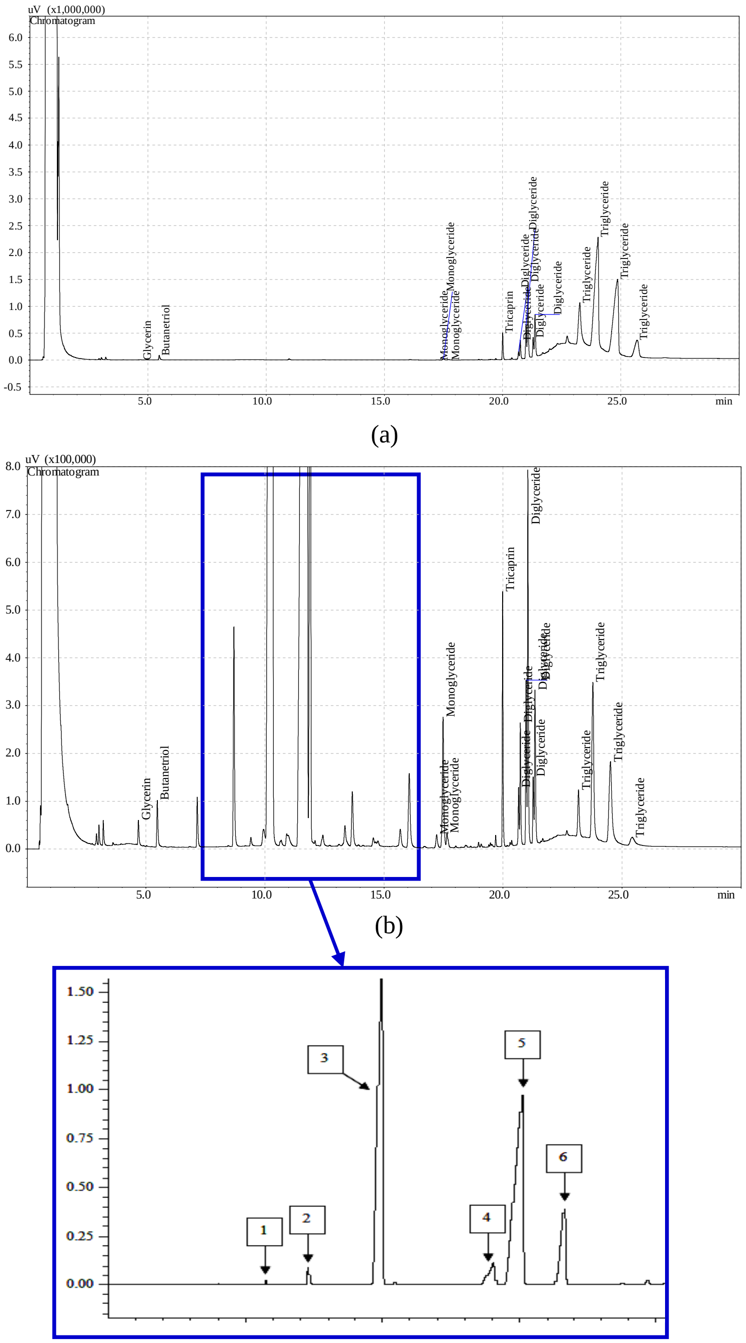
* Average of triplicate results

The quantification of GL, MG, DG and TG is necessary to ensure that the quality of oil meets the biodiesel specifications. The esters and glycerol contents in CPO were analyzed by GC methods according to ASTM D6751 [261] and EN 14214 [23].

Figure 5.29a presents the GC chromatogram of CPO sample before starting the transesterification reaction. The GC response (presented in Figure 5.29a) showed that the CPO contains small traces of glycerine and high amount of TG.

Figure 5.29b presents the analyzed compounds peaks progression of derivatized glycerine, butanetriol standard, methyl esters, derivatized MG, tricaprin second standard, derivatized DG, and TG. Small peaks of minor components, such as sterols, are also detected by the GC.

Figure 5.29c presents the esters content in the CPO biodiesel. The chromatogram for FAME content in CPO biodiesel indicates the presence of methyl laurate, methyl myristate, methyl palmitate, methyl stearate, methyl oleate, and methyl linoleate in the produced CPO biodiesel.



(a)

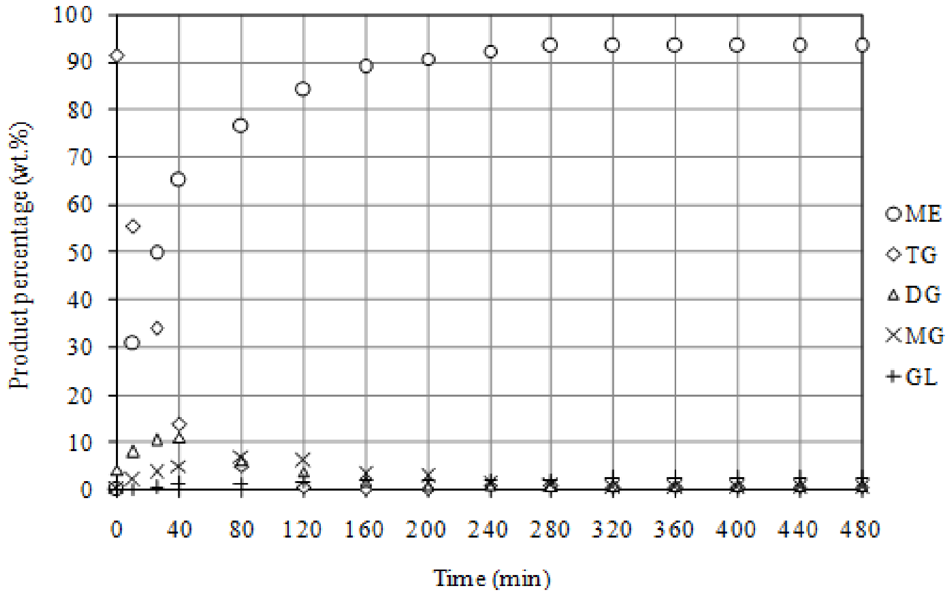
(b)

(c)

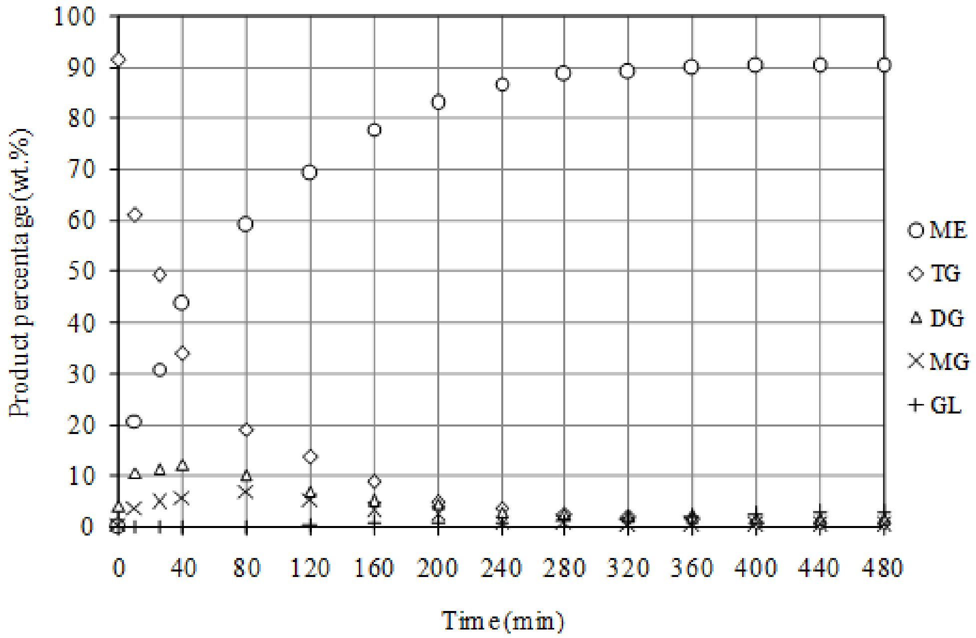
Figure 5.29 GC chromatograms of (a) Crude palm oil; (b) Transesterified crude palm oil ; (c) FAME of crude palm oil; Peaks 1- methyl laurate, 2 - methyl myristate, 3 - methyl palmitate, 4 - methyl stearate, 5 - methyl oleate, and 6 - methyl linoleate.

