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# Oxidative Desulfurization of Jet and Diesel Fuels Using Hydroperoxide Generated in Situ by Catalytic Air Oxidation

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The objective of this work is to explore the potential of carrying out oxidative desulfurization using air as an oxidant. The liquid fuels to be desulfurized were first contacted with air to produce hydroperoxides in situ, which were then used as selective oxidants to oxidize the sulfur compounds. Unsupported CuO was tested as a catalyst for producing hydroperoxides in the fuel at 120 °C in the presence of air. Air oxidation was also carried out in the presence of $Al_2O_3$-supported CuO and also noncatalytically. Unsupported CuO was substantially more active than the other two cases. The yield of the hydroperoxides depends strongly on the catalyst and the reaction temperature; the yield decreased in the order of 120 °C > 140 °C ≫ 100 °C but the rate of oxidation to produce hydroperoxides decreased in the order of 140 °C > 120 °C ≫ 100 °C. It was found that more hydroperoxides could be generated in diesel fuel than in jet fuel, which might be related to the higher concentration of alkyl aromatics in diesel fuel when compared to JP-8 jet fuel. The hydroperoxides generated in situ were then used to oxidize the sulfur compounds in the fuel in the presence of $SiO_2$-supported $MoO_3$ catalyst. Hydroperoxides generated in situ were effective in oxidizing the alkyl-substituted benzothiophene and dibenzothiophene present in jet and diesel fuels to their corresponding sulfones which were then removed by adsorption on beta zeolite. On the other hand, the amount of cumene hydroperoxide required per mole of S for oxidation to sulfone was 1.5 and 10 times higher than the stoichiometric amounts for JP-8 jet fuel and diesel fuel, respectively. This study demonstrates that oxidative desulfurization can be effectively carried out by using air as an oxidant for generating hydroperoxides in situ, which can then be used to selectively oxidize the sulfur compounds to sulfones, thereby eliminating the need for use, storage, and handling of expensive liquid-phase peroxide oxidants.

## 1. Introduction

“U.S. EPA Tier 2” emissions specifications and “EU Euro IV” standards called for sulfur in diesel fuel to be reduced to a maximum of 15 and 10 ppmw S, respectively, and many countries around the world are pursuing toward ultralow sulfur diesel (ULSD) fuels.[1−4] These strict sulfur mandates led to a surge of development of alternative desulfurization technologies because of the increased difficulty in removing the last few alkyl substituted dibenzothiophenes, especially 4,6-dimethyl dibenzothiophene (4,6 DMDBT) from diesel fuels.[3,5] Given the long lead times involved for developing alternative technologies, most refiners made investment plans for meeting these tight specifications by employing conventional hydrodesulfurization (HDS), which is a simple and proven process for the refiners. This has led to HDS units operating at increased severity and/or with higher catalyst volumes contributing to higher operating costs but with diminishing returns for ultralow sulfur fuels.[1,6]

Among the alternative technologies proposed in the literature, oxidative desulfurization (ODS) has gained attention because of its mild operating conditions coupled with no hydrogen requirement for ULSD. More importantly, the substituted dibenzothiophenes such as 4,6-DMDBT, which is the least reactive for HDS, could show increased oxidation activity under certain conditions. So implementation of ODS as a finishing step to ULSD that complements HDS has also been discussed in the literature.[7]

Most of the ODS approaches reported in the literature involve selective oxidation of sulfur compounds to corresponding sulfones by liquid oxidants followed by adsorption or extraction to remove them for ULSD. The use of liquid oxidants has plagued ODS technology because of the increased cost in handling and storage of the liquid oxidants. Some examples of liquid oxidants used in prior studies include hydrogen peroxides, *tert*-butyl hydroperoxide, *tert*-butyl hypochlorite, and nitric acid, etc.[8−15] To overcome the issue of usage of these expensive oxidants, the use of oxygen and ozone has been proposed in the literature but the issue of selectivity to sulfur compounds was not addressed clearly.[16,17] Use of oxygen as an oxidant with sacrificial aldehyde has also been proposed in the literature for selective oxidation of sulfur compounds,[18] and a novel process based on catalyst free, solvent assisted oxidative desulfurization of fossil fuels by air was reported recently.[19] However, the use of expensive oxidants, oil-insoluble oxidants which result in biphasic reaction and the use of sacrificial agents, has rendered ODS as an unfavorable technology.

