A novel method for oxidative desulfurization of liquid hydrocarbon fuels based on catalytic oxidation using molecular oxygen coupled with selective adsorption

Xiaoliang Ma, Anning Zhou, Chunshan Song

Abstract

The present study explored a novel oxidative desulfurization (ODS) method of liquid hydrocarbon fuels, which combines a catalytic oxidation step of the sulfur compounds directly in the presence of molecular oxygen and an adsorption step of the oxidation-treated fuel over activated carbon. The ODS of a model jet fuel and a real jet fuel (JP-8) was conducted in a batch system at ambient conditions. It was found that the oxidation in the presence of molecular oxygen with Fe(III) salts was able to convert the thiophenic compounds in the fuel to the corresponding sulfone and/or sulfoxide compounds at 25°C. The oxidation reactivity of the sulfur compounds decreases in the order of 2-methylbenzothiophene > 5-methylbenzothiophene > benzothiophene > dibenzothiophene. The alkyl benzothiophenes with more alkyl substituents have higher oxidation reactivity. In real JP-8 fuel, 2,3-dimethylbenzothiophene was found to be the most refractory sulfur compound to be oxidized. The catalytic oxidation of the sulfur compounds to form the corresponding sulfones and/or sulfoxides improved significantly the adsorptivity of the sulfur compounds on activated carbon, because the activated carbon has higher adsorptive affinity for the sulfones and sulfoxides than thiophenic compounds due to the higher polarity of the former. The remarkable advantages of the developed ODS method are that the ODS can be run in the presence of O$_2$ at ambient condition without using peroxides and aqueous solvent and thus without involving the biphasic oil–aqueous-solution system.

1. Introduction

Deep desulfurization of liquid hydrocarbon fuels has become an increasingly important subject worldwide [1–3]. The sulfur content in the transportation fuels is a very serious environmental concern because the sulfur in fuel is converted to toxic SO$_x$ and contributes to acid rain. The SO$_x$ also poisons the catalysts for the conversion of NO$_x$, CO, and particulate matter for exhaust gas treatment in vehicles. Furthermore, the development of fuel cells makes deep desulfurization an even more challenging issue for making fuel-cell grade fuel [1,2]. Because of their higher energy density, liquid hydrocarbon fuels such as gasoline, jet fuel and diesel, are considered to be promising fuels for fuel cells, particularly for transportation applications and portable power applications. These liquid fuels are catalytically reformed to produce hydrogen-rich gas that can be fed into the fuel cell stacks for electricity generation. However, the presence of even trace amounts of sulfur at the level of parts per million by weight (ppmw) is a poison to both fuel processing as well as fuel cell catalysts. Therefore, the petroleum refining industry and the fuel cell industry are facing a major challenge to produce the ultra-clean liquid hydrocarbon fuels to meet the new and stricter sulfur specification and to meet the need of fuel cell applications.

Existing processes and emerging approaches to desulfurization have been discussed in recent reviews [1–6]. Hydrodesulfurization (HDS) at high temperature (320–380 °C) and high pressure (3–7 MPa) over sulfided CoMo or NiMo catalysts
is currently a major process in petroleum refining industry to reduce the sulfur in liquid hydrocarbon fuels. The major sulfur compounds existing in current liquid hydrocarbon fuels are thiophenic compounds and their alkyl-substituted derivatives. Some of them have been considered to be the refractory sulfur compounds in the fuels due to the steric hindrance of the alkyl groups in HDS [2,4–7]. Consequently, it is difficult or very costly to use the existing HDS technology to reduce the sulfur in the fuels to less than 10 ppmw. In order to meet the need of ultra-clean fuels for environmental protection and H₂ production, it is necessary to develop new approaches to ultra-deep desulfurization of liquid hydrocarbon fuels.