From the GC analyses of the products and intermediates sampled during the duration of the transesterification reaction, a plot of product yield and intermediates concentration was generated for each IL catalyst. Figures 5.30a, b, c and d show the changes in the reaction mixture compositions and the drop of TG concentration during the course of the reaction. In all cases, the concentration of ME increases and then the rate of formation started to reduce indicating that the reaction is coming to a stop. The same observations were also made by Noureddini and Zhu [132] and Vicente *et al*. [189] for the methanolysis reaction of soybean and sunflower oil, respectively. As the reaction progressed, the concentration of DG and MG intermediates increased and the concentration of TG decreased due to the formation of ME.

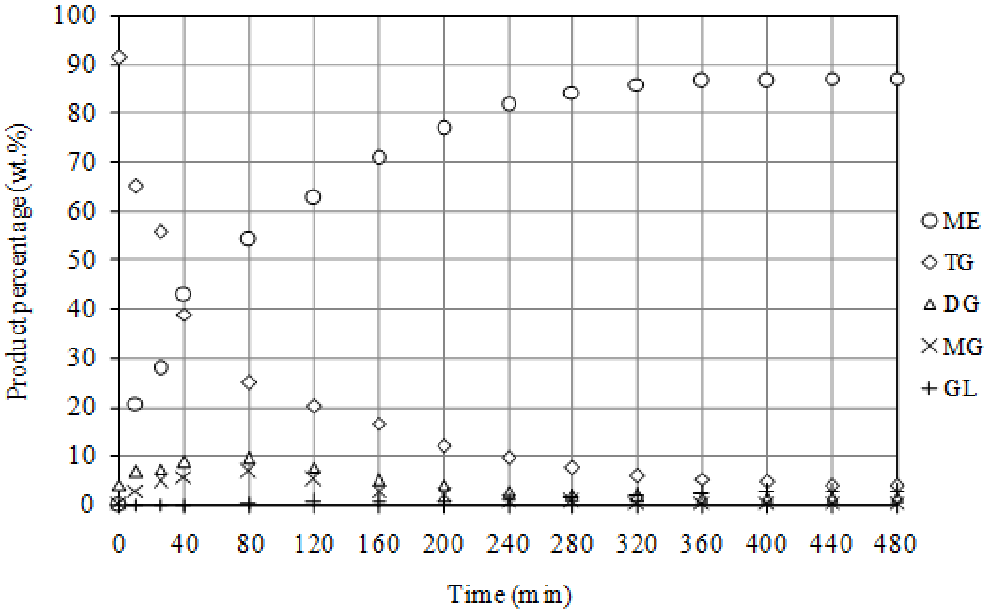
Eventually, the concentrations of DG, MG, TG and ME stayed almost constant as the reaction reached equilibrium. Since excess methanol was used, the final concentration of ME exceeds that of TG. This is the expected behavior of homogeneous reaction where the concentration of TG ultimately falls below the concentration of DG and MG [259].



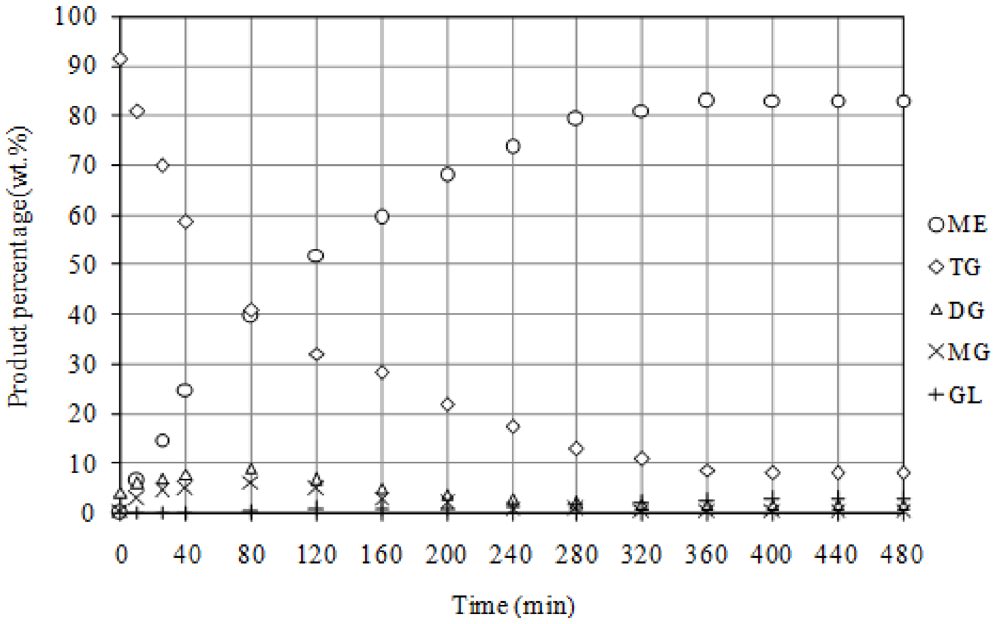
(a) Catalyst type- $BSBIMHSO_4$



(b) Catalyst type-MSBIMHSO$_4$



(c) Catalyst type-BSPIMHSO$_4$



(d) Catalyst type-MSPIMHSO$_4$

Figure 5.30 The concentration of product and intermediates during the transesterification of CPO at optimum conditions (a) 5.0 wt.% of BSBIMHSO$_4$; (b) 5.0 wt.% of MSBIMHSO$_4$; (c) 5.2 wt.% of BSPIMHSO$_4$; (d) 5.2 wt.% of MSPIMHSO$_4$.

The final purification step of biodiesel synthesis is the removal of free glycerol from the biodiesel, which can be achieved by washing with solvents. In this work two types of solvent and de-ionized water were used.

Table 5.7 Free glycerol content in biodiesel samples after washing

	Free glycerol content (wt%)		
Catalyst	Ethyl acetate	DI	Ethanol
MSPIMHSO$_4$	0.011	0.026	0.144
MSBIMHSO$_4$	0.017	0.023	0.083
BSPIMHSO$_4$	0.014	0.031	0.102
BSBIMHSO$_4$	0.009	0.024	0.053

Table 5.7 presents the content of free glycerol in the biodiesels obtained by imidazolium catalyzed transesterification using MSPIMHSO$_4$, MSBIMHSO$_4$, BSPIMHSO$_4$ and BSBIMHSO$_4$ after washing.

From the table, the free glycerol content in biodiesel samples after washing with ethyl acetate is well within the accepted range (≤0.02 wt). This might be because glycerol is extremely soluble in ethyl acetate [21] while the ILs are not. However, biodiesel is also extremely soluble in this solvent, therefore there might be some product lost during the washing. On the other hand, washing with deionized water (DI) showed results near to the accepted value.

Table 5.8 compares the total glycerides of the produced biodiesel using the four ILs before and after the distillation. As expected, after being washed with Ethyl acetate, the results obtained for the distilled samples show lower total glycerides content, which agree with the biodiesel specifications of EN 14214 and ASTM D 6751.

It was observed that biodiesel yield for un-distilled samples containing high total glycerol content. A trend of decreasing yield was observed as the total glycerol content increases.

Table 5.8 Total glycerol content in four biodiesel samples before and after distillation

	Total glycerol content (wt%)	
Catalyst	Un-distilled sample	Distilled sample
MSPIMHSO$_4$	0.71	0.28
MSBIMHSO$_4$	0.61	0.20
BSPIMHSO$_4$	0.56	0.11
BSBIMHSO$_4$	0.54	0.10

5.5.3. Kinetics of Transesterification

The kinetic study in this work takes the following assumptions:

(a) The reaction was assumed to take place in the oil phase.

(b) The use of excess methanol (>3:1) ensures the forward reaction.

(c) The backward reaction is neglected since excess methanol is used to ensure the forward reaction, thus the product concentration by the backward reaction is considered negligible. Thus, the transesterification kinetics was only calculated for the forward reactions.

To correlate the experimental results for four ILs based on the reaction time and five different temperatures, the kinetics analysis came out with a set of three rate constants for each temperature.