In this study, ODS was carried out by a two-step in situ air oxidation procedure coupled with adsorption, and the scheme of the process is shown in Figure 1. In the first step, the fuel is mixed with air in the presence of a catalyst to produce hydroperoxides in situ. The hydroperoxide generated in the fuel then oxidizes the sulfur compounds present to their corresponding sulfones in the second step in the presence of a catalyst. The generated sulfones were then removed by adsorption for ultralow sulfur fuels. In regard to this, a commercial JP-8 jet fuel with 520 ppmw S and a commercial diesel fuel with 41 ppmw S were tested for ODS by the process scheme as described in Figure 1. JP-8 jet fuel was also employed here because of the renewed interest in using jet fuel feedstock as a precursor for fuel cell applications, which calls for very low levels of sulfur as the sulfur compounds are detrimental to the fuel processor and to the fuel cell itself.[20,21]

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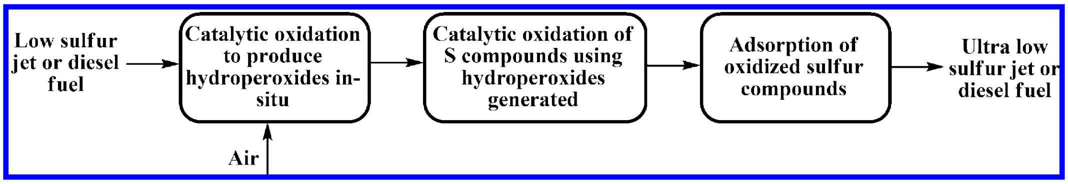

**Figure 1.** Scheme of the ODS process used in this study.

**Table 1. Key Properties of JP-8 Jet Fuel (JP-8-520) and Diesel Fuel (LSD-41)**

| | JP-8-520 | LSD-41 |
|---|---|---|
| initial boiling point, °C | 156−293 | 173−351 |
| paraffins, wt % | 52.8 | 57.4 |
| cycloparaffins, wt % | 30.8 | 24.4 |
| aromatics, wt % | 15.9 | 18.3 |
| sulfur, ppm | 520 | 41 |

## 2. Experimental Section

**2.1. Real Fuels.** JP-8 jet fuel (JP-8-520) containing 520 ppmw S and diesel fuel (LSD-41) containing 41 ppmw S were obtained from Altex Technologies Corporation, Sunnyvale, California, and from BP, respectively. Some of the key properties of JP-8 jet fuel and diesel fuel used in this study are listed in Table 1.

**2.2. Oxidants.** Ultrahigh purity (UHP) air was used as an oxidant in most parts of this study. The 80% cumene hydroperoxide in cumene purchased from Sigma Aldrich was also tested as an oxidant in a few cases and was used as such without further purification.

**2.3. Catalysts and Adsorbent. 2.3.1. CuO and CuO/$Al_2O_3$ for Low-Temperature Air Oxidation to Produce Hydroperoxides.** Copper nitrate hemipentahydrate was used as the copper precursor, which was purchased from Sigma Aldrich and used without further purification. $\gamma$-Alumina (LaRoche VGL-15) supplied by UOP was used as the support. The 12 wt % Cu was loaded on $\gamma$-alumina by the method of wet impregnation, and the catalyst was calcined at 450 °C before oxidation experiments. Unsupported CuO was prepared by direct calcination of the precursor at 300 °C.

**2.3.2. $MoO_3/SiO_2$ for Sulfur Oxidation Using Hydroperoxides.** Ammonium molybdate tetrahydrate was used as the molybdenum precursor, which was bought from Sigma Aldrich and used without further purification. Untreated fumed silica (M-5) purchased from Cabot was used as the support. The 12 wt % Mo was loaded on M-5 silica by the method of wet impregnation, and the catalyst was calcined at 450 °C before oxidation experiments.

**2.3.3. Beta Zeolite for Sulfone Adsorption.** Beta zeolite [CP 814C] with $SiO_2/Al_2O_3 = 38$ was obtained from Zeolyst. The catalyst was calcined at 550 °C to convert the ammonium form into the proton form before adsorption experiments.

**2.4. Oxidation and Adsorption Procedures.** Oxidation and adsorption experiments were carried out in a 20 mL batch reactor equipped with a temperature controller, condenser, and magnetic stirrer.

**2.4.1. Low-Temperature Air Oxidation to Produce Hydroperoxides.** In a typical experiment, 5 g of fuel was heated up to the desired temperature along with 0.5 g of catalyst. After the desired condition was reached, air was bubbled at the rate of 5 cc/min and samples were collected periodically. Air oxidation was tested at temperatures between 100 and 140 °C under atmospheric pressure.

**2.4.2. Oxidation of Sulfur Compounds by Hydroperoxides Generated in Situ.** In a typical experiment, 5 g of fuel from low-temperature air oxidation was heated up to 85 °C along with 0.1 g of catalyst. Oxidation was carried out for 60 min without any air bubbling at atmospheric pressure.

**2.4.3. Adsorption of Sulfones.** In a typical experiment, 4 g of fuel was heated up to 85 °C along with 0.8 g of adsorbent to remove the oxidized sulfur compounds produced in the fuel after the two step oxidation. Adsorption was carried out for 60 min at atmospheric pressure.