Using adsorbents to selectively remove the sulfur compounds in liquid hydrocarbon fuels is one of the promising approaches, as the process can be conducted at ambient conditions without using costly hydrogen [1,2]. As well known, the liquid hydrocarbon fuels contain not only sulfur compounds but also a large number of aromatic compounds that have aromatic skeleton structure similar to the coexisting sulfur compounds, this inherent problem makes a great challenge in development of an effective adsorbent with high adsorptive selectivity for the sulfur compounds. In addition of many approaches in development of the selective adsorbents for the adsorptive desulfurization [1,8–14], many oxidative desulfurization (ODS) methods, which convert the thiophenic compounds in the fuels to the sulfoxides and/or sulfones, and then, remove them by abstraction, distillation or adsorption, have been explored. Early work in ODS of thiophenic compounds in the presence of 30% hydrogen peroxide (H₂O₂) was reported by Gilman and Esmay [15] and Heimlich and Wallace [16]. Other reported ODS systems include H₂O₂ (oxidant)/polyxometalate (catalyst) [17], H₂O₂/formic-acid [18–21], H₂O₂/phosphotungstic acid [22], NO₂ oxidation [23,24], H₂O₂/12-tungstophosphoric-acid [25], H₂O₂/iron-complexes (TAML, activators) [26], H₂O₂/N₂O₅ [27], H₂O₂/acetic-acid [28,29], and CF₃COOH/titano silicates [30]. H₂O₂/solid bases [31], H₂O₂/TiSi [32], H₂O₂/catalyst [33–36], and H₂O₂/ (activated-carbon plus formic acid) [37]. The advantages of the ODS are that it avoids the use of hydrogen and allows the process to be conducted at ambient conditions, which is more efficient energetically. However, as shown above, most of the reported ODS systems involve use of the oil-insoluble oxidants, H₂O₂ or peroxides, which results in a biphasic oil–aqueous-solution system. This biphasic system limits the mass transfer through the biphasic interface in the oxidation process, which leads to decrease the oxidation rate. The liquid–liquid phase separation after the oxidation usually causes a loss of the fuel oil in the process. The remained sulfones in the oil phase need to be removed further by adsorption and/or abstraction, which also results in a loss of the fuel oil [23,38]. The water-soluble acid or base used as a catalyst in the biphasic system also corrodes the equipments. In order to avoid these problems, some researchers explored the systems using oil-soluble oxidants, such as peracid/Co(II) [38], tert-ButOCl/Mo-Al₂O₃ [39], and tert-ButOOH/Mo–Al₂O₃ [40–42]. Nevertheless, the reaction safety and the cost for the oxidant are still greatly concerned for developing a commercially feasible ODS process.

Our objective in the present study is to explore a novel ODS method of liquid hydrocarbon fuels, which is more energy efficient, cost effective and environment friendly. This ODS method combines a catalytic oxidation step in the presence of molecular oxygen at ambient condition and an adsorption step using carbon-based material. The potential advantages of this novel ODS method are that (1) the process attempt to use molecular oxygen or air as an oxidant, which are readily available, cheap, and suitable for on-board or on-site desulfurization applications; (2) the process does not use peroxides and aqueous solutions and thus it does not involve the biphasic oil–aqueous-solution system, which will significantly simplify the process and reduce the loss of fuel in the liquid–liquid phase separation. The key point in development of this novel ODS process is whether the thiophenic compounds in the fuels can be catalytically oxidized in the presence of molecular oxygen (or air). Fe(III) salts and iron complexes have been reported as the good catalysts for many oxidation reactions at ambient conditions [43–47]. Rossi and Martin have comparatively studied the catalytic and selective sulfoxidation reaction of methylphenylsulfide in the presence of metallic nitrates and bromides [43]. They found that a combination of Fe(III) nitrate and Fe(III) bromide is favorable for oxidation of sulfides into sulfoxides.

In the present study, Fe(III) nitrate and Fe(III) bromide with and without carbon support were examined for ODS of a model jet fuel (MJF) and a real jet fuel (JP-8) in the presence of molecular oxygen in a batch system at ambient conditions. The adsorptive desulfurization of the oxidation-treated fuels over an activated carbon was also conducted at ambient conditions. In this work, a jet fuel, JP-8, was selected as a feed for ODS study, as JP-8 is a logistic fuel and the deep desulfurization of JP-8 on-board or on-site without using hydrogen for fuel cell applications has attracted a great attention recently [48].