The initial content of TG, DG and MG in crude palm oil measured using the GC was 91.5%, 4.4%, and 0.56%, respectively. The molecular weights of TG, DG, and MG of the crude palm oil, and its ME and GL were calculated from the determined fatty acid composition. They are found to be 845.6, 597.0, 347.5, 270.8 g/mol, when BSBIMHSO$_4$ was used, and the molecular weight for GL was 92.1 g/mol, respectively.

The configuration of surface active compounds of MG, DG and soaps favours the formation of very little but stable emulsion. Therefore, the reaction mixture can be considered as a pseudo-homogeneous media and the reaction kinetics was controlled by the transesterification reaction.

5.5.3.1. *First-Order Kinetics*

According to the first order reaction kinetics, the first forward reaction of the CPO transesterification can be expressed as follows:

$$-\frac{d[TG]}{dt} = k_{TG}[TG][MeOH] \cdots\cdots (5.4)$$

Freedman *et al.* [187] calls pseudo-first-order to the condition of when the molar ratio of methanol to triglyceride is high, then the rate of reaction is dependent only on the concentration of TG and the concentration of methanol is assumed to be constant and the reverse reaction is neglected, thus the rate law equation becomes:

$$-\frac{d[TG]}{dt} = k_{TG}[TG] \cdots\cdots (5.5)$$

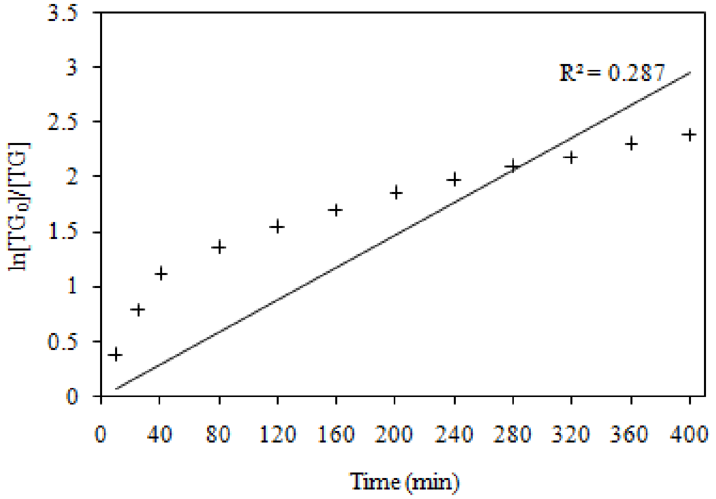
Integration of Equation 5.5 gives:

$$\ln \frac{[TG]_o}{[TG]} = k_{TG.}t \cdots\cdots (5.6)$$

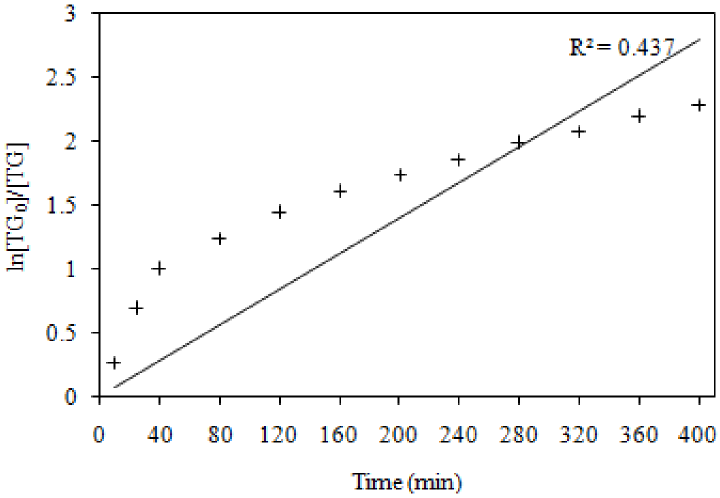
Where k_{TG} is the pseudo rate constant, [TG] is the triglycerides concentration after a "t" time, and $[TG]_o$ is the initial concentration of triglycerides.

Using equation 5.6, the triglycerides concentrations were calculated for each reaction temperature. Then a plot of pseudo first order was plotted as shown on Figures 5.31a, b–f.

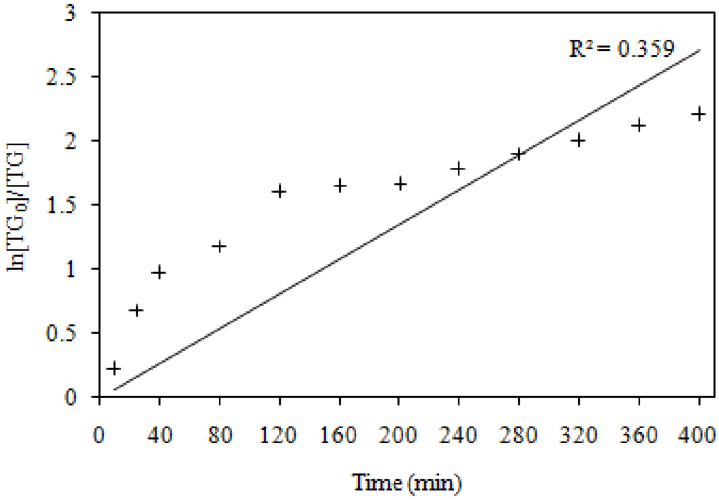
A plot of $\ln[TG]_o/[TG]$ vs. time should be a straight line for the reaction to be a first order with slope of k_{TG}. However, as shown in Figure 5.31 (a–f), the plots did not yield straight lines for the reactions using $BSBIMHSO_4$ as the catalyst. Likewise for the other two catalysts, the plots did not give straight lines and their corresponding correlation coefficient values are not well fitted, as presented in Table 5.9. Therefore, first-order kinetics was not considered.



