Deep Desulfurization of Light Oil through Extraction and Oxidation Processes using H₂O₂/Tungstophosphoric Acid in Room-temperature Ionic Liquids

Li-Lin Chuang,^a Jung-Fu Huang,^a Wen-Hen Lo^b and Guor-Tzo Wei^{a,*}

^aDepartment of Chemistry and Biochemistry, National Chung Cheng University, Ming-Hsiung, Chia-Yi, 62102 Taiwan ^bCPC Refining & Manufacturing Center, Chia-Yi, 60036, Taiwan

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In this research, using room-temperature ionic liquids (RTILs) as the solvents to combine solvent extraction and chemical oxidation processes in one-pot operation for the desulfurization of fuel oil was pursued. In this solvent extraction and chemical oxidation desulfurization (SECOD), RTILs as media are immiscible with oil; sulfur compounds in oil are extracted into RTILs and oxidized thereafter to the corresponding sulfones by H_2O_2/TPA (tungstophosphoric acid). During SECOD, these high polar sulfones partition mainly in the ionic liquid phase. Hence, it results in their continuous removal from oil, which leads to deep desulfurization. To study the SECOD, we employed dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) in hexadecane as model oil systems and compared the effects of RTILs on the removal of DBT and 4,6-DMDBT. The desulfurization rates followed the order OMIM⁺PF₆⁻ > BMIM⁺PF₆⁻ > BMIM⁺PF₆⁻ are water-immiscible and form three-phase (oil–water–ionic liquid) reaction systems; these three-phase systems offer higher removal efficiencies of sulfur compounds from oil. Under the optimized conditions, SECOD process reduced the sulfur content of diesel light oil from 897 to 42 ppm (i.e., 95% desulfurization efficiency) in a one-batch operation.

Keywords: Room-temperature ionic liquid; Oxidative desulfurization; Fuel oil.

INTRODUCTION

Petroleum-derived middle feedstocks, such as light oils, usually contain a high amount of sulfur impurity. The sulfur compounds in diesel light oils are converted by combustion to SO_x, which are the major source of acid rain and air pollution.¹ Regulations limit sulfur content in light oil to reduce the air pollution.² The production of light oils containing very low sulfur is, therefore, an important task for oil refineries. The removal of sulfur compounds in oils is carried out industrially by a catalytic hydrodesulfurization (HDS) method. This method is operated at both high temperature and high pressure of hydrogen gas. HDS is generally carried out under much sever conditions like higher temperature, higher hydrogen pressure and more active catalysis to produce the light oil that has lower content of sulfur compounds to meet the requirements of new regulations. Meanwhile the desulfurization efficiency of HDS is limited, especially for polyaromatic sulfur containing compounds such as DBT and its derivative 4,6-DMDBT, etc. To overcome this problem, alternative non-HDS desulfurization methods have been reported. These non-HDS approaches include adsorption,³⁻⁵ solvent extraction,^{6,7} biodesulfurization,⁸ oxidative desulfurization (ODS)^{1,9-19} and so on. Among them, ODS has attracted wildly interest because it is carried out under mild conditions: at low temperature and under atmospheric pressure, etc. ODS method has great potential to be a complementary process of traditional HDS for producing very low sulfurs of diesel oils.¹⁴

The ODS process usually involves oxidizing the sulfur compounds in oils thus transforming them into sulfones in the first step. The sulfones are then removed by a selective extraction in a second step. Different catalysis and oxidants have been employed in the first step of ODS, such as H₂O₂/HCOOH,¹⁸ H₂O₂/CH₃COOH,⁹⁻¹¹ H₂O₂/CF₃COOH,¹⁹ $\mathrm{H_2O_2/methyltrioxorhenium(VII)},^{20}\ \mathrm{H_2O_2/TPA},^{14,21\text{-}24}\ \mathrm{H_2O_2/}$ vanadium peroxocomplexes,²⁵⁻²⁶ H₂O₂/vanadiumsilicate,²⁷ H_2O_2/T itanium silicalite²⁸ and other non- H_2O_2 system (eq. Ozone, t-BuOOH, etc.).^{29,30} A polar organic solvent, such as acetonitrile, dimethyl sulfoxide, or N,N-dimethylformamide, is usually utilized as extraction solvent in the second step.⁸ These solvents are generally flammable and volatile organic compound (VOCs). The use of VOCs causes environmental and safety concerns, such as hazardous gas emission and fire hazard.