2. Experimental

2.1. Catalysts and adsorbents

A mixture of iron salts, which contained Fe(NO₃)₃·9H₂O and FeBr₃ with Fe(NO₃)₃·H₂O/FeBr₃ ratio of 3 in weight, denoted as Fe–Fe, was prepared by a mechanochemical method. A series of Fe–Fe supported on an activated carbon (ACMB) with the (Fe–Fe) to-ACMB weight ratio of 1/1, 1/2 and 1/3, respectively, denoted as Fe–Fe/ACMB-1/1, Fe–Fe/ACMB-1/2 and Fe–Fe/ACMB-1/3, were also prepared by the mechanochemical method. A certain amount of Fe(NO₃)₃·9H₂O and FeBr₃ were mixed and milled into fine powders in a mortar, and then, a certain amount of ACMB was added into the mixture and was further milled by about 5 min. After mixing and milling, the powder mixture was sealed in a bottle for use. The adsorbents (ACMB and ACC) were dried at 110 °C in an oven for 2 h before using in the oxidation or adsorption experiments. Fe(NO₃)₃·9H₂O and FeBr₃ were purchased from Aldrich Chemical Co. Fe(NO₃)₃·9H₂O/ACC (Fe/ACC) was also prepared by the similar method, but the mixture was dried in a vacuum oven at 60 °C for 18 h. ACMB and ACC were
commercial activated carbons with the surface area of 2202 and 899 m²/g, respectively. The detailed pore structure of ACMB and ACC was measured by BET method, and the results are listed in Table 1.

2.2. Model jet fuel and real JP-8

In order to facilitate the comparison of the oxidative and adsorptive selectivity for various sulfur compounds, a model jet fuel (MJF) was prepared by adding sulfur compounds into liquid alkanes for the present study. MJF contained the same molar concentration of benzothiophene (BT), 2-methylbenzothiophene (2-MBT), 5-methlybenzothiophene (5-MBT) and dibenzothiophene (DBT). MJF also contained 10 wt% of butylbenzene to mimic the mono-aromatics in commercial jet fuel. The detailed composition of MJF is shown in Table 2. The total sulfur content in MJF was 412 ppmw. All compounds added in MJF were purchased from Aldrich Chemical Co. used as such without further purification. A real jet fuel, JP-8, was supported by the U.S. Air Force Wright Patterson Laboratory. The fuel contained 717 ppmw sulfur. The major sulfur compounds in JP-8 were alkyl benzothiophenes with one to three carbon atoms in the substituted alkyl groups.

2.3. Oxidation and adsorption experiments

The oxidation was conducted by contacting MJF or JP-8 with the catalyst at a fuel-to-catalyst weight ratio of 21 in a 20 ml vial with a magnetic stirrer at 25 °C and different reaction times, 5, 30 and 60 min, respectively. The PFPD chromatograms of MJF and the oxidized MJF samples with identification are shown in Fig. 1. As PFPD signal is non-linear and there might be a quenching effect in the analysis [8], in the present paper a semi-quantitative analysis according to the peak area of PFPD chromatograms was conducted. It is clear that the peak area for BT, 2-MBT and 5-MBT decreased with increasing reaction time, whereas the peak area corresponding to 1-dioxobenzothiophene (BTO2, retention time: 11.45 min), 1-dioxo-2-methylbenzothiophene (2-MBTO2, retention time: 12.65 min) and 1-dioxo-5-methylbenzothiophene (5-MBTO2, retention time: 13.03 min) increased with increasing reaction time. No

<table>
<thead>
<tr>
<th>Name</th>
<th>Purity</th>
<th>Concentration (wt%)</th>
<th>Concentration (mmol/kg)</th>
<th>S concentration (ppmw)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BT</td>
<td>0.99</td>
<td>0.0427</td>
<td>3.18</td>
<td>102</td>
</tr>
<tr>
<td>2-MBT</td>
<td>0.98</td>
<td>0.0675</td>
<td>3.20</td>
<td>103</td>
</tr>
<tr>
<td>5-MBT</td>
<td>0.96</td>
<td>0.0480</td>
<td>3.24</td>
<td>104</td>
</tr>
<tr>
<td>DBT</td>
<td>0.97</td>
<td>0.0595</td>
<td>3.23</td>
<td>104</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>0.99</td>
<td>0.0398</td>
<td>3.11</td>
<td>104</td>
</tr>
<tr>
<td>2-Methylnaphthalene</td>
<td>0.97</td>
<td>0.0447</td>
<td>3.14</td>
<td>104</td>
</tr>
<tr>
<td>Tert-butylbenzene</td>
<td>0.99</td>
<td>9.996</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Decane</td>
<td>0.99</td>
<td>44.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Hexadecane</td>
<td>0.99</td>
<td>0.0592</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Tetradecane</td>
<td>0.99</td>
<td>44.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Others (impurity)</td>
<td></td>
<td>1.06</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| Total              | 100.0  |                     |                         | 412                    

