

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1. Conclusions

This research has investigated the prospect of ionic liquid catalysis in the synthesis of palm biodiesel from crude palm oil. The optimization and characterization of biodiesel produced from crude palm oil in presence of a variety of promising ILs catalysts was investigated. CPO is an economic source for biodiesel production. The research findings have shown that palm biodiesel methyl esters can be synthesized by ionic liquid-catalyzed transesterification with a 94.6% yield.

Investigations on the activities of 24 ILs, with imidazolium, ammonium and pyrazolium based cations have shown that SO_3H functionalized Brønsted imidazolium, with HSO_4^- anion, catalysts are most active for these reactions than the other route cations; and longer chains imidazolium IL showed greater activity for the transesterification compared to the other synthesized imidazolium ILs. However, all ILs with functionalized sulfonate straight chains anions did not show any catalytic activity.

The acidity of the Brønsted RTILs according to their catalytic activity is in the order of imidazolium > pyrazolium > ammonium with the same side chain and anion. These results indicate that heterocyclic ILs with two nitrogens have higher acidity than the single N located in the middle of ammonium one.

Analyses were performed to assess the effect of methanol to CPO molar ratio, IL concentration, agitation intensity and temperature on the esters content for the time period of 8 h. The effect of temperature on the performance of IL catalysts for biodiesel forming reactions was further studied for CPO transesterification. The experimental results show that temperature has significant effect on esters formation. The maximum esters content obtained was achieved at a higher temperature, further increased in the temperature, i.e. 180 °C didn't show increasing in the esters content.

The ester content in the final product depended on the amount of catalyst as same as the temperature. A direct correlation between catalyst concentration and yield is observed in the IL catalyzed transesterification up to the optimum concentration. Increasing the catalyst

amount beyond the optimum concentration did not show further increase in the conversion, in fact a noticeable reduction in the product yield was observed. This behavior is similar to the processes using conventional catalysts.

The results obtained also indicate that molar ratio of methanol to oil has a significant effect on the yield; generally yield increases with molar ratio. Maximum conversions in the IL-catalyzed transesterification were achieved at the molar ratio range of 12:1 – 15:1. The amount of alcohol used depends on the IL viscosity. Higher amount of alcohol is needed when the viscosity of IL is also higher. Further increase of the molar ratio did not significantly increase the amount of FAME; rather it complicates the removal of IL since biodiesel, glycerol, and ILs are highly soluble in methanol.

Agitation intensity is important in transesterification reaction to lead the reactions to proceed to completion. At lower agitation speed, the oil and methanol-IL mixture appeared as re-separated layers; therefore high stirring speed is required to achieve high conversion. The immediate separation of IL from the product media indicates the quenching steps, required in traditional processes, can be omitted. This is an advantage of that the product required shorter time to be purified since no extensive purification steps are required.

Results from the comparison study at optimized reaction conditions, suggested that increasing the sulfonate chain from propyl, of 1-butyl-3-(3-sulfopropyl) imidazolium hydrogensulfate to butyl, of 1-butyl-3-(4-sulfobutyl) imidazolium hydrogensulfate increases the catalytic activity of IL.

Reaction time is found to affect the transesterification of CPO too. The rate of reaction was fast during the first 3 hour, and then it started to slow down. The reduction in reaction rate is due to rapid formation of water from the reaction of FFA with alcohol, and possibly from the IL moisture content.

The negative effect of IL water content on transesterification rate was observed in the IL (BSBIMHSO₄), where the catalyst seems to be deactivated when the water content reached 200 ppm. Hence, efficient drying and anhydrous handling must be insured since most fully water miscible-ILs are used as catalysts in high moisture-sensitive reactions. After their applications, the ILs afforded complete recovery of their original catalytic activity, which suggests that this type of catalyst could be used for cycles with similar activity.

The kinetics of IL-catalyzed transesterification reactions follow a second order reaction with reaction rate constants of MG>DG>TG, while the activation energies decrease in the reverse order. A new reaction mechanism is proposed since the reaction mechanism does not follow neither acidic nor basic catalyst.

The optimum parameters for 1-butyl-3-(4-sulfobutyl) imidazolium hydrogensulfate catalyzed-methanolysis were found to be 5.0 wt% catalyst concentration, reaction temperature of 170 °C, molar ratio of 12:1 of methanol to CPO, and 800 rpm agitation intensity, producing esters yield of 94.6%.

As compared to H₂SO₄, the 4 types of imidazolium based ILs show activity closed to this corrosive acid. It was found that the high performance was obtained from BSBIMHSO₄-catalyzed transesterification. The results obtained showed it as the most potential and promising IL H₂SO₄ substitution.

Most of the fuel properties of palm biodiesel synthesized in this work are within the range prescribed in the ASTM standards for biodiesel. However, the biodiesel produced from MSPIMHSO₄ catalyst does not meet the prescribed ASTM specifications for Flash point, Acid value and glycerides contents.

6.2. Recommendations

In order to enhance the understanding of the importance of Brønsted RTIL-catalyst to biodiesel synthesis, the following studies are recommended:

- Since water has a serious impact on quenching the IL catalytic activity or the transesterification progress, a continuous two stage reactor is recommended for the transesterification reaction. After completion of the first stage, the dried-unreacted TG and the intermediates can be transferred to the second reactor where the reaction can be continued while water from the first stage reaction somehow can be removed.
- In this work, the effect of side chain length, especially the sulfonate chain on the catalytic activity was investigated for the propyl to butyl. The findings have shown increase in catalytic activity with increasing chain length, but a decrease of thermal stability and an increase of viscosity. In order to enhance the understanding of the effect of side chain length on the catalytic activity and other ILs properties, investigations of chain length longer than butyl is recommended. Also, occupying the alkyl side chain with sulfonate chain may increase the catalytic activity.
- In order to decrease the transesterification reaction temperature for high yield, a high pressure reactor such as autoclave reactor should be used. However, taking care of the changes in the IL under high pressure must be one of the first checks before starting any reaction.

- Since not much report available in using microwave assisted transesterification, it is important to optimize the parameters for production of methylesters.