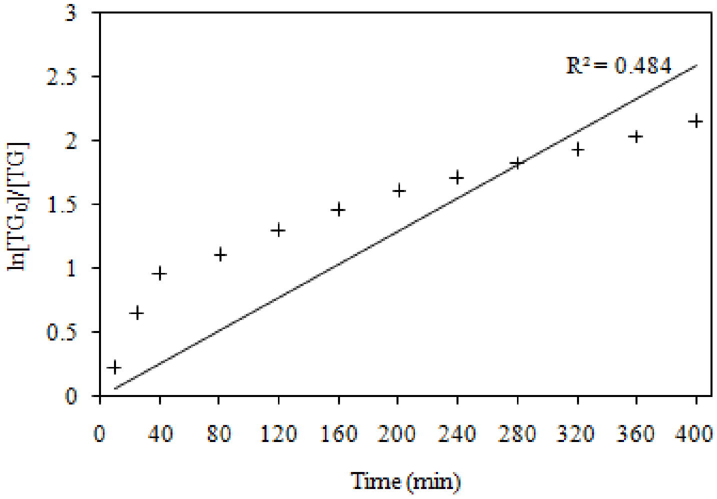
(a) T = 120 °C



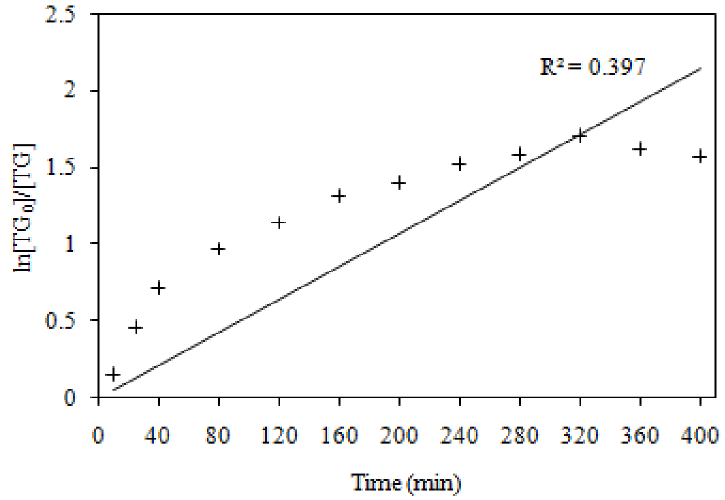
(b) T = 130 °C



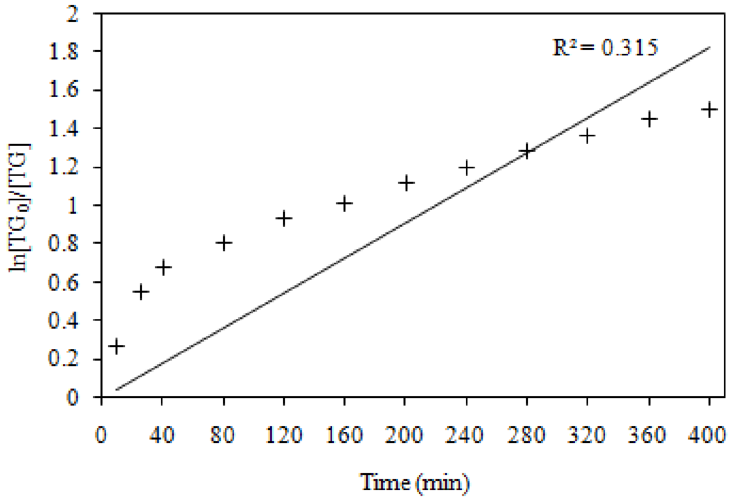
(b) T = 140 °C



(d) T = 150 °C



(d) T = 160 °C



(f) T = 170 °C

Figure 5.31 Plots of the pseudo first order reaction model for the transesterification reaction of crude palm oil with a 12:1 methanol/oil molar ratio and 5.0 wt.% $BSBIMHSO_4$ catalyst at various temperatures: (a) 120 °C, (b) 130 °C, (c) 140 °C, (d) 150 °C, (e) 160 °C, (f) 170 °C.

Table 5.9 The correlation coefficient values obtained at 6 different temperatures and 4 different types of ILs

R^2 (%)

	120 °C	130 °C	140 °C	150 °C	160 °C	170 °C
$MSBIMHSO_4$	26.2	31.3	27.9	19.8	22.2	22.7
$BSPIMHSO_4$	13.6	29	26.8	20.7	15.4	18.8
$MSPIMHSO_4$	19.9	34.5	28.4	22.9	17.4	14.2
$BSBIMHSO_4$	28.7	43.7	35.9	48.4	39.7	31.5

5.5.3.2. Second-Order Kinetics

A second order kinetics was considered following Darnoko and Cheryan [186] who assumed that the forward reaction was a pseudo second-order and the reverse reaction was neglected because the alcohol was in excess. Then the equation for a pseudo second-order reaction rate for TG can be expressed as follows:

$$\frac{d[\mathrm{TG}]}{dt} = -k_{\mathrm{TG}}[\mathrm{TG}]^2 \cdots\cdots (5.7)$$

After integration of Equation 5.7, a new expression is obtained;

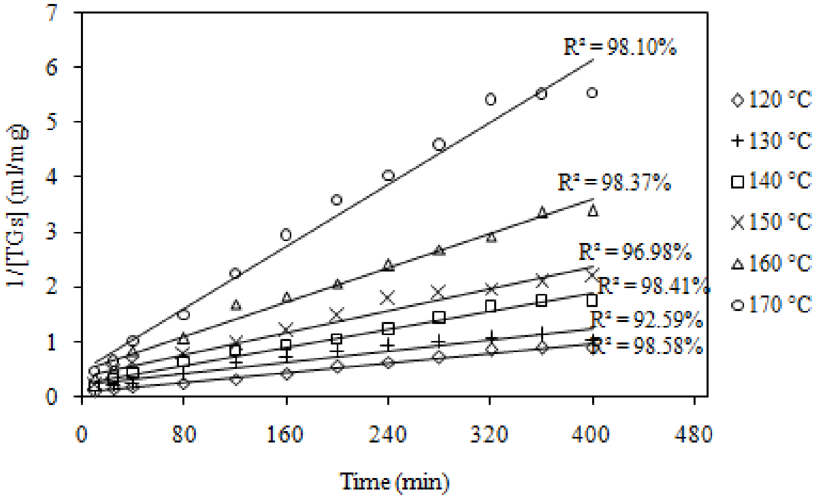
$$\frac{1}{[\mathrm{TG}]} - \frac{1}{[\mathrm{TG}]_o} = k_{\mathrm{TG}}.\mathrm{t} \cdots\cdots (5.8)$$

Similarly, the same set of expression as in 5.7 can be written for the intermediates, DG and MG, and by integrating the expressions, a new expressions as in 5.8 can be written as given in 5.9 and 5.10.

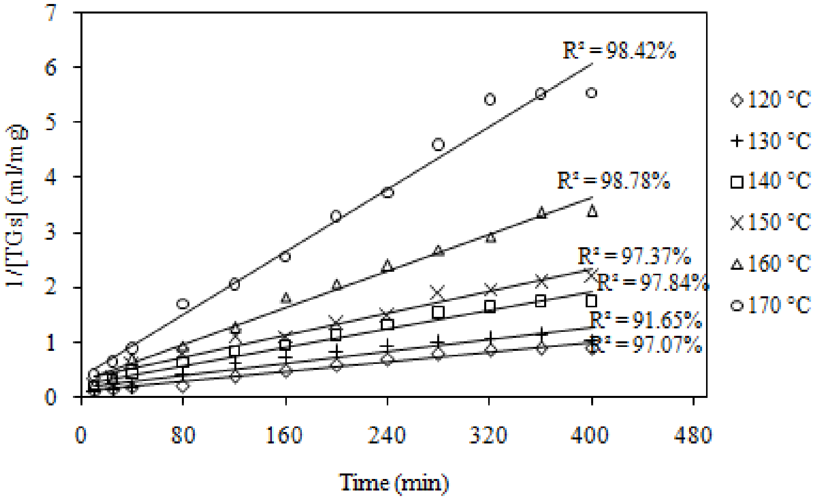
$$\frac{1}{[\mathrm{DG}]} - \frac{1}{[\mathrm{DG}]_o} = k_{\mathrm{DG}}.\mathrm{t} \cdots\cdots (5.9)$$

$$\frac{1}{[\mathrm{MG}]} - \frac{1}{[\mathrm{MG}]_o} = k_{\mathrm{MG}}.\mathrm{t} \cdots\cdots (5.10)$$

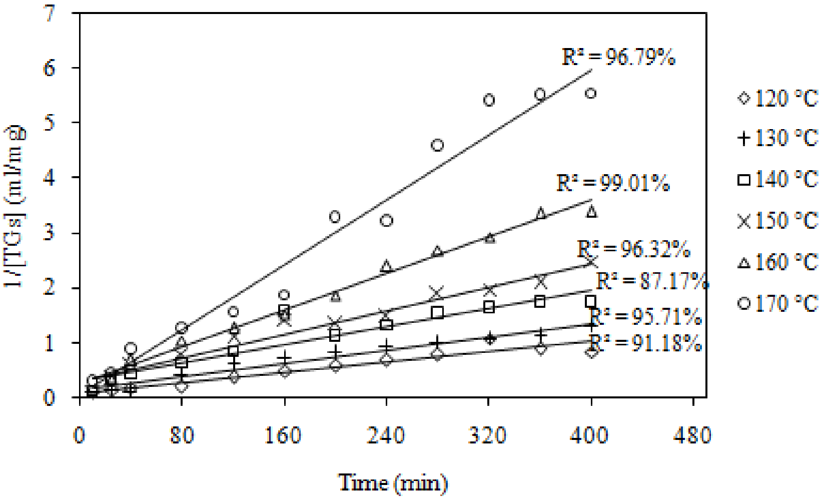
Where “t” is the reaction time, $[\mathrm{TG}]_o$ is the initial concentration of TG; $[\mathrm{DG}]_o$ and $[\mathrm{MG}]_o$ are the initial concentrations of di and monoglycerides, respectively.