The total sulfur concentration of the treated fuel samples was analyzed by using ANTEK 9000 series sulfur analyzer. The detailed analysis method was reported in our previous paper [8]. The identification and semi-quantification of the various compounds in the treated MJF and JP-8 was analyzed by a HP 5890 gas chromatograph with a capillary column (XTI-5, Restek, 30 m in length, 0.25 mm in internal diameter) and a pulsed flame photometric detector (PFPD).

3. Results and discussion

3.1. Oxidation of thiophenic compounds

Oxidation of the sulfur compounds in MJF on Fe–Fe was conducted in the batch reaction system with O2 gas bubbling at 25 °C and different reaction times, 5, 30 and 60 min, respectively. The PFPD chromatograms of MJF and the oxidized MJF samples with identification are shown in Fig. 1.

Table 1

<table>
<thead>
<tr>
<th></th>
<th>( S_{\text{BET}} ) (m² g⁻¹)</th>
<th>( S_{\text{mic}} ) (m² g⁻¹)</th>
<th>( S_{\text{meso}} ) (m² g⁻¹)</th>
<th>( V_{\text{total}} ) (cm³ g⁻¹)</th>
<th>( V_{\text{mic}} ) (cm³ g⁻¹)</th>
<th>( V_{\text{meso}} ) (cm³ g⁻¹)</th>
<th>Average pore size (nm)</th>
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<tbody>
<tr>
<td>ACC</td>
<td>899</td>
<td>709</td>
<td>190</td>
<td>0.492</td>
<td>0.368</td>
<td>0.124</td>
<td>2.19</td>
</tr>
<tr>
<td>ACMB</td>
<td>2202</td>
<td>1175</td>
<td>1027</td>
<td>1.192</td>
<td>0.629</td>
<td>0.564</td>
<td>2.17</td>
</tr>
</tbody>
</table>

Table 2

Composition of model jet fuel (MJF)
peak for BT, 2-MBT and 5-MBT was observed in the treated fuel after 60 min reaction, indicating that all of BTs had been converted into the oxidized BTs. The major oxidation products from BTs was 1-dioxobenzothiophenes, but a few other oxidation products corresponding to retention times at 14.6, 15.6 and others were also observed, as shown in Fig. 1 for the treated fuel after 60 min reaction. In comparison with BTs, DBT was less reactive for oxidation, as considerable amount of DBT still remained in the treated fuel after 60 min reaction. The different disappearance rates of the sulfur compounds according the peak area, as shown in Fig. 1, indicate that the oxidation reactivity of these sulfur compounds decreases in the order of 2-MBT > 5-MBT > BT > DBT. The methyl group on BT increases the oxidation reactivity, probably because the methyl group on the aromatic rings is an electron donator, which enhances the electron density of the sulfur atom attacked by the active oxygen within the oxidation. It should mention that the oxidation reactivity of DBT in the present study is much less than that of BT. The relative oxidation reactivities for BT and DBT appear to be contrary to the previous finding by others [19,32,36]. The present study involves a heterocatalysis in the presence of molecular oxygen, while the previous studies involve a biphasic oil–aqueous-solution system using H2O2 as an oxidant. This may be one of the reasons for the different reactivity order.

In order to examine whether the molecular oxidation joins the oxidation of the sulfur compounds, the oxidative desulfurization of JP-8 over ACC and Fe/ACC with and without O2 bubbling was conducted at 65 °C. The results are listed in Table 3. It clearly shows that though the reaction in the absence of O2 took place for even 5 h, the sulfur concentration in the treated JP-8 was still much higher than that of the treated fuel from the oxidative desulfurization of JP-8 in the presence of O2 for 2 h, especially for the case over Fe/ACC catalyst. The results indicate that the molecular oxygen directly join the oxidation of the sulfur compounds and accelerate the conversion of sulfur compounds to sulfone and/or sulfoxide compounds. It leads to a significantly decrease of sulfur concentration in the treated JP-8 since the formed sulfone and/or sulfoxide compounds are easy to be adsorbed on activated carbon. In this reaction system, the oxidation may take place on the Fe(III) center with nitrate/nitrite and/or bromide/bromine.