**2.5. Analysis of Fuel Samples. 2.5.1. Hydroperoxide Analysis.** Hydroperoxides in the air-oxidized samples were estimated by the ASTM D 3703-99 procedure (standard test method for peroxide number of aviation turbine fuel). In a typical analysis, a known amount of oxidized fuel dissolved in carbon tetrachloride was contacted with aqueous potassium iodide in an acidic medium. The hydroperoxides present in the fuel are reduced by the potassium iodide. The equivalent amount of iodide liberated was titrated with sodium thiosulfate solution. Hydroperoxides in the fuel are expressed as milligrams of peroxide per kilogram of fuel (ppm).

**Repeatability of Hydroperoxide Analysis.** The difference between two successive test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would, in the long run, in the normal and correct operation of the test method, exceed the following values only in 1 case in 20: $r = 0.15X$, where $X$ is the average of two test results.

**2.5.2. Sulfur Analysis.** Qualitative analysis of the sulfur compounds in real fuel was conducted with an HP 5890 gas chromatograph (XTI-5 column from Restek, 30 m in length and 0.25 mm in internal diameter) equipped with a pulsed flame photometric detector (PFPD). The total sulfur concentration in real fuel was analyzed by using an Antek 9000 series total sulfur analyzer. The detailed analytical method was reported previously.[22]

## 3. Results and Discussion

**3.1. Effect of Catalyst on Liquid Phase Air Oxidation for in Situ Hydroperoxide Generation.** To test the activity of the catalyst for generating hydroperoxides in the fuel, air

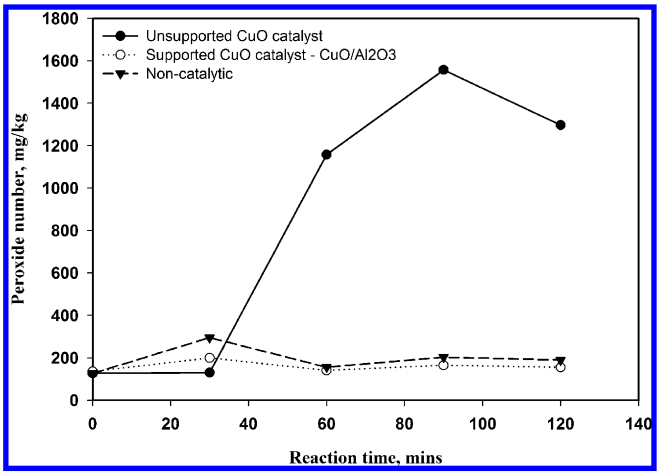

**Figure 2.** Effect of catalyst on liquid phase air oxidation of jet fuel (JP-8-520) to produce hydroperoxides in situ. (Reaction conditions: 5 g of fuel; oil/catalyst (w/w), 10; oil/air (v/v), 1.25 $min^{-1}$ at 120 °C).