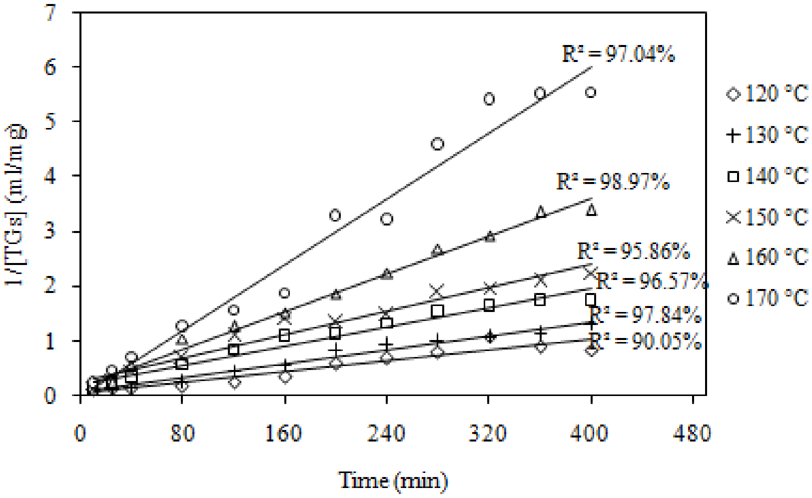
(a) Catalyst type- BSBIMHSO$_4$



(b) Catalyst type - MSBIMHSO$_4$



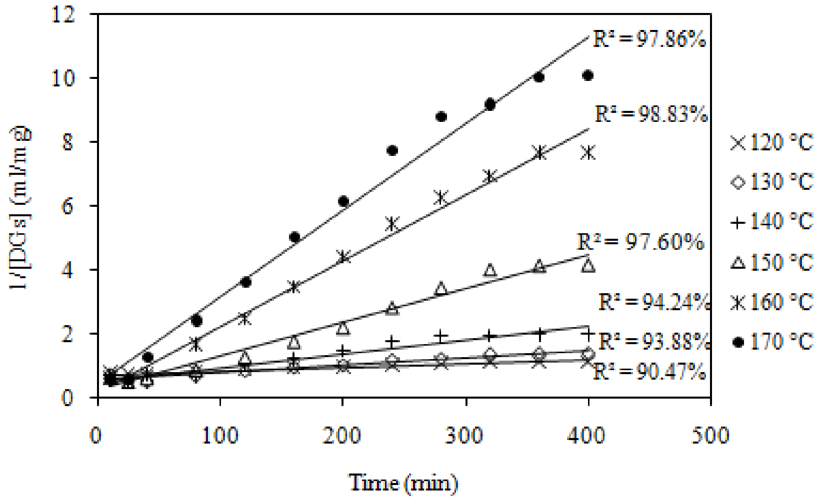
(c) Catalyst type - $BSPIMHSO_4$



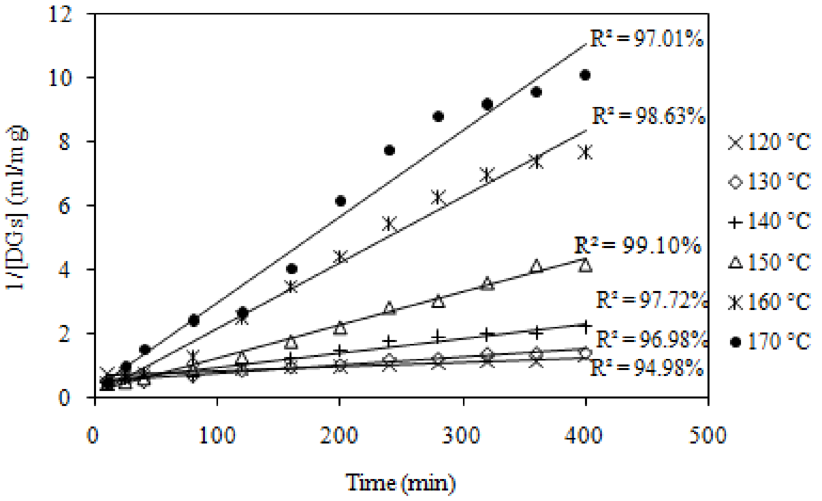
(e) Catalyst type - $MSPIMHSO_4$

Figure 5.32 Plots of 1/[TG] vs. time of pseudo second order reaction model for alcoholysis of crude palm oil at 6 different temperatures, 12:1 methanol/CPO molar ratio, 800 rpm mixing intensity: (a) 5.0 wt.% of $BSBIMHSO_4$; (b) 5.0 wt.% of $MSBIMHSO_4$; (c) 5.2 wt.% of $BSPIMHSO_4$; (d) 5.2 wt.% of $MSPIMHSO_4$.

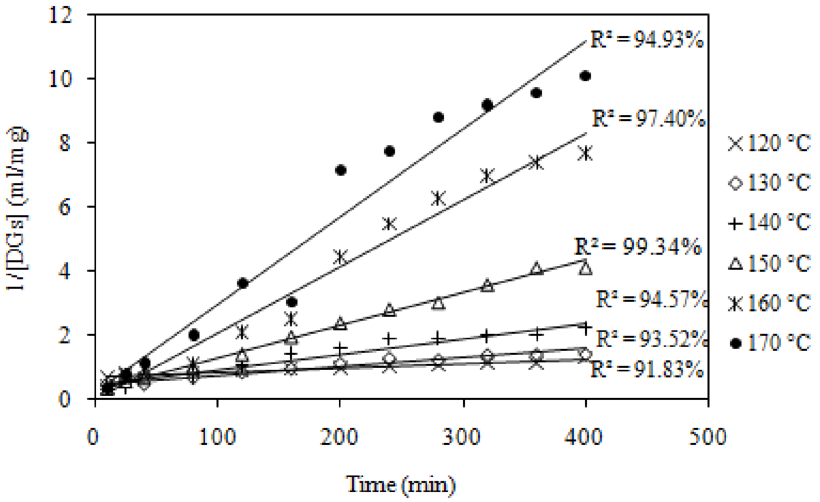
The concentrations of TG, DG and MG for all four catalyst types used in the transesterification of CPO are presented in Figures 5.32, 5.33, and 5.34 respectively, as a function of time at various reaction temperatures. The plots of 1/TGs vs. reaction time show acceptable straight lines, indicating compliance to second order reaction.