Dedicated to the memory of Professor Yung-Son Hon (1955–2011).

* Corresponding author. Tel: +886-5-2428121; Fax: +886-5-2721040; E-mail: chegtw@ccu.edu.tw

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Compared with VOCs, RTILs have many unique properties, such as non-volatile, negligible vapor pressure, non-explosive, easy to recycle, and high thermal stability etc. RTILs are regarded as green solvents and have recently gained recognition as environmentally benign alternative solvents for synthesis, separation, electrochemistry, catalysis, etc.³¹⁻⁴³ RTILs were also employed for removing sulfurs from fuels by solvent extractions recently.^{7,44-47} However, the efficiency of sulfur removal by solvent extraction is limited and multiple-extraction is required to obtain the fuels with low content of sulfurs. Although, multiple-extraction with special ionic liquid can effectively remove sulfurs from oils, it has the problem of cross-solubility of oil, i.e. portion of oil is extracted by ionic liquid.⁴⁴ Our previous work demonstrated that we were able to reduce the oil sulfur content from 8040 ppm down to 1000 ppm by SECOD method with $BMIM^+PF_6^{-.11}$ Although the sulfur content is still high, an order of magnitude improvement in the desulfurization yield was obtained by SECOD method using RTILs, as compared with that of merely extraction. The major advantages of using RTILs in SECOD method over traditional ODS are: (1) it combines oxidation and separation operation to one operation, (2) the benefits of RTILs over VOCs for chemical operation can be realized because of no emission loss with RTILs in an open reactor at ambient pressure, (3) it simplified the reaction system due to the solubility properties of RTILs, and (4) water immiscible RTILs provide favor reaction conditions for ODS. For example, phase transfer reagent is not required for catalytic reaction because RTILs are able to dissolve non-polar, polar and charged compounds.^{21,25} This process has been widely investigated recently.48-58

Further investigations of SECOD for desulfurization of oil with RTILs are essential to realize its potential application for the desulfurization of light oils. Here, the use of H₂O₂/TPA as catalytic oxidation reagents and 1-butyl-3methylimidazollium tetrafluoroborate (BMIM⁺BF₄⁻), 1butyl-3-methylimidazollium hexafluorophosphate (BMIM⁺PF₆⁻) or 1-octyl-3-methylimidazollium hexafluorophosphate (OMIM⁺PF $_{6}$) as the solvent for the desulfurization of light oils of SECOD method was carried out. Hydrogen peroxide/Polyoxometalates reaction system have long been studied for oxidation reactions,¹²⁻¹⁷ while the solution of H₂O₂/TPA was shown to have the highest reactivity of H₂O₂/polyoxometalate reaction system.²³ In this work, DBT and 4,6-DMDBT dissolved in hexadecane were employed as model oils to study the effect of various parameters on the desulfurization. The desulfurization behavior of SECOD is discussed and the effectiveness of this method for the desulfurization of light oils is presented to demonstrate the capability of SECOD to produce low sulfurs of fuel oils.