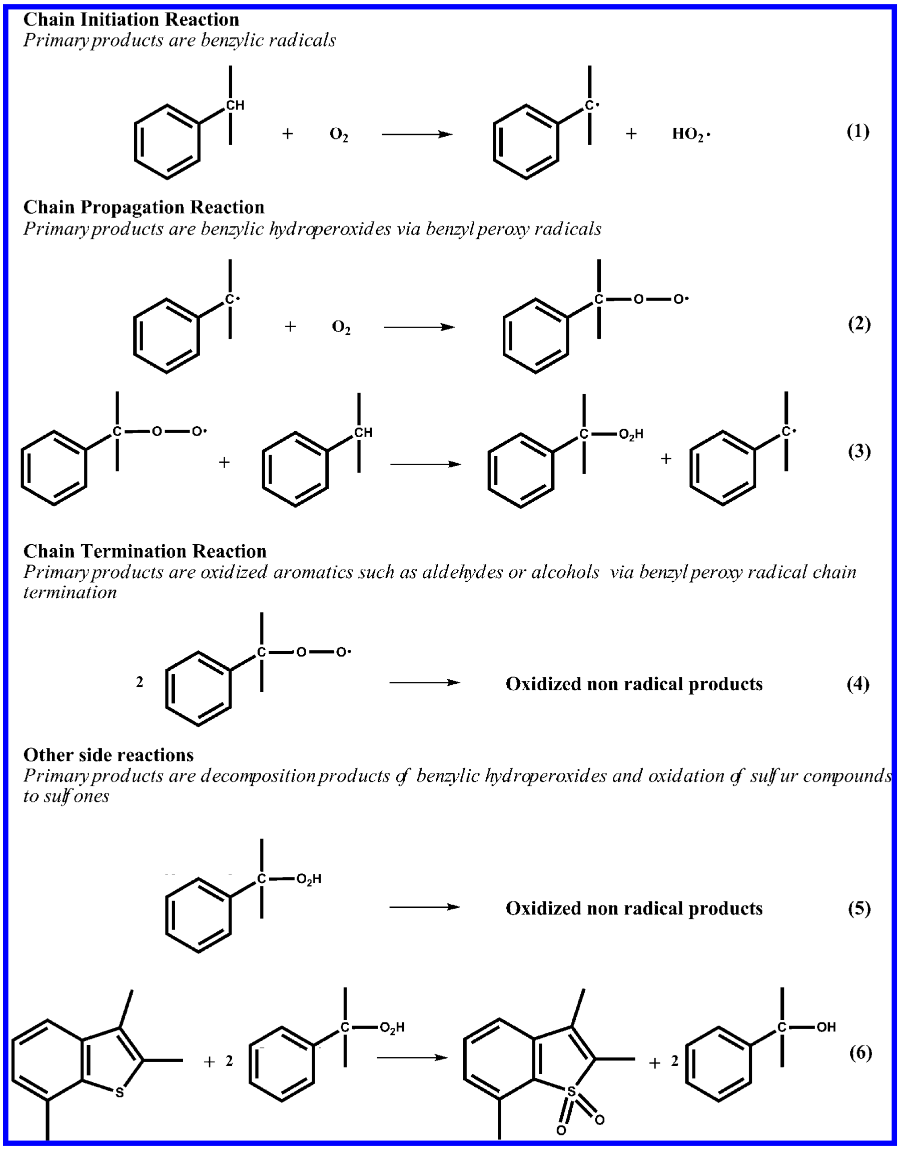

**Figure 3.** Typical reaction scheme of low-temperature liquid phase air oxidation of jet fuel (with cumene and 2,3,7-trimethyl benzothiophene as representative aromatic and sulfur compounds, respectively) to obtain hydroperoxide as the main product.

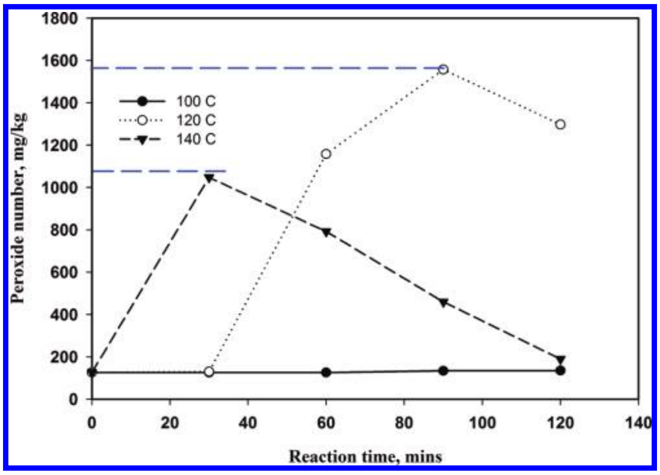

**Figure 4.** Effect of temperature on liquid phase air oxidation of jet fuel (JP-8-520) to produce hydroperoxides in situ catalyzed by unsupported CuO catalyst. (Reaction conditions: 5 g of fuel; oil/catalyst (w/w), 10; oil/air (v/v), 1.25 min$^{-1}$ at 120 °C).

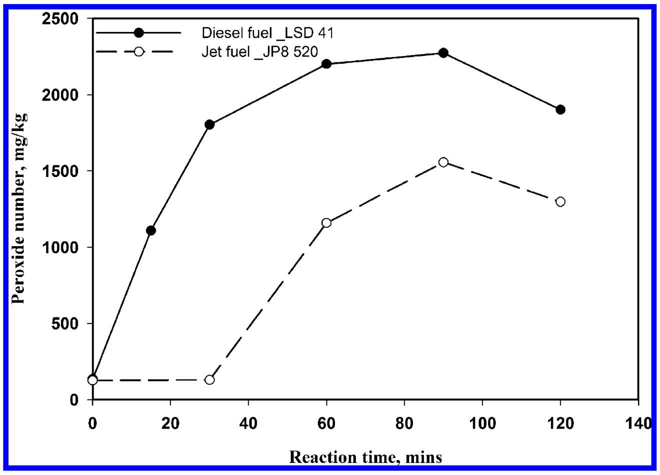

**Figure 5.** Liquid phase air oxidation of jet fuel (JP-8-520) and diesel fuel (LSD-41) to produce hydroperoxides in situ catalyzed by unsupported CuO catalyst. (Reaction conditions: 5 g of fuel; oil/catalyst (w/w), 10; oil/air (v/v), 1.25 at 120 °C).

oxidation of JP-8-520 was carried out in the presence of unsupported CuO, $Al_2O_3$-supported CuO catalysts,[23] and also noncatalytically. Results shown in Figure 2 in terms of peroxide number demonstrate that hydroperoxides were indeed produced in the fuel at different reaction times in the presence and absence of catalyst. As seen from Figure 2, in the presence of