![Fig. 1. PFPD chromatograms of MJF and the oxidized MJF samples over Fe–Fe at 25 °C for different reaction times.](image)

Table 3
Effect of the O2 bubbling on sulfur removal from JP-8

<table>
<thead>
<tr>
<th>With O2 bubbling(^a)</th>
<th>Without O2 bubbling(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(S) in treated fuel (ppmw)</td>
<td>(S) removal (%)</td>
</tr>
<tr>
<td>ACC</td>
<td>633</td>
</tr>
<tr>
<td>Fe/ACC</td>
<td>442</td>
</tr>
</tbody>
</table>

\(^a\) Conditions: fuel/adsorbent: 21/1 (wt), 65 °C, 2 h.

\(^b\) Conditions: fuel/adsorbent: 21/1 (wt), 65 °C, 5 h.
redox cycles as mediators, as proposed previously by Rossi and Martin [43]. More investigations are necessary to understand further this oxidation mechanism. An important message got from this study is that the molecular oxygen can be used directly as an oxidant for ODS instead of H2O2, which involves a biphasic oil–aqueous-solution system and results in the loss of oil in the liquid–liquid separation.

It has been reported that some activated carbons are able to catalyze the oxidation of some sulfur compounds [49,50] and activated carbons usually have very high surface area. Loading Fe–Fe on some activated carbon might improve the oxidation performance of the catalyst. With this in mind, we prepared new catalysts by mixing Fe–Fe and ACMB with different (Fe–Fe)-to-ACMB ratios in weight, and conducted the oxidative desulfurization of JP-8 over the Fe–Fe/ACMB in the batch reactor in the presence of oxygen gas at 25 °C for 2 h. The PFPD chromatograms of the oxidation-treated JP-8 samples on different Fe–Fe/ACMB and Fe–Fe are shown in Fig. 2. The identification of the sulfur compounds in JP-8 was conducted by comparing the relative retention time with the data from literature [51]. The major sulfur compounds in the JP-8 included 2,7-dimethylbenzothiophene (2,7-DMBT), 2,6-dimethylbenzothiophene (2,6-DMBT), 2,4-dimethylbenzothiophene (2,4-DMBT), 2,3-dimethylbenzothiophene (2,3-DMBT), 2,4,7-trimethylbenzothiophene (2,4,7-TMBT), 2,3,7-trimethylbenzothiophene (2,3,7-TMBT), and 2,3,5 (or 6)-trimethylbenzothiophene (2,3,5/6-TMBT). It was found that even at room temperature the prepared Fe–Fe/ACMB catalysts were able to convert the benzothiophenic compounds in JP-8 to their corresponding sulfones and/or sulfoxides. By comparing the disappearance rate of the benzothiophenic compounds on the basis of the corresponding peak area in the PFPD chromatograms for the treated JP-8 samples (see Fig. 2), it was found that Fe–Fe/ACMB-1/1 catalyst presented the best catalytic activity for the oxidation, as the product from the oxidation over Fe–Fe/ACMB-1/1 gave the least peak area for alkyl benzothiophenes. In comparison of C3BTs and C2BTs, it is clear that C3BTs presented higher oxidation reactivity than C2BTs in general, which indicates that the methyl groups increase the oxidation reactivity of benzothiophenes. This is agreement with the finding for the oxidation of MJF. Among C2BTs, 2,3-DMBT was found to be the most refractory compound to be oxidized, while among C3BTs, 2,3,7-TMBT was found to be the most refractory one. It is still unclear why 2,3,7-DMBT is the most refractory sulfur compound. Both the electronic and steric effects of the methyl groups may play an important role in determining the oxidation reactivity. To clarify this, more investigations are necessary.