EXPERIMENTAL

RTILs synthesis

The synthesis of $BMIM^+PF_6^-$, $OMIM^+PF_6^-$ and BMIM⁺BF₄⁻ were prepared by a literature procedure.³² BMIM⁺Cl⁻ or OMIM⁺Cl⁻ was prepared by adding equimolar amounts (0.3 mole) of 1-methylimidazole and chlorobutane or chlorooctane to a round-bottom flask fitted with a reflux condenser and heated at 70 °C for 48~72 h. The resulting viscous and vellowish liquid was cooled to room temperature and then washed three times with ethyl acetate. The remaining ethyl acetate was removed by rotary evaporation. The residue was poured into acetone or water (150 mL), the equimolar amount (0.3 moles) of the NaBF₄ (in acetone) or KPF_6 (in water) was needed, and the mixture was stirred for 24 h at room temperature. The resulting precipitate of NaCl (from BMIM⁺BF₄⁻) was filtered off; KCl (from $BMIM^+PF_6^-$ and $OMIM^+PF_6^-$) was washed off with water until no precipitation occurred when the sample tested with AgNO₃ solution. The solvent (acetone or water) was removed through rotary evaporation under vacuum. NMR spectroscopy was employed to verify the structures and purities of the RTILs. The purity and structure of final product was characterized with ¹H-NMR.

Oxidation/extraction desulfurization

Desulfurization of model oil was carried out as follows: Weight 0.110 g DBT or 4,6-DMDBT dissolve in 100 mL $C_{16}H_{34}$ as a stock solution. The sulfur stock solution (5 mL) was mixed with an equal volume of RTIL and then a 35% H_2O_2 solution (0.583 mL) containing TPA (3.5 µmol) was added. The mixture was stirred and heated to 70 °C. The upper phase ($C_{16}H_{34}$) was withdrawn periodically for analysis of its sulfur content using a UV–Vis spectrometer (Shimadzu UV-3170PC) with detection at 320 nm.

Oxidations of DBT and 4,6-DMDBT in the RTILs were performed as follows: DBT or 4,6-DMDBT (0.011 g) was dissolved in an RTIL stock solution (10 mL). The DBT or 4,6-DMDBT stock solution (2.5 mL) was mixed with a 35% H₂O₂ (0.291 mL) solution containing TPA (1.75 μ mol) to form the sulfur-containing RTIL mixture. The mixture was heated to 70, 80, and 90 °C and stirred vigorously during the reaction. The solutions were periodically with-

drawn and analyzed for their sulfur content using reversed-phase high-performance liquid chromatography (RP-HPLC; Shimadzu LC-6A equipped with a SPD-6A detector) with detection at 241 nm.

Desulfurization of light oil was carried out as follows: 10 mL light oil mixed with 10 mL ionic liquid and added 6.99 mL containing 12.5 *u*mole TPA. The mixture was stirred at 70 °C. The amount of sulfur in the light oil was determined by Antek pyroreactor 771, which was equipped with an Antek UV fluorescence detector 714. The total contents of saturated hydrocarbon and one-, two-, poly-ring aromatic hydrocarbons in the light were analyzed by reversed-phase HPLC (Shimadzu LC-6A equipped with a refractive-index detector RID-6A).

RESULT AND DISCUSSION

Effect of ionic liquids on desulfurization

DBT or 4,6-DMDBT dissolved in C₁₆H₃₄ was employed as a sulfur containing model oil. Mixing an ionic liquid with the model oil forms a biphasic liquid-liquid system because of immiscibility between ionic liquid and oil. Sulfur compounds will participate in both oil and ionic liquids. This leads to the extraction of sulfurs compounds from oil. This approach has been employed in several reports.44-47 However, the efficiency of solvent extraction remains limited. In this SECOD method, DBT and 4,6-DMDBT in the model oil were extracted into the ionic liquid phase, where they were oxidized by TPA/H₂O₂ to their sulfones (hexavalent sulfur species), as indicated in Scheme I.¹¹ These oxidized sulfones have high polarities and, therefore, they are highly partitioned in the ionic liquid phase. Consequently, a continuous decrease in the concentration of sulfurs in hexadecane was observed during