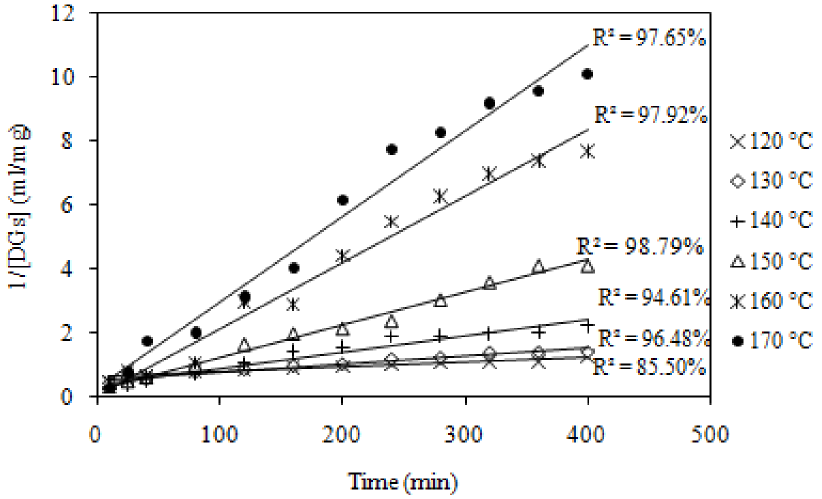
(a) Catalyst type- $BSBIMHSO_4$



(b) Catalyst type - $MSBIMHSO_4$



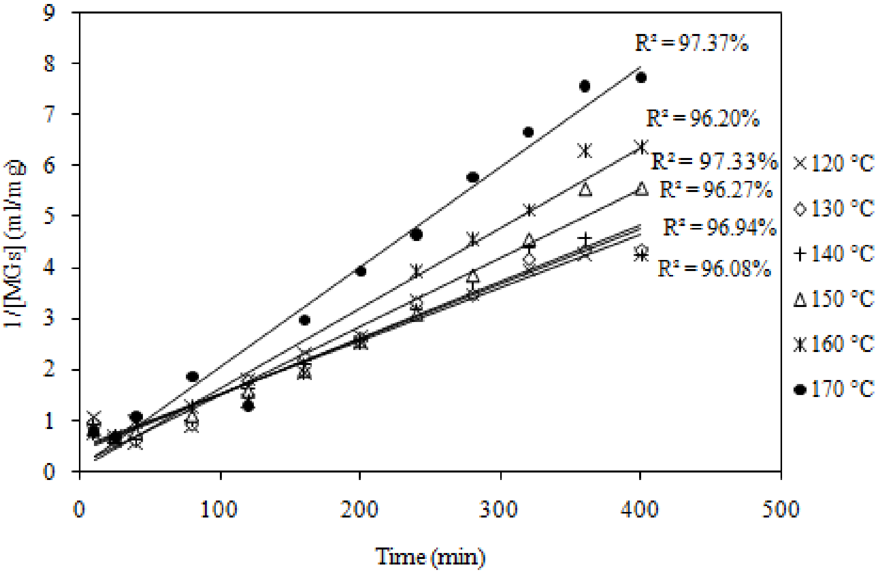
(c) Catalyst type - BSPIMHSO$_4$



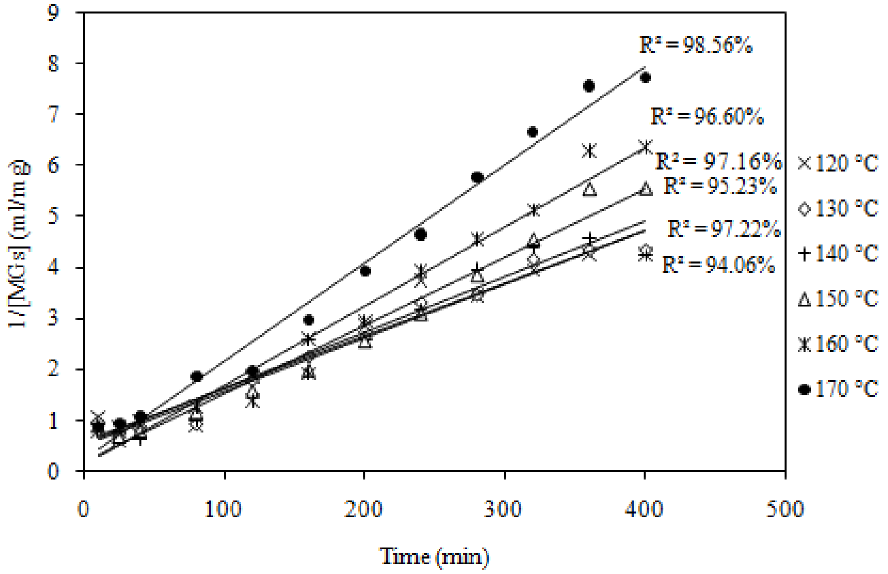
(d) Catalyst type - MSPIMHSO$_4$

Figure 5.33 Plots of 1/[DG] vs. time of pseudo second order reaction model for DGs reaction with methanol at 6 different temperatures, 12:1 MeOH/CPO molar ratio: (a) 5.0 wt.% of BSBIMHSO$_4$; (b) 5.0 wt.% of MSBIMHSO$_4$; (c) 5.2 wt.% of BSPIMHSO$_4$; (d) 5.2 wt.% of MSPIMHSO$_4$.

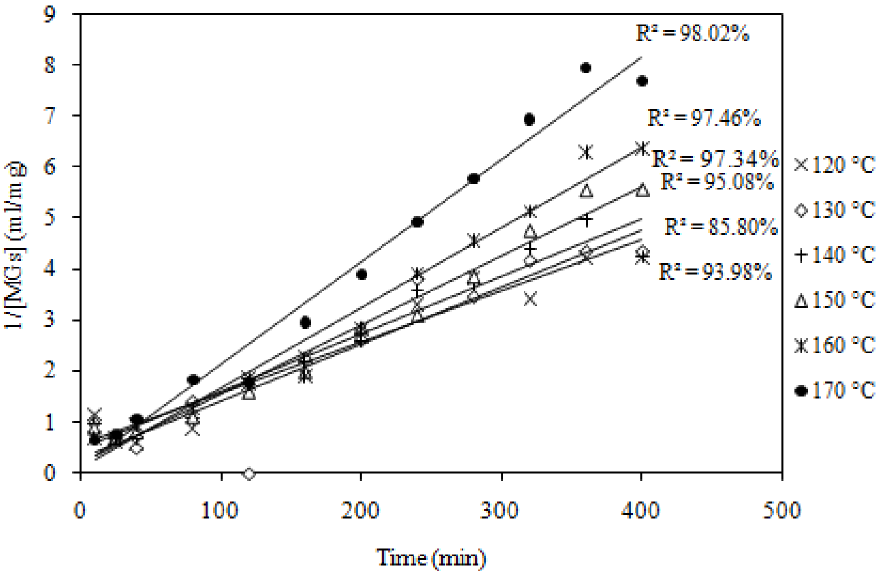
The equations obtained from the fitted graphs were used to calculate the forward kinetic constants. Then the parameters were defined. Where, the rate constant (k, L/mol.s) is determined from the slopes of the line. The forward k values for TG, DG and MG at 6 different temperatures, 4 different types of ILs are tabulated in Table 5.10.



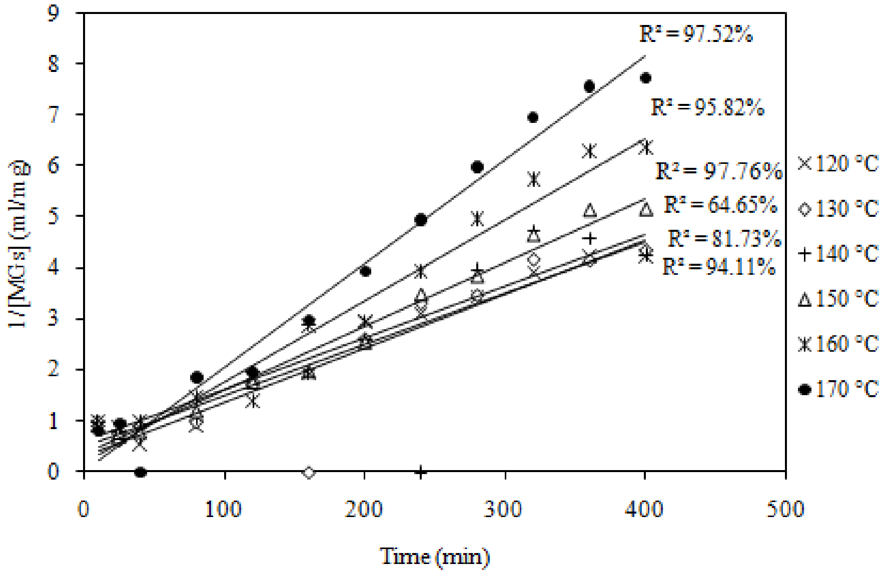
(a) Catalyst type- $BSBIMHSO_4$



(b) Catalyst type - $MSBIMHSO_4$



(c) Catalyst type - BSPIMHSO$_4$



(d) Catalyst type - MSPIMHSO$_4$

Figure 5.34 Plots of the pseudo second order reaction model at 6 different temperatures studied for the MGs reaction with methanol, using a 12:1 molar ratio of MeOH to CPO and catalyst concentration of: (a) 5.0 wt.% of BSBIMHSO$_4$; (b) 5.0 wt.% of MSBIMHSO$_4$; (c) 5.2 wt.% of BSPIMHSO$_4$; (d) 5.2 wt.% of MSPIMHSO$_4$.

The values in the table are average of triplicate runs for each set of conditions. From the table, the values of reaction constant are observed to increase at higher temperature.

It is also observed that the reaction constant for MG is higher than the reaction constant for DG, which is higher than the reaction constant for TG. These observations are in agreement with Darnoko and Cheryan [186] and Leevijit *et al.*, [205] in their kinetic investigations of alkali-catalyzed transesterification of refined palm oil with KOH and NaOH, respectively.

