

Effect of 1-Butyl-3-Methylimidazolium Tricyanomethane in Extractive Desulphurization Process on Model Oil

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ABSTRACT – Driven by regulatory requirements to reduce the content of sulphur in fuels, the demand to find an alternative process to hydrodesulphurization is on the rise. In this study, experiments were conducted for the removal of sulphur compound (present as benzothiophene or BT) with concentration of 2000 ppm in the model oil (present as n-dodecane or n-C12) using 1-butyl-3-methylimidazolium tricyanomethane ([bmim][TCM]) as the extractant. The effects of stirring speed, extraction time and water content on the extraction efficiency were investigated. In the end, the loading factor of the [bmim][TCM] is also discussed where it can be concluded that, more than one mole of [bmim][TCM] may interacted with one mole of BT during extractive desulphurization process.

KEYWORDS

Extractive
desulphurization,
sulphur removal,
ionic liquids,
model oil,
[Bmim][TCM]

INTRODUCTION

The main goal In every oil refinery, the central separation step is distillation process where petroleum is separated into various fractions according to their volatility. Unfortunately, the sulphur compounds present in the crude oil will also be collected in the fractionated distillation products. In order to meet market regulation, the sulphur content in each product obtained from different fractionation temperatures is required to be removed. For commercial diesel especially, due to the tightening of air quality act all over the world, the maximum allowable limit of sulphur content has been reduced drastically (Zhao et al. 2007; Dai et al. 2008; Liu et al. 2008).

For instance, European Union (EU) imposed a restriction on sulphur content in fuels at 350 ppm in 2004, followed by a drastic reduction to 50 ppm in 2006, when later reduced it further to 10 ppm in 2010. In general, after 2010, the limit for sulphur content in fuel has been reduced to within the range of 15 to 10 ppm in Japan, United States of America (USA), Canada, Australia, New Zealand, Singapore and Hong Kong. Currently, many of the other countries in the world, especially those with high fuel consumption such as China, India, Russia, Brazil and Iran, are taking steps to follow the standard fuel product specification that is presently in place in the USA and Europe. Some countries in Asia, Middle East and South America such as Thailand, Bahrain, Oman, Kuwait, Argentina, Chile and Peru are currently contemplating a more drastic action in ratcheting down the standards which would bring them at par with the USA Environmental Protection Agency (EPA) and Euro IV standard, where the limit for sulphur content is 50 ppm (Lo et al. 2003; Lu et al. 2007; Rheinberg et al. 2008; Zhao et al. 2008; Li et al. 2009; Adzamic et al. 2009; Kulkani and Afonso, 2010; Taib and Murugesan, 2011; Wang et al. 2011).

In Malaysia, since 2006 petroleum companies have adopted Euro II standard where the sulphur content is kept at 500 ppm. However, due to stringent environmental requirement imposed by the government recently, petroleum refineries are forced to comply with a new requirement to further reduce the sulphur content up to 50 ppm in accordance to Euro IV requirement which will commence in 2015 (ACFA, 2012).

ILs are made up of at least two components namely cation and anion. The most commonly used cations in ILs is imidazolium whereas most popular anions are BF₄ and PF₆. Imidazoles are favorable species for investigation because of their stability towards air and water, ability to stay in liquid form over a wide range of temperature and their relatively favorable density and viscosity.

Although various kinds of ILs have been used as extractive solvent, their direct applications for sulphur removal have not been extensively studied due to lack of information on the behavior of ILs itself. This also hampers efforts in designing and selecting appropriate ILs for extractive desulphurization of fuels which needs to be addressed before possible applications such as desulphurization of petroleum products can be implemented (Davis and Forrester, 1999; Tian et al. 2007; Liu et al. 2008). Taking this into consideration, the present study investigated the behavioral of ILs in n-C12.

MATERIALS AND METHODS

In this study, all extraction experiments were conducted using batch system in atmospheric environmental. The 25mL extractor was filled with known amounts of BT (sulphur compound) in n-C12 (major component in fuels especially diesel) as the model oil. The extractor's cap was fabricated to install the thermometer in order to measure temperature during the extraction process. Due to the hygroscopic nature of ILs, the water content of all ILs were checked before using in the extraction process. If the measured water content of ILs is higher than 500ppm, the ILs was dried in a vacuum oven and its water content re-determined before proceeding for extraction.

During the extractive desulphurization process, the mixture of ILs and model oil was stirred at a desired speed and time to attain equilibrium at atmospheric conditions. The two layers were observed. The ILs, which usually having higher density than the model oil, form the lower phase. Thus, the upper phase, which is model oil, could be easily withdrawn for quantitative assay analysis of BT in model oil phase using high performance liquid chromatography (HPLC). The HPLC (HP1100, Agilent, US) was equipped with an auto-sampler, a reverse-phase Zorbax SB-C18 column (4.6 mm X 150 mm; 5 μ m) and a diode array detector (DAD). Detail of the HPLC analysis conditions is shown in Table 1. The external standard method at 280nm was used to quantify BT composition the oil phase. Agilent 1200 Series LC software was used for system programming and data retrieval. Based on the measured values, the material balance of BT in model ILs phase was made.