Scheme I Reaction mechanism of DBT and 4,6-DMDBT in the H_2O_2/TPA system



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the oxidation process, as shown in Fig. 1 and Fig. 2. These findings are similar to those of our previous report in which we employed acetic acid/ H_2O_2 as the catalyst/oxidant.¹¹ The sulfur content at time zero reflects the ability of each ionic liquid to extract sulfur from model oil. Fig. 1 reveals that BMIM⁺BF₄⁻, BMIM⁺PF₆⁻, and OMIM⁺PF₆⁻ extract 53, 52 and 64%, respectively, of DBT from model oil. Fig. indicates that BMIM⁺BF₄⁻, BMIM⁺PF₆⁻, and 2 OMIM⁺PF₆⁻ extract 28, 27 and 48%, respectively, of 4,6-DMDBT from model oil. Figs. 1 and 2 both indicate that OMIM⁺PF₆⁻ has the best extraction efficiency of these three RTILs. Nevertheless, the yields of these solvent extractions are limited and multiple extractions would be required to obtain low-sulfur oils.⁴⁵ The data also show that sulfur concentration in oil continuously decreases after adding chemical oxidation to solvent extraction. This situation arises because chemical oxidation of the sulfur com-







Fig. 2. Oxidation/Extraction of 4,6-DMDBT in the H_2O_2 /TPA system at 70 °C.

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pounds in the ionic liquid phase to their corresponding sulfones results in a shift in the partition equilibrium of the sulfur compounds between the oil and ionic liquid phases, which leads to further extraction from the oil. Consequently, a continuous extraction and oxidation cause the continuous decrease of sulfur concentration in oil. In less than an hour, this process could remove more than 99% of DBT in model oil with $BMIM^+PF_6^-$, and $OMIM^+PF_6^-$. It took somewhat longer to decrease the yield of 4,6-DMDBT accordingly. The efficiencies of the sulfur removals using these three RTILs followed the order $OMIM^+PF_6^- >$ $BMIM^+PF_6^- > BMIM^+BF_4^-$. This order results, in part, from the fact that OMIM⁺PF₆⁻ has the highest extraction efficiency, but it might also reflect the different reaction activities of the sulfur compounds in the different RTILs (see below).

Oxidation reactivity of DBT and 4,6-DMDBT in ionic liquids

The reactivity of DBT and 4,6-DMDBT in oil are low with HDS method because of their steric hindrance. These low reactivity compounds in HDS method are called refractory sulfurs. HDS process has the difficulty to produce low sulfur oil because it is unable to remove the refractory sulfurs from oils effectively. Conversely, ODS method has been described to be a potential alternative or complementary method of HDS for its high efficiency to remove the refractory sulfurs from oils.¹⁴ In order to understand the oxidation reactivity of DBT and 4,6-DMDBT in SECOD process, we directly dissolved DBT and 4,6-DMDBT in RTILs and then added H_2O_2/TPA for oxidation. The oxidation rates of DBT and 4,6-DMDBT in RTILs are shown in Fig. 3 and Fig. 4. The data indicate that the reactivity of DBT and 4,6-DMDBT in different ionic liquids are in the order of $OMIM^+PF_6^- > BMIM^+PF_6^- > BMIM^+BF_4^-$. As the results of Fig. 1-4 indicate that $OMIM^+PF_6^-$ not only has the highest extraction efficiency and also has the highest oxidation reactivity, thus has the best performance for removing refractory sulfurs from oil, as shown in Fig. 1 and Fig. 2. The reason of the highest oxidation reactivity of OMIM⁺PF₆ can be attributed to its lowest concentration of water. Previous works indicated that oxidation of DBT by H₂O₂/ CH₃COOH was a reciprocal of H₂O concentration.¹¹ In previous report, BMIM⁺PF₆⁻ (a water immiscible ionic liquid) has better yield of sulfur removal than that of BMIM⁺BF₄⁻ (a water miscible ionic liquid). Here, similar trend was observed with TPA/H_2O_2 . Therefore, water concentration has strong influence on the reactivity of refractory sulfurs with TPA/H_2O_2 and $OMIM^+PF_6^-$ is the most water immiscible of all three RTILs employed. As a result, OMIM⁺PF₆⁻ has the highest desulfurization yield and reactivity.