3.2. Adsorption of the oxidized thiophenic compounds over Fe–Fe/ACMB and ACMB

It should be pointed out that the function of Fe–Fe/ACMB was not only as an oxidation catalyst, but also as an adsorbent for the sulfur removal. The total sulfur concentration of the JP-8 samples treated by the different catalysts was measured, and the adsorptive capacity of the Fe–Fe/ACMB on the basis of the

![Fig. 2. PFPD chromatograms of JP-8 and the oxidized JP-8 samples over different catalysts at 25 °C for 2 h.](image-url)
total catalyst weight was calculated. The adsorptive capacity as a function of Fe–Fe/(Fe–Fe + ACMB) weight ratio is shown in Fig. 3. This relationship is not a linear. There is the maximum capacity value of 9.6 mg of sulfur per gram of adsorbent (mg S/g A) corresponding to a Fe–Fe/ACMB weight ratio around 1/2, which is about 4 times higher than that for ACMB and about 1.4 times higher than that for Fe–Fe alone.

In order to understand why the addition of Fe–Fe to ACMB can significantly improve the adsorptive capacity, the adsorptive desulfurization of MJF and the oxidation-treated MJF over ACMB were also conducted in the batch adsorption system at 25 °C for 2 h. The PFPD chromatograms of the adsorption-treated MJF (b), the oxidation-treated MJF (c), the product after the adsorption treatment of the oxidation-treated MJF(d) as well as MJF (a) are shown in Fig. 4 together for easy comparison. By comparison of Fig. 4a and b, it was found that ACMB has higher adsorptive selectivity for DBT than for BTs, and the methyl substituents increased the adsorptive selectivity of ACMB for the thiophenic compounds, which is in agreement with our previous study [52]. The major difference between MJF and the oxidation-treated MJF is that the later contains the oxidized BTs instead of BTs. The adsorption treatment over ACMB was only able to reduce the sulfur in MJF to 106 ppmw, as ACMB has lower adsorptive affinity for benzothiophenic compounds, especially for BT, which was also found in our previous study [53]. However, after converting the most of benzothiophenic compounds to the corresponding sulfones and/or sulfoxides, as shown in Fig. 4c, the adsorption treatment of the oxidation-treated MJF over ACMB reduced the sulfur in the fuel to 2 ppmw, indicating that ACMB has much higher adsorptive affinity and selectivity for the sulfones and sulfoxides than for benzothiophenic compounds. By comparing the adsorptive desulfurization over ACMB and the ODS by the oxidation over Fe–Fe followed by the adsorption over ACMB, as shown in Table 4, the former can only remove 74.3% sulfur, while the latter is able to remove 99.5% sulfur. The sulfur removal in the first step (oxidation) of the ODS process is only 13.3%, probably through precipitation, adsorption on Fe–Fe, or complexation with Fe–Fe. The results indicate that the oxidation step and the adsorption step work together to improve deep desulfurization performance significantly.

In order to understand the different adsorptive capacity of the activated carbon for thiophenic compounds and their
corresponding sulfones, the electrostatic potential and the dipole magnitude of BT, DBT and their corresponding sulfones were estimated by a semi-empirical quantum chemistry method, MOPAC-PM3, in CAChe (Version 6.1.1). The results are shown in Fig. 5. The oxidation of the sulfur compounds significantly increased the polarity of the molecules. The dipole magnitude increases from 1.091 D for BT to 5.577 D for 1-dioxobenzothiophene, and from 0.901 D for DBT to 5.453 D for 5-dioxodibenzothiophene. A very high negative electrostatic potential was found on dioxobenzothiophene and dioxodibenzothiophene, which is located on the two oxygen atoms. The stronger adsorptive affinity of the activated carbons towards dioxobenzothiophene and dioxodibenzothiophene could be attributed to their higher polarity and negative electrostatic potential. Thus, the remarkably higher adsorptive capacity of Fe–Fe/ACMB than that of ACMB can be ascribed to the oxidation of the thiophenic compounds to the corresponding sulfones and/or sulfoxides, and ACMB has much higher adsorptive affinity for the produced sulfones and/or sulfoxides than for the thiophenic compounds.