Table 1. Analytical conditions for HPLC analysis.

	Description
Flow rate	0.7 ml/min
Mobile phase	90% methanol in water (v/v %)
Oven temperature	40°C
Injection volume	10 μ L

The composition of BT (sulphur compound) in model oil determined by HPLC analysis was then used to calculate the partition coefficient, K_d which defines the extent of the mobility of BT into ILs phase using the following relationships:

$$K_d = \frac{[C]_{s,IL}}{[C]_{s,MO}} \quad (1)$$

where, $[C]_{s,IL}$ is the concentration of BT in the ILs phase after extraction (ppm) and $[C]_{s,MO}$ is the concentration of BT in the model oil phase after extraction (ppm).

The effect of three process variables namely stirring speed, extraction time and water content was studied. The optimum value of each variable was then further used in the study.

EXPERIMENTAL RESULTS

The effect of stirring speed on sulphur extraction efficiency (K_d value) was firstly investigated. As shown in Figure 1, there is a drastic extraction efficiency increment with an increase of stirring speed from stagnant to 100 rpm. A very low extraction occurred during the stagnant period where only interfacial extraction of both oil and ILs took place. Then the K_d value continued to linearly increase with the increase of stirring speed from 100 rpm to 500 rpm. The maximum allowable speed of the extractor vial is 500 rpm, therefore the experiment was limited up to 500 rpm as the optimum stirring speed in order to achieve higher sulphur extraction efficiency.

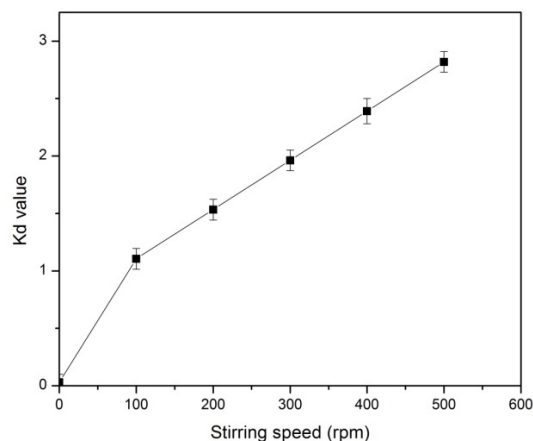


Figure 1. The effect of stirring speed on sulfur extraction efficiency (K_d value) by [bmim][TCM]. (Conditions: Extraction time – 10 min, mass ratio ILs/model oil – 1/1, room temperature, initial BT concentration in model oil – 2000 ppm).

In an effort to understand the effect of extraction time, experiments were repeated at the optimum stirring speed condition and the results are displayed in Figure 2. As can be seen from Figure 2, the sulphur extraction efficiency increased with an increase in extraction time for the first 30 minutes. Extending the extraction time longer than 30 minutes did not result in extracting more BT from the model oil phase, indicating that the extraction process has reached equilibrium state. Similar results were obtained by other researchers, where the required extraction time ranged from 25 min to 30 min [Liu *et al.* 2008; Taib and Murugesan, 2011]. It was also observed that there is no marginal increase in extraction efficiency by increasing the extraction time of unstirred samples.

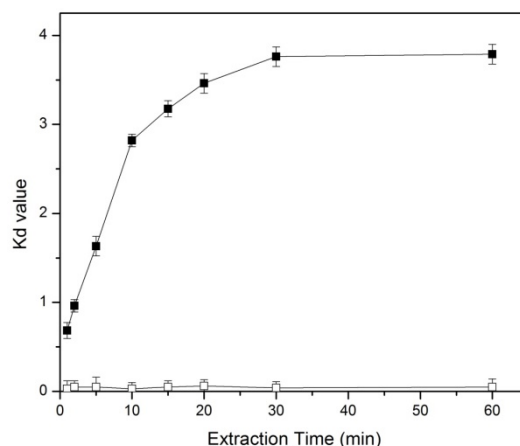


Figure 2. The effect of extraction time on sulfur extraction efficiency (Kd value) by [bmim][TCM] (Conditions: Stirring speed – 500 rpm, mass ratio ILs/model oil – 1/1, room temperature, initial BT concentration in model oil – 2000 ppm)

As shown in Figure 3, the sulphur extraction efficiency decreased dramatically as the water content in [bmim][TCM] increased, for instance 2.5% of water content in [bmim][TCM] can drop the K_d value by about 1.5 from 3.672 at 0.000233% (233 ppm) water content. This implies that the efficiency of BT extraction using [bmim][TCM] from the model oil decreases drastically with the presence of more water in [bmim][TCM]. On the other hand, this also suggests that the sulphur compounds dissolved in the spent ILs can be regenerated by water dilution process, which will be later discussed.