For oxidation, pseudo-first-order is carried out because excess H_2O_2 was employed. The oxidation rate constants of the DBT and 4,6-DMDBT in Fig. 3-4 were calculated from a plot of $\ln(C_t/C_0)$ versus reaction time, where C_0 is the initial sulfur concentration and C_t is the sulfur concentration at oxidation t (min). The slopes of the plot are the rate constants and listed in Table 1. The data indicate that reactivity of DBT is higher than that of 4,6-DMDBT. The same reactivity trend was reported by using H_2O_2 solutions of TPA.²² However, this is in reversed order to that of catalytic oxidation by HOOH¹⁸ and CH₃COOH.⁹⁻¹¹ Te et al. has described the detail about the difference of these two oxidant/catalyst systems for the oxidation of refractory sulfurs.²² They attributed the difference in reactivities of two



Fig. 3. Oxidation of DBT in the H_2O_2/TPA system at 70 °C.



Fig. 4. Oxidation of 4,6-DMDBT in the H_2O_2/TPA system at 70 °C.

Table 1. DBT and 4,6-DMDBT oxidation rate constant at 70 °C

Reactants	IL	Rate constants (mim ⁻¹)	Correlation factor (R ²)
DBT	C ₄ MIMBF ₄	0.0089	0.9917
	C ₄ MIMPF ₆	0.2096	0.9931
	C ₈ MIMPF ₆	0.4344	0.9681
4,6-DMDBT	C ₄ MIMBF ₄	0.0772	0.9982
	C ₄ MIMPF ₆	0.1186	0.9962
	C_8MIMPF_6	0.1229	0.9892

oxidation systems is due to the molecular sizes of catalysts not the intrinsic reactivities of sulfurs. TPA is a large molecular catalyst while HOOH or CH₃COOH is a small molecular catalyst. Steric effect of the sulfurs plays important role for the oxidation with large molecular catalyst, such as TPA. While the reactivity results from small molecular catalyst, such as HCOOH, reflect the intrinsic reaction of sulfurs. Table 1 also indicates that the reactivities of both sulfurs in three RTILs are in the order of OMIM⁺PF₆⁻ > BMIM⁺PF₆⁻ > BMIM⁺BF₄⁻. The reason of this sequence has been described in last paragraph.

The rate constants of DBT and 4,6-DMDBT in $C_4MIM^+PF_6^-$ at different temperatures were also performed, as shown in Fig. 5. Using these rate constants at different temperature, a plot of -ln k verse 1/T for the oxidative reaction gave a straight line, as shown in Fig. 6. The activation energy (Ea) of DBT and 4,6-DMDBT are estimated from the Arrhenius equation to be 51.2 and 56.7 kJ/mole, respectively. These values are slightly lower than those of reported by Te et al. (53.8 and 58.7 kJ/mol for DBT and 4,6-DMDBT, respectively). These reactivity studies



Fig. 5. Pseudo-first order rate for DBT and 4,6-DMDBT oxidation rate at 70 °C in different ILs.

indicate that SECOD is strongly temperature-dependent. Because the RTILs are stable at rather high temperatures and because the reactivities of the sulfur compounds toward oxidation are strongly temperature-dependent, higher temperature can be employed in the SECOD method to accelerate these reactions.