Table 5.10 Reaction constants for TG, DG and MG at six temperatures

IL	Temp. (ºC)	TG → DG	DG → MG	MG → GL
		k_{TG} (L/mol.s)	k_{DG} (L/mol.s)	k_{MG} (L/mol.s)
BSBIMHSO_4	120	0.000855	0.00295	0.302
	130	0.00112	0.00375	0.391
	140	0.00284	0.00731	0.45
	150	0.00599	0.00937	0.592
	160	0.0118	0.0173	0.688
	170	0.0152	0.0208	0.826
MSBIMHSO_4	120	0.000831	0.00282	0.295
	130	0.000996	0.00359	0.381
	140	0.00265	0.00709	0.438
	150	0.00588	0.00922	0.576
	160	0.0106	0.0162	0.676
	170	0.0137	0.0191	0.801
BSPIMHSO_4	120	0.000812	0.00273	0.296
	130	0.000984	0.00324	0.367
	140	0.00235	0.00696	0.429
	150	0.00572	0.00904	0.563
	160	0.0093	0.0145	0.663
	170	0.0122	0.0174	0.78
MSPIMHSO_4	120	0.000777	0.00267	0.289
	130	0.000906	0.0031	0.356
	140	0.00221	0.00688	0.41
	150	0.00553	0.00897	0.552
	160	0.0081	0.0123	0.617
	170	0.0104	0.0161	0.777

It is also observed that the forward kinetic constants are dependent on the type of catalyst. The k-values for BSBIMHSO_4 catalyzed reaction are the highest followed by the k-values for MSBIMHSO_4, BSPIMHSO_4 and MSPIMHSO_4. This suggests that the reaction constants for TG, DG and MG increase with increasing catalytic activity. The reaction rates were calculated using equation (5.8) and the data tabulated above. The rate law equation according to equation (5.8) is as follows:

$$\text{Rate} = -r_A = -\frac{d[\text{TG}]}{dt} = k_{TG}[\text{TG}]^2 \cdots\cdots\cdots\cdots (5.11)$$

Table 5.11 The reaction rates for ILs catalyzed-transesterification at the investigated temperature

IL type	Temp. (ºC)	$-r_A \times 10^{-1}$ (M/s)
$BSBIMHSO_4$	120	2.557877
	130	3.311217
	140	3.848881
	150	5.080205
	160	5.998115
	170	7.210117
$MSBIMHSO_4$	120	2.498038
	130	3.225197
	140	3.745079
	150	4.9442
	160	5.878504
	170	6.974241
$BSPIMHSO_4$	120	2.505491
	130	3.105068
	140	3.666202
	150	4.832619
	160	5.744673
	170	6.771822
$MSPIMHSO_4$	120	2.446145
	130	3.011236
	140	3.505438
	150	4.738435
	160	5.331472
	170	6.720799

Table 5.11 presented the reaction rate at the applied temperatures (120 – 170 °C) for the 4 used catalysts. The reaction rates for all the functionalized imidazolium IL-catalyzed reactions are found to be in the order of $BSBIMHSO_4$> $MSBIMHSO_4$> $BSPIMHSO_4$> $MSPIMHSO_4$, which is the order of increasing catalytic activity. The rate of reaction is also temperature dependent and this is observed for every catalyst type.

The Svante Arrhenius theory give quantitative basis for the relationship between the activation energy, reaction rate constant and temperature, and takes the form of a linear equation expressed as follows:

$$k = Ae^{-E_a/RT} \qquad (5.12)$$

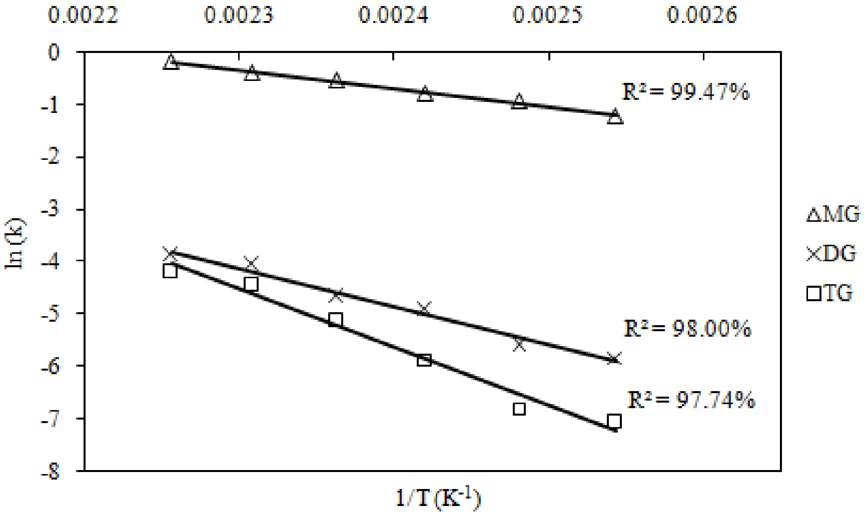
Integration of Equation 5.12 yields:

$$\ln k = \ln A - \frac{Ea}{R} \times \frac{1}{T} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (5.13)$$

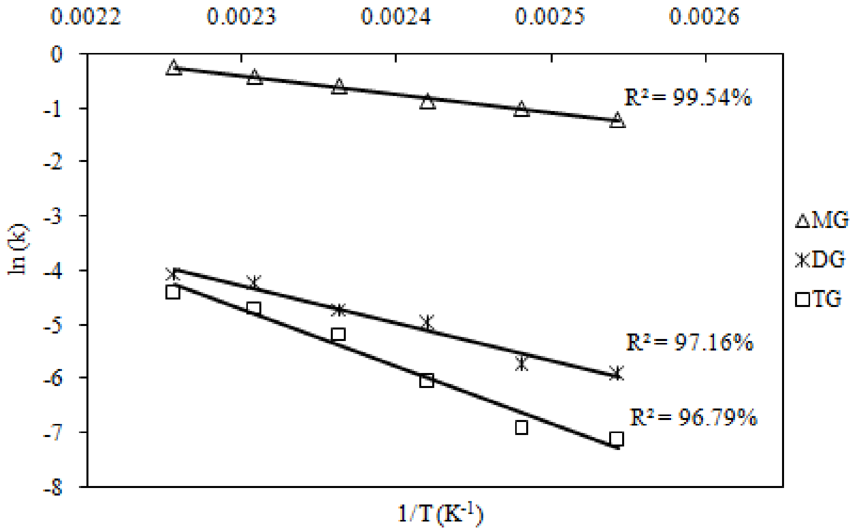
Where E_a is the activation energy (kcal/mol), k is the average overall reaction rate constant, A is an Arrhenius constant, R is the universal gas constant (cal/mol.K) and T is the absolute temperature (K).

The calculated reaction constants data along with the Arrhenius equation were used to determine the activation energy for MG, DG, and TG of the reactions catalyzed with H_2SO_4, $BSBIMHSO_4$, $MSBIMHSO_4$, $BSPIMHSO_4$, and $MSPIMHSO_4$. The plot of ln *k* versus 1/T gives a straight line with a slope of $-E_a/R$ as shown in Figures 5.35a, b, c, d and e, respectively.

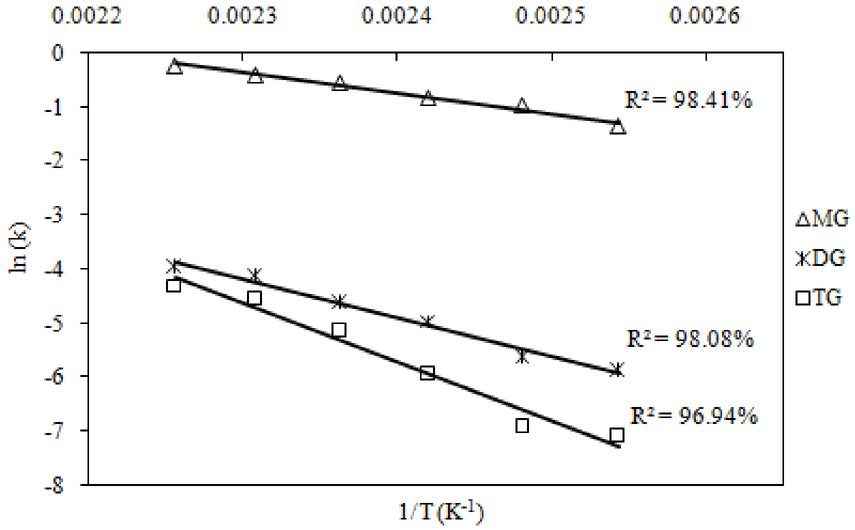
Table 5.12 presents the calculated activation energies for the three forward reactions. The activation energies were found to be highest for TG followed by DG and MG. Even though $MSPIMHSO_4$ catalyzed transesterifications required the highest activation energies to reach the transition states; the activation energies with other types of catalyst, including H_2SO_4, are found to be very close to each other.



