CHAPTER 6
CONCLUSIONS

The study on removal of sulfur compounds from diesel by liquid-liquid extraction technique using ILs as the solvent at lab-scale single batch extraction process that operates under mild conditions without requiring H_2, O_2, catalyst and oxidant has been successfully completed. In this study, the anions and cations were selected from COSMO-RS database. Inconsistent results between the experimental and COSMO-RS prediction toward extractive desulfurization led for further investigation.

ILs with different combination of anion and cation were used as extractant for removing the sulfur compounds. Investigations of the unique interaction mechanism between ILs and the targeted sulfur compounds using Raman spectroscopy provided evidence that π-π interaction was involved during the extraction process. Based on π-π interaction mechanism which linked to aromaticity effect, a new complementary method using aromaticty index (AI) and double-bond equivalent (DBE) was introduced. The AI values were calculated for the cations while DBE values for the anions. The results showed that ILs with high AI and DBE usually will give good performance during extractive desulfurization process. Validation of desulfurization performance using model oil of 25 selected ILs based on their AI and DBE values can be a useful complementary method for screening ILs for extractive desulfurization of diesel in addition to COSMO-RS technique.

13 ILs were successfully synthesized in-house whereby these ILs together with 12 of purchased ILs were characterized accordingly. The significant effect of physical properties against desulfurization performance was explored. A mapping of density (ρ) against the molecular weight (M_w) produced specific and discrete group classification which provides a quick and simple approach for estimating the potential of ILs performance for diesel desulfurization. Four groups were identified which are

fluoro-based, cyano-based, phosphate-based and sulfate-based ILs, all of which showed linear correlation towards desulfurization performance.

The study on the effect of stirring speed and extraction time on the performance of extractive desulfurization using model oil showed that increasing the stirring speed contributed to increase the desulfurization performance. On the other hand, an optimum extraction time was observed, whereby in this work the optimum extraction time was 30 minutes at the maximum stirring speed of 500 rpm. Again it should be mentioned here that the maximum stirring speed in this work is limited by the equipment limit. Extending the extraction time longer than 30 minutes did not result any significant removal of sulfur compounds from the model oil. Another factor that affects desulfurization performance is water content in ILs. The water content should be minimized as low as possible in order to optimize the desulfurization performance, even at part per million (ppm) levels.

Response Surface Methodology (RSM) was successfully applied to model and analyse the process as well as determination of the optimum operational conditions for extractive desulfurization of model oil. At a comparable range of mass ratio (model oil/ ILs), temperature and initial concentration, both temperature and initial concentration showed slight effect on desulfurization performance but for mass ratio, significant effect was observed. The optimum conditions for extractive desulfurization were determined at mass ratio of 0.92, temperature of 30°C and initial concentration of 2000 ppm. The experimental findings were in close agreement with the model prediction. From the present study, it is evident that the use of statistical optimization approach, RSM has helped to earmark the most significant operating parameters and optimum levels with minimum effort and time.

During the extractive desulfurization process of actual diesel, certain amount of short chain aliphatic and aromatic hydrocarbons was removed from the diesel phase. Observation using ternary diagram approach revealed that both short chain aliphatic and aromatic hydrocarbons are partially miscible in [bmim][TCM] phase. However, results from the desulfurization of model fuel which contained both aromatic hydrocarbon as well as sulfur compound using [bmim][OSO_4], [bmim][DCA],

[bmim][SCL], [bmim][BZT] and [bmim][TCM] showed higher affinity for removal of sulfur compounds up to 11 times higher than aromatic hydrocarbons.

The desulfurization results of two commercial diesel at the optimum conditions using three ILs namely [bmim][OSO_4], [bmim][DCA] and [bmim][TCM] showed success in removing sulfur compounds identified by GC-MS . Among the seven studied compounds namely *n*-C_{12}, *n*-C_6, benzene, toluene, *p*-xylene, BT and DBT, the highest removal was attained for BT and DBT by all three ILs systems. Comparing the three types of ILs, [bmim][TCM] showed the best extractant for extractive desulfurization of commercial diesel. A study of desulfurization cycle has succeeded at reducing the total sulfur concentration significantly, where in Diesel A for example, about 874 ppm have been removed after two cycles from initial of the total sulfur concentration of 1128 ppm. This result indicated the possibility of reducing the total sulfur concentration further, possibly to 50 ppm, by increasing the number of cycle. [bmim][DCA] also showed great potential as an extractant for sulfur compounds as it can be regenerated from BT using simple electrochemical approach.

CHAPTER 7
RECOMMENDATIONS FOR FUTURE RESEARCH

In the present study, the extractive desulfurization was conducted in an extractor (using vial that has the maximum capacity of 25 mL) which limits the stirring speed. On this basis, if the extractor can be designed to attain an easier equilibrium state which will also improve the contact time between model oil and the studied ILs. The effect of extractor size to stirring speed or stirrer size ratio on the desulfurization performance can also be studied.

The study of interaction mechanism between sulfur compound and ILs should be expanded to include other sulfur compounds and ILs. In addition, an advanced two dimensional correlation of infrared (2D IR) spectroscopy method should be explored. By using this method, the interacting site could be displayed in a contour map representation for better understanding.

Further study on new emerging cations and anions can be carried out in searching for the best combination of ILs for extractive desulfurization process. Particular focus can be given to sulfur-containing ILs which will provide information pertaining to the extent of interaction between this type of ILs and sulfur compounds.

Other combinations of aliphatic hydrocarbons and sulfur compounds for model fuel can be investigated for further understanding of the behaviour of sulfur compounds extraction in the presence of aliphatic hydrocarbons since short chain and long chain aliphatic hydrocarbons have different selectivity and capacity for desulfurization.

The present study has investigated only two regeneration methods; further research should be conducted to identify the most suitable method of recycling spent ILs for industrial purposes.