3.3. Oxidative desulfurization of real JP-8

Oxidative desulfurization of real JP-8 by a combination of the catalytic oxidation and adsorption over ACMB was performed at ambient conditions. The oxidation of JP-8 on Fe–Fe/ACMB-1/1 to convert the sulfur compounds to the corresponding sulfones was conducted in the batch system with a JP-8/catalyst weight ratio of 21 at 25 °C under bubbling of oxygen gas for 2 h. The oxidation-treated JP-8 was further treated by the adsorption over ACMB with a JP-8/ACMB weight ratio of 21 at 25 °C for 3 h. The PFPD chromatograms of the oxidation-treated JP-8, the adsorption-treated JP-8 after the oxidation as well as JP-8 are shown together in Fig. 6 for easy comparison. The total sulfur concentration in the oxidation-treated JP-8 and the adsorption-treated JP-8 were measured, and the corresponding S removal in each step was calculated. The results are summarized in Table 4. In the oxidation step, majority of sulfur compounds was oxidized to form the sulfones and/or sulfoxides, and then, the formed sulfones and/or sulfoxides were adsorbed partly on the Fe–Fe/ACMB. The sulfur concentration in the fuel was reduced from the initial
717–279 ppmw. About 61% of the total sulfur in JP-8 was removed in the oxidation step. The corresponding adsorptive capacity of Fe–Fe/ACMB was 9.2 mg S/g.

In the second step (the adsorption step), the sulfur concentration was further reduced from 279 to 126 ppmw. The corresponding adsorptive capacity of ACMB was 3.2 mg S/g. Most of the sulfones and/or sulfoxides were removed, and the major remaining sulfur compounds in the final fuel is 2,3-DMBT, an unoxidized sulfur compounds. It indicates that if one is able to convert more benzothiophenic compounds to the sulfones, such as by increasing the catalyst activity or reaction temperature, the sulfur removal can be further improved.

For comparison purpose, the adsorptive desulfurization of JP-8 over ACMB in the absence of both the Fe–Fe catalyst and oxygen gas was also conducted at the same conditions. The results are also listed in Table 4. In this case only 16.0% of sulfur in JP-8 can be removed, and the corresponding adsorptive capacity is only 2.4 mg S/g, which was four times less than that over Fe–Fe/ACMB in the presence of molecular oxygen. These results make it clear that the conversion of benzothiophenic compounds to the corresponding sulfones significantly improves the adsorptive performance of the activated carbon for sulfur removal, which is in agreement with the observation for MJF.

The above results demonstrate that the two-step ODS method proposed in the present study is able to oxidize the sulfur compounds in ambient condition in the presence of Fe–Fe/ACMB and molecular oxygen, and then to remove them from real jet fuel (JP-8). It should be pointed out that the proposed ODS method may also be applied for other liquid hydrocarbon fuels in comparison with the ODS process reported in literature.

4. Summary

The present study has demonstrated a novel oxidative desulfurization method for jet fuel. This method combines the oxidation of the sulfur compounds in the presence of molecular oxygen and the Fe(III) salts at ambient conditions, and the adsorptive desulfurization of the oxidation-treated fuel over the activated carbon.

Fe(III) salts are effective in conversion of the benzothio-phenic compounds existing in the liquid hydrocarbon fuel to the sulfones and/or sulfoxides in the presence of molecular oxygen at ambient conditions. The results indicate that molecular oxygen joins the oxidation directly. The oxidation reactivity of the sulfur compounds over the Fe(III) salts increases in the order of DBT < BT < 5-MBT < 2-MBT. The alkyl benzothiophenes with more alkyl substituents have relatively higher oxidation reactivity. 2,3-DMBT is the most refractory sulfur compound in the JP-8 to be oxidized in the present study. Loading of Fe(III) salts on the activated carbon (ACMB) increases further the oxidation activity of the Fe(III) salts.

The catalytic oxidation of the sulfur compounds existing in the liquid hydrocarbons to form the corresponding sulfones and/or sulfoxides improves significantly the adsorptivity of the sulfur compounds over activated carbon, because the activated carbon has higher adsorption affinity for the sulfones and sulfoxides than thiophenic compounds due to the higher polarity of the former than the latter.

The remarkable advantages of the developed ODS method in this study are that the method can oxidize the sulfur compounds in the fuel in the presence of molecular oxygen at ambient condition without involving the biphasic oil–aqueous-solution system. Consequently, this ODS method might be more energy efficient, cost effective and environment friendly in comparison...
with other ODS methods reported in literature, and thus could be a more promising process for deep desulfurization of the liquid hydrocarbon fuels.

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