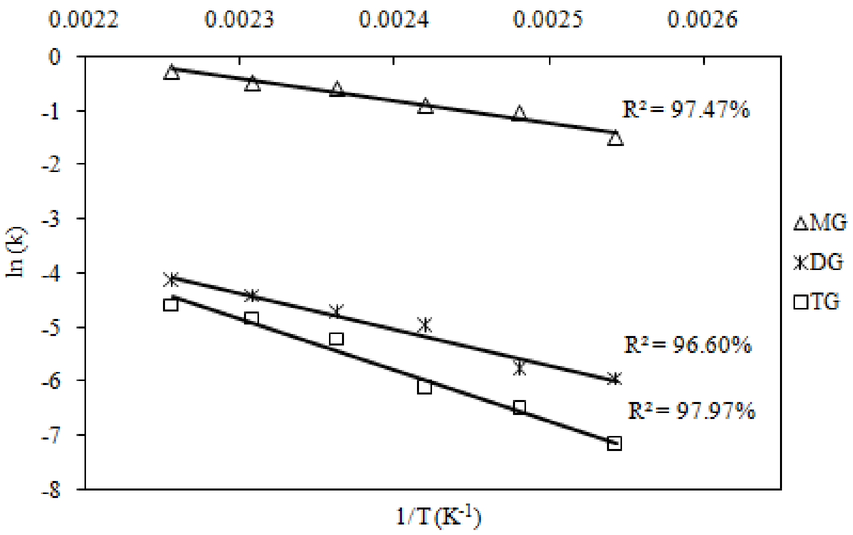
(a) Catalyst type - $BSBIMHSO_4$



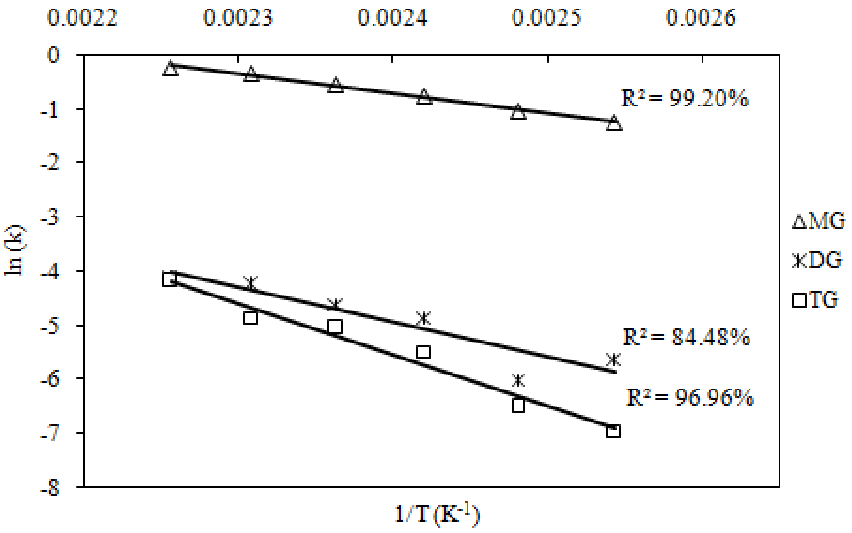
(b) Catalyst type - MSBIMHSO$_4$



(b) Catalyst type - BSPIMHSO$_4$



(d) Catalyst type - $MSPIMHSO_4$



(d) Catalyst type – H_2SO_4

Figure 5.35 Plots of the natural log of the rate constant (ln k) versus the inverse of temperature (1/T) in kelvin for the transesterification reactions catalyzed by: (a) $BSBIMHSO_4$; (b) $MSBIMHSO_4$; (c) $BSPIMHSO_4$; (d) $MSPIMHSO_4$; and (e) H_2SO_4.

This is observed for TG, DG and MG. At the end of each transesterification reaction at the higher temperatures, as expected, the concentration of MG was higher than TG and DG. Therefore, the third reaction (Equation 5.10) was found to be having lower activation energy than the others. These results are in conformity and within the range of results found by Noureddini and Zhu [132] and Darnoko and Cheryan [186] for alkali-catalyzed transesterification of soybean and palm oil, respectively.

Table 5.12 Arrhenius activation energy E_a in cal/mol for TG, DG and MG

IL	$E_{aTG} \pm 0.22$ (kcal/mol)	$E_{aDG} \pm 0.14$ (kcal/mol)	$E_{aMG} \pm 0.01$ (kcal/mol)
$MSPIMHSO_4$	22.0	14.4	6.9
$BSPIMHSO_4$	21.7	14.2	6.9
$MSBIMHSO_4$	20.9	13.9	6.8
$BSBIMHSO_4$	20.4	13.3	6.8
H_2SO_4	19.2	12.8	6.6

5.6. POME characterization

The experimental data on basic fuel properties of POME samples obtained from acid-catalyzed and imidazolium-catalyzed transesterifications of palm biodiesels are summarized in Table 5.13 together with the biodiesel standard specifications of ASTM D6751-03 and EN 14214.

The imidazolium catalysts were $MSPIMHSO_4$, $BSPIMHSO_4$, $MSBIMHSO_4$, and $BSBIMHSO_4$. However, there is not much difference in the some properties of the biodiesel samples, regardless of the catalyst type. The densities, viscosities and specific gravities are found to be within the specified ranges with slightly high values when $MSPIMHSO_4$ was applied as catalyst.

All the biodiesel passed the EN 14214 flash point limits with the exception of IL $MSPIMHSO_4$ biodiesel which shows lower flash point (122 °C) than the ASTM limit. However, it is within the accepted range of European standard ($\geq$120 °C).

The water contents in the produced biodiesel were 0.0207, 0.0201, 0.0203, 0.0203, and 0.0270 mg/kg when the transesterified oil was catalyzed with $MSPIMHSO_4$, $BSPIMHSO_4$, $MSBIMHSO_4$, $BSBIMHSO_4$, and H_2SO_4 respectively. The presence of large amount of water in biodiesel can cause fouling in vehicle engine fuel system. According to ASTM D 2709, the specification for water in biodiesel is 0.05 wt.% [23]. The presence of water of more than this specified amount in biodiesel can cause the formation of emulsions leading to hydrolytic oxidation. In addition, sediment reduces oil flow to the combustion chamber [23].

Acid value is limited to a maximum of 0.50 mg KOH /g sample in both ASTM D 6751 and EN 14214. The four ILs samples did not meet this requirement, where the lowest value of 1.724 mgKOH/g oil was showed with BSBIMHSO$_4$-catalyzed transesterification. This due to that the ILs were quenched before finishing the esterification reaction because of the formation of water.

As can be seen in Table 5.14, all the produced biodiesels have lower free and total glycerol contents than the EN 14214 limited amount of being less than 0.02 and 0.25 %, respectively.

Table 5.15

This due to the efficient procedure used for recovering the valuable glycerol. However, not all the produced biodiesels have passed the glycerides contents limit specified by the EN 14214 standard. The biodiesels produced with $BSPIMHSO_4$ and $MSPIMHSO_4$ showed monoglycerides contents of 1.072 and 1.043 %, respectively. Accordingly, the EN 14214 specified the amount of MG content to be less than 0.8%. Similarly, the TG and DG contents of $BSPIMHSO_4$ and $MSPIMHSO_4$-catalyzed transesterifications were failed to pass the specified amounts of TG and DG content, which limited for each to be less than 0.2%. This is may be due to that the transesterifications using $BSPIMHSO_4$ and $MSPIMHSO_4$ were quenched earlier than the other IL catalysts (see Figures 5.30c and 5.30d).

Overall the biodiesels produced using $BSBIMHSO_4$ and $MSBIMHSO_4$ ILs met the investigated ASTM D 6751 requirements. However, some of biodiesel samples failed to meet the EN 14214 stringent required for European market, due to excess the ester content specification.