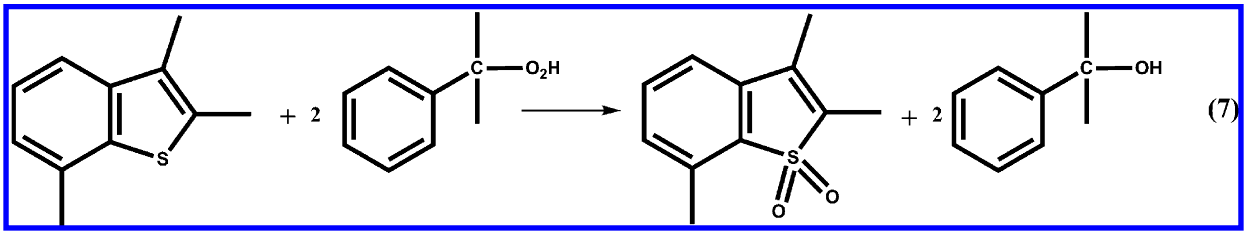

**Figure 6.** Typical reaction scheme of sulfur compound oxidation by hydroperoxide generated in situ representing the second step of the ODS process (with cumene hydroperoxide and 2,3,7-trimethyl benzothiophene as representative alkyl benzene hydroperoxide and sulfur compounds, respectively) to form sulfones.

unsupported CuO catalyst, oxidation proceeded at a substantial rate to produce hydroperoxides. This is in contrast to the $Al_2O_3$-supported CuO catalyst which showed no activity for hydroperoxide generation using air as an oxidant, exhibiting a trend similar to noncatalytic air oxidation. It can be seen from Figure 2 that the concentration of hydroperoxide gradually increases with reaction time and then it decreases after reaching a peak value. This might be due to the fact that the hydroperoxides which are thermally unstable have begun to decompose to other oxygenated products.

Figure 3 shows the reaction scheme of a catalytic air oxidation of a fuel. Attack by elementary oxygen on an alkyl benzene based compound in fuel is a free radical reaction, and the activation to produce a free radical can be accomplished by light, heat, catalysts, or by initiators which decompose to give a free radical (reaction 1 in Figure 3).[24] Aromatics air oxidation to hydroperoxides occurs in two steps. The first step is a “chain initiation reaction” where the active benzylic radicals are produced followed by the “chain propagation step” in which the oxygen reacts with benzylic radicals to form hydroperoxides via benzyl peroxy radical formation shown by reactions 2 and 3 in Figure 3. The chain initiation and the propagation step represent the hydroperoxide formation where the concentration of hydroperoxide increases gradually with time. The point where the hydroperoxide concentration begins to decrease is where the “chain termination reaction” begins to dominate and the free radicals begin to form other oxidized nonradical products as shown in reaction 4 in Figure 3. During this stage, the chain propagation reaction recedes dramatically. Also hydroperoxides which are intermediates of the air oxidation process are not thermally stable and start to decompose, which can be either catalytically or thermally driven or by both, reaction 5 in Figure 3.

**3.2. Effect of Temperature on Liquid Phase Air Oxidation of JP-8-520.** To examine the effect of temperature on oxidation activity, air oxidation of JP-8-520 was carried out in the presence of unsupported CuO catalyst at three different operating temperatures (100, 120, and 140 °C) and the results are shown in Figure 4. Even in the presence of catalyst at 100 °C, oxidation did not proceed to the formation of hydroperoxides. At 120 °C, significant generation of hydroperoxides took place with increasing reaction time up to 90 min. At 140 °C, oxidation proceeded at a rapid rate and the hydroperoxide concentration peaked much earlier in comparison to oxidation at 120 °C, as shown in Figure 4. However, the peak hydroperoxide value at 120 and 140 °C are 1047 and 1557 ppmw, respectively (see in Figure 4). This might be because of the increased kinetic rate of the chain termination reaction (reaction 4 in Figure 3) to form other nonradical oxidized products at 140 °C. Temperature is critical for liquid phase air oxidation of fuel. The hydroperoxide yield decreased in the order of 120 °C > 140 °C ≫ 100 °C and the rate of oxidation decreased in the order of 140 °C > 120 °C ≫ 100 °C. So at higher temperatures, the benzylic radicals generated in the reaction can potentially form other oxidized nonradical products (reaction 4 in Figure 3) or the hydroperoxides generated in situ undergo thermal decomposition to other oxidized products (reaction 5 in Figure 3), which decrease the overall selectivity of the ODS process.

**3.3. In Situ Hydroperoxide Generation in Diesel Fuel.** Commercial diesel LSD-41 was also air oxidized at low temperature in liquid phase for in situ hydroperoxide generation. Since unsupported CuO catalyst showed good activity for JP-8-520 at 120 °C, the same conditions were used for air oxidation of LSD-41. Figure 5 shows the concentrations of hydroperoxides produced in LSD-41 with reaction time in terms of the peroxide number. For reference, air oxidation of JP-8-520 under the same conditions is also included. LSD-41 shows a better activity for hydroperoxide generation when compared with JP-8-520 under the same conditions. But both LSD-41 and JP-8-520 reach a peak hydroperoxide value in 90 min, beyond which the peroxide number of both the fuels began to drop, as can be seen from the lower values at 120 min, probably due to the chain termination. The difference in hydroperoxide yield for LSD-41 and JP-8-520 may be related to the different concentration and types of aromatic hydroperoxide precursors present in the fuels. Some of the key properties of jet and diesel fuel used in this study are shown in Table 1. Investigation of a surrogate fuel containing various concentrations and types of aromatic compounds will provide a better insight for this change in oxidation activity. The high concentration of alkyl benzene may result in a higher concentration of benzylic radicals which are precursors for hydroperoxide formation. The higher concentration of sulfur compounds in JP-8-520 than that in LSD-41 may be another reason for the low concentration of hydroperoxide in JP-8-520, as the generated hydroperoxides in the air oxidation of JP-8-