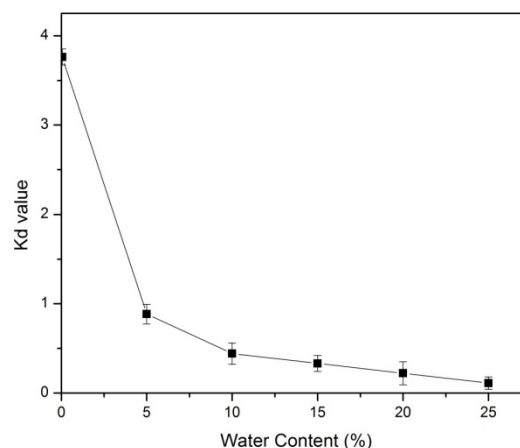


Figure 3. The effect of water content on sulfur extraction efficiency (Kd value) by [bmim][TCM]. (Conditions: Stirring speed – 500 rpm, extraction time – 30 min, mass ratio ILs/model oil – 1/1, room temperature, initial BT concentration in model oil – 2000 ppm).

The choice of a suitable composition for the ILs (extractant) was carried out experimentally, and [bmim][TCM] was chosen. The effect of [bmim][TCM] concentration in water, as the extracting solvent, on sulphur extraction efficiency is shown in Figure 4. A drastic reduction in K_d value can be seen as the [bmim][TCM] concentration dropped from 4.36 mM to 4.14 mM; but, from 3.93 mM down to 3.27 mM of [bmim][TCM] concentration, the K_d value was linearly reduced. This suggests that at the initial stage of extraction process, which shows major influence toward extraction efficiency, the presence of water in [bmim][TCM] should be avoided. In the presence of both water and BT, the interaction of ILs is much more favourable for water instead of BT via hydrogen bonding, by means a stronger interaction than π - π bonding.

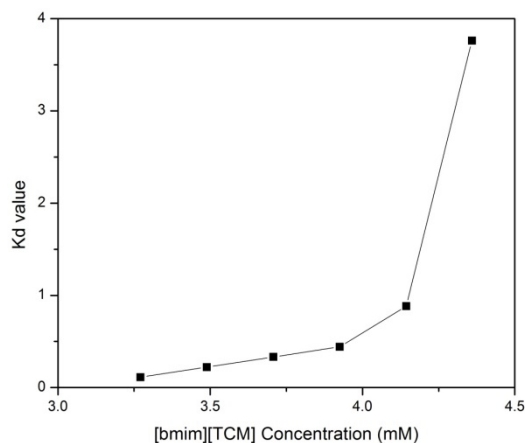


Figure 4. Relationship between Kd value and [bmim][TCM] concentration.

In the case of loading factor, when $R > 1$ it is called overloading. It means that more than two moles of solutes (represented by BT) react with one mole of extractant (represented by [bmim][TCM]). On the other hand, in the case of $R < 1$, it means that several mole of extractant interact with one mole of solute [Yunhai et al. 2006]. As seen in Figure 5, at any point the R values for BT extraction is lower than 1. This indicates that more than one mole of [bmim][TCM] may interacted with one mole of BT during the extractive desulphurization process.

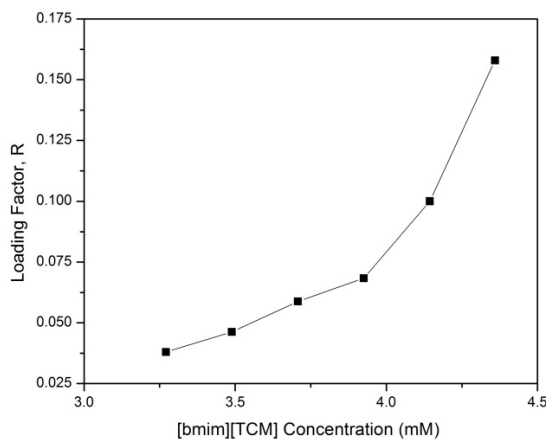


Figure 5. Relationship between loading factor and initial concentration of [bmim][TCM] (Conditions: Stirring speed – 500 rpm, extraction time – 30 min, mass ratio ILs/model oil – 1/1, room temperature, initial BT concentration in model oil – 2000 ppm).

CONCLUSION

The study on the effect of stirring speed and extraction time on the performance of extractive desulphurization using model oil for [bmim][TCM] showed that increasing the stirring speed contributed to increase the desulphurization 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 sulphur compounds from the model oil. Another factor that affects desulphurization performance is water content in ILs. The water content should be minimized as low as possible in order to optimize the desulphurization performance.

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