Desulfurization of light oil with SECOD

We used a light oil containing 897 ppm sulfur to evaluate the performance and capability of SECOD process with different RTILs. The component of the raw oil and treated oil are shown in Table 2. The sulfur contents are 803, 786, and 675 ppm after extracted with BMIM⁺BF₄⁻, BMIM⁺PF₆⁻, and OMIM⁺PF₆⁻, respectively. The sulfur contents were reduced to 365, 113, and 42 ppm after treated the oil by SECOD process using BMIM⁺BF₄⁻, BMIM⁺PF₆⁻, OMIM⁺PF₆⁻, respectively. The desulfurization yields of SECOD are 59.3, 87.4, and 95.3% with BMIM⁺BF₄⁻, BMIM⁺PF₆⁻, and OMIM⁺PF₆⁻, respectively. The results in Table 2 clearly demonstrate the effectiveness of the SECOD process.

We were interested to find out what types of sulfur compounds remained in the oil after performing the SECOD process. We employed sulfur-specific gas chromatography to measure the sulfur compounds within the light oil before and after SECOD with $OMIM^+PF_6^-$ (Fig. 7). The residual sulfur compound present in the oil after SECOD processing appears to be alkyl benzothiophene (C₄-BT). A previous report indicated that BTs are difficult to be removed when using the ODS method.³⁰

In addition, we noted a difference between the aromatics in the light oil after desulfurization. The composi-





Oxidative Desulfurization in Ionic Liquids

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Sample		Saturated hydrocarbon (vol %)	One-ring aromatics (vol %)	Two-ring aromatics (vol %)	Poly-ring aromatics (vol %)	Sulfur content (ppm)	Desulfurization yield (%)
Feed	Untreated	81.0	13.0	5.8	0.2	897	
Extraction ^a	With C ₄ MIMBF ₄	82.2	12.9	4.1	0.2	803	10.5
Extraction/Oxidation ^b	With C ₄ MIMBF ₄	81.8	12.7	5.4	0.1	365	59.3
Extraction ^a	With C ₄ MIMPF ₆	82.5	12.8	3.5	0.1	786	12.4
Extraction/Oxidation ^b	With C ₄ MIMPF ₆	82.6	12.7	4.6	0.1	113	87.4
Extraction ^a	With C ₈ MIMPF ₆	83.6	12.8	3.5	0.1	675	24.7
Extraction/Oxidation ^b	With C ₈ MIMPF ₆	83.7	13.5	2.8	0	42	95.3
Extraction ^a Extraction/Oxidation ^b Extraction ^a Extraction/Oxidation ^b	With C_4 MIMPF ₆ With C_4 MIMPF ₆ With C_8 MIMPF ₆ With C_8 MIMPF ₆	82.5 82.6 83.6 83.7	12.7 12.8 12.7 12.8 13.5	3.5 4.6 3.5 2.8	0.1 0.1 0.1 0	786 113 675 42	12.4 87.4 24.7 95.3

Table 2. Constants of aromatic and sulfur compounds in light gas oil before and after contact with ionic liquid

^a No oxidation reagents; ^b With oxidation reagents added to the extraction system.

tion of aromatic hydrocarbons after desulfurization was lower than that in the feed light oils. This situation arose because these aromatic hydrocarbons were extracted into the ionic liquid phase. After the oxidative reaction, the aromatic compounds in the light oils were highly oxidized.⁷ The effect that extraction has on the composition of the polyaromatic hydrocarbons in the oxidized oil is more significant than those of the mono- and bicyclic aromatic hydrocarbons. This situation leads to a larger reduction in the content of aromatic hydrocarbons in the light oil after performing sulfur removal.

Regeneration/recycling of RTILs

We followed the approach that we had described previously to recycle the ionic liquids.¹¹ At the end of each run, the reacted ionic liquids were washed out with water and then the ionic liquid phase was filtered, the volatiles were evaporated, and the residue extracted with diethyl ether. ¹H NMR spectroscopy confirmed that the purities of BMIM⁺BF₄⁻, BMIM⁺PF₆⁻, and OMIM⁺PF₆⁻ were retained.





The system was recharged with the oxidizing agent (H_2O_2) with OMIM⁺PF₆⁻, the yield was maintained for four cycles of operation.

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