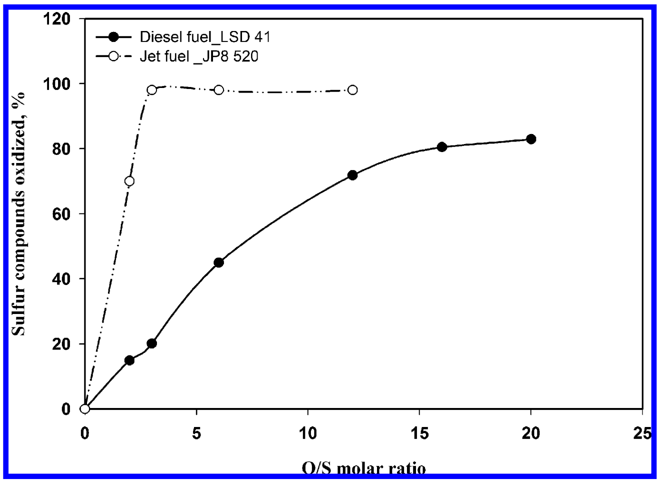

**Figure 7.** Oxidant (hydroperoxide) requirement for complete oxidation of sulfur compounds in JP-8-520 and LSD-41 (Reaction conditions: 5 g of fuel; oil/catalyst (w/w), 50; no air bubbling at 85 °C).

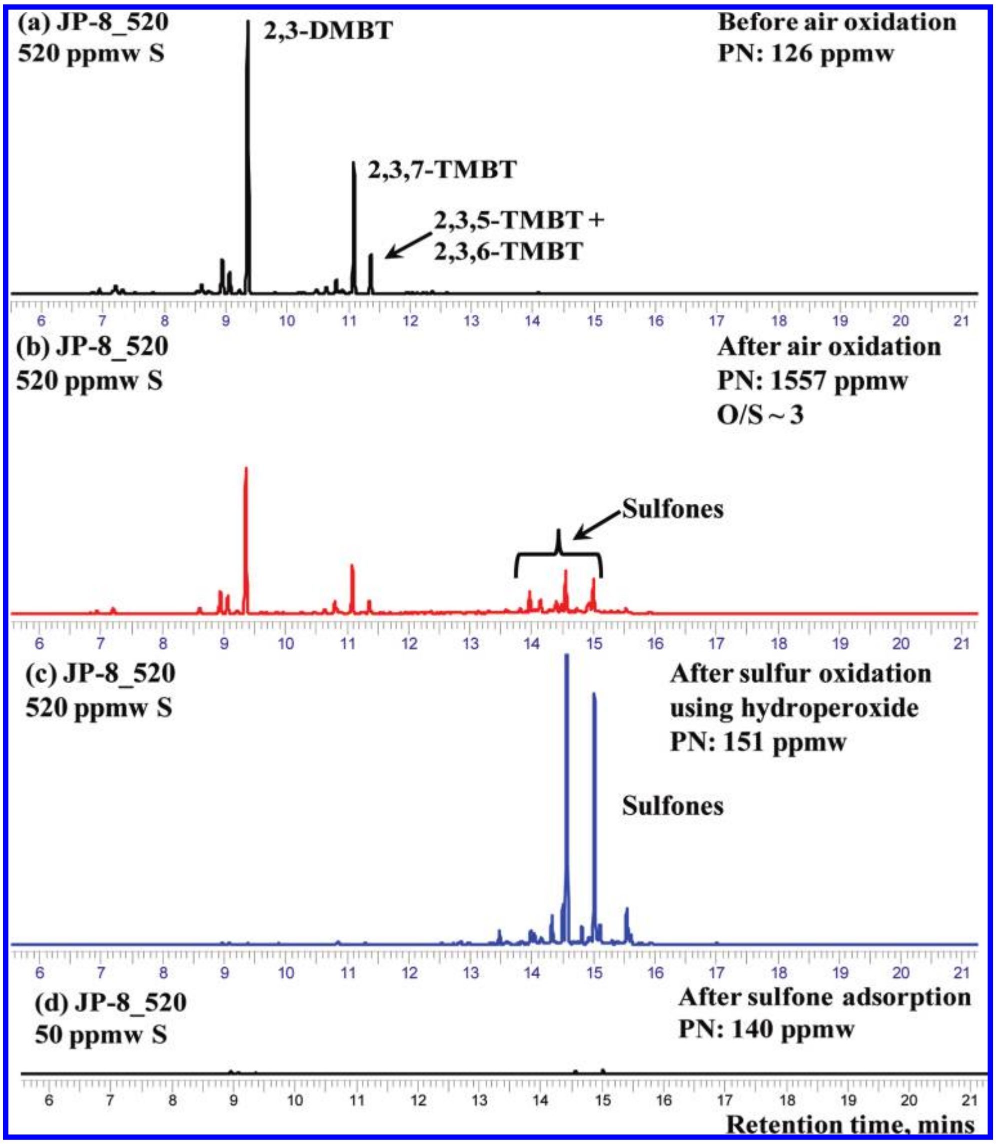

**Figure 8.** PFPD chromatogram of JP-8-520 jet fuel at different stages of oxidation and after adsorption. (a) JP-8-520 jet fuel, (b) after air oxidation to produce hydroperoxides in situ using the CuO catalyst (reaction conditions, see Figure 2), (c) after sulfur compound oxidation by hydroperoxides using $MoO_3/SiO_2$ catalyst (reaction conditions, see Figure 7) and (d) JP-8-520 after sulfone adsorption (reaction conditions, 4 g of fuel; oil/adsorbent (w/w), 5 at 85 °C for 60 min). PN, peroxide number. The sulfur concentration and peroxide number of the fuel during the different stages of the reaction are shown on the left top corner and right top corner of Figures parts a−d, respectively.

520 were partially consumed in oxidation of the sulfur compounds in JP-8-520, which will be further discussed later.

**3.4. Effect of Oxidant to Sulfur Molar Ratio [O/S] on Oxidation of Sulfur Compounds in JP-8-520 and LSD-41.** Theoretically to oxidize one mole of sulfur compound to their corresponding sulfone, two moles of hydroperoxide are required (reaction 7 in Figure 6). However, there might be other competitive compounds in the fuel for oxidation by hydroperoxides which can cause an increase in the oxidant consumption for real fuels. For example, it has been well documented that nitrogen compounds present in the fuel inhibit hydroperoxide-based oxidation, resulting in the formation of other lighter nitrogen compounds.[25] Therefore, to estimate the hydroperoxide required for oxidation of sulfur compounds in JP-8-520 and LSD-41, cumene hydroperoxide was used as a model oxidant in various amounts to oxidize the sulfur compounds present in the fuel. Also, it has been well documented in the literature that an impregnated $MoO_3$ based catalyst is an active catalyst for dibenzothiophenic compounds present in diesel fuel.[25,26] Therefore, the O/S molar requirement was estimated here using cumene hydroperoxide in the presence of $SiO_2$-supported $MoO_3$ catalyst. Oxidation of sulfur compounds in JP-8-520 and LSD-41 was carried out at different O/S molar ratios, and the results are shown in Figure 7. Sulfur compounds oxidized by cumene hydroperoxide were estimated by selective removal of the sulfones that were produced followed by analysis of total sulfur content in the fuel by using a total sulfur analyzer as described in the Experimental Section. To achieve complete oxidation of sulfur compounds in JP-8-520, only 3 (1.5 times the theoretical O/S requirement) mol of oxidant is required to convert 1 mol of sulfur compounds. However, for LSD-41, ~20 mols of oxidant is required per mole of S, which is 10 times the theoretical O/S requirement. The increased oxidant consumption might be due to the presence of nitrogen and polyaromatic compounds present in LSD-41 causing an increase in the oxidant requirement for LSD-41. Also, the influence of other aromatics and the type of sulfur compounds present in jet and diesel fuel might play a critical role in the desulfurization performance. Even though LSD-41 was more reactive toward forming peroxides, reactivity for oxidation of sulfur compounds was poor

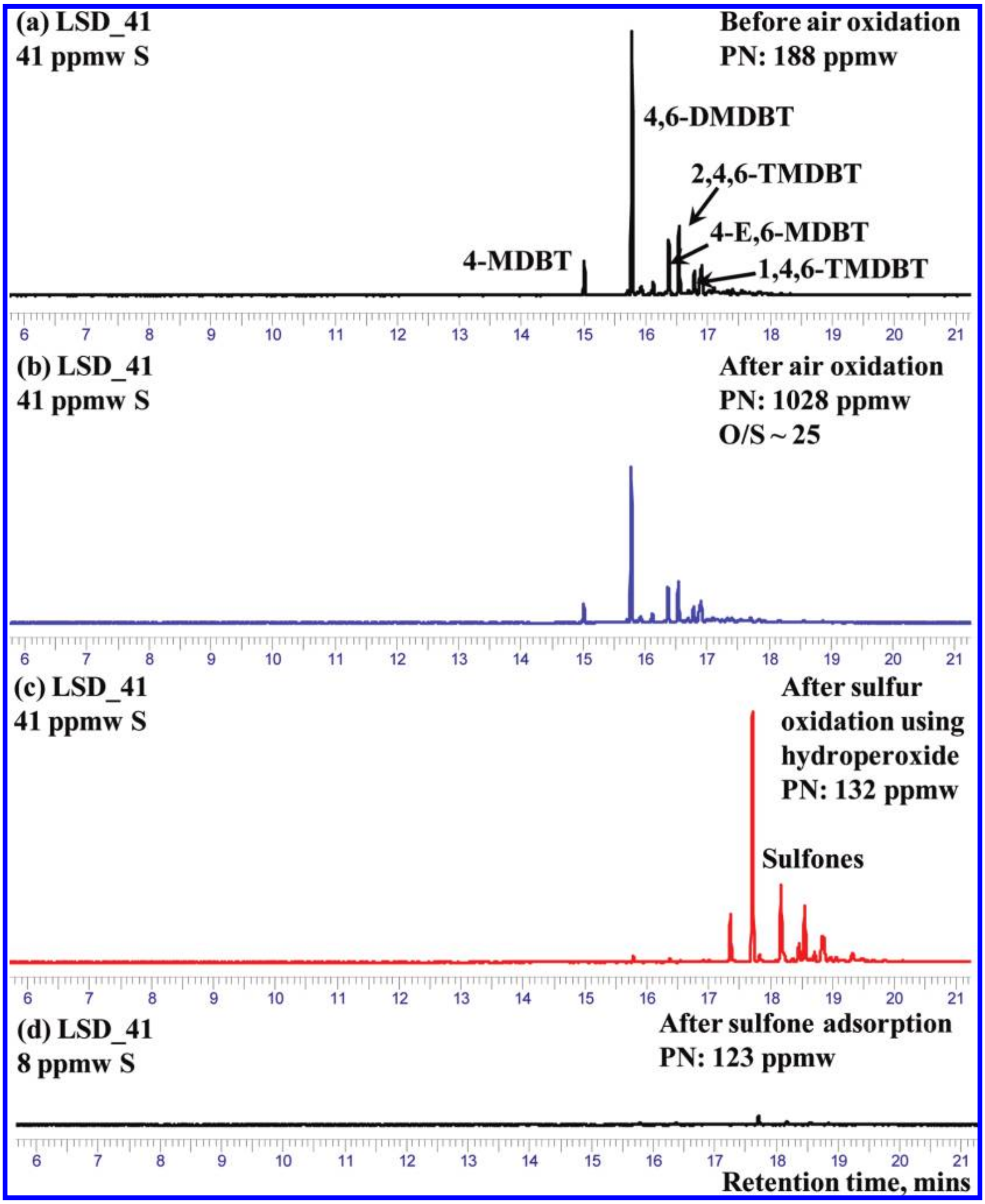

**Figure 9.** PFPD chromatogram of LSD-41 diesel fuel at different stages of oxidation and after adsorption. (a) LSD-41 diesel fuel, (b) after air oxidation to produce hydroperoxides in situ using CuO catalyst (reaction conditions, see Figure 2), (c) after sulfur compound oxidation by hydroperoxides using the $MoO_3/SiO_2$ catalyst (reaction conditions, see Figure 7), and (d) LSD-41 after sulfones adsorption (reaction conditions, 4 g of fuel; oil/adsorbent (w/w), 5 at 85 °C for 60 min). PN, peroxide number. The sulfur concentration and peroxide number of the fuel during the different stages of the reaction are shown on the left top corner and right top corner of parts a−d, respectively.

when compared to jet fuel as seen from Figure 7. It is also interesting to note that, even though the sulfur compounds present in JP-8-520 are benzothiophenic compounds, almost 98% of the sulfur compounds were oxidized at O/S = 3 but only 82% of the sulfur compounds in LSD-41 were oxidized at O/S = 20. This is interesting given the fact that typical dibenzothiophene-type sulfur compounds in diesel fuels have higher electron density on the S atom than benzothiophene-type compounds in jet fuel.[27] More investigation is necessary to elucidate this behavior.

**3.5. ODS of JP-8-520.** ODS of JP-8-520 was carried out by a two step oxidation coupled with adsorption as shown in Figure 1. JP-8-520 was air oxidized in the presence of CuO, and the peroxide number at the end of reaction was 1557 ppmw (peroxide number after 90 min of reaction in Figure 1). This represents the first stage of oxidation. Figure 8a shows that the sulfur compounds present in JP-8-520 are the substituted benzothiophenic compounds such as 2,3- dimethyl dibenzothiophene (2,3-DMBT) and 2,3,7-trimethyl dibenzothiophene (2,3,7-TMBT). Also from the PFPD chromatogram in Figure 8b, during air oxidation of JP-8-520 to produce hydroperoxides in situ, ~8% of organic sulfur compounds present in JP-8-520 were already converted to their corresponding sulfones. Conversion of organic sulfur compounds during this step was estimated by selectively adsorption of sulfones that were generated. This can be represented by reaction 5 in Figure 3. JP-8-520 containing in situ generated hydroperoxides (peroxide number, 1557 ppmw) was then used for selective oxidation of the rest of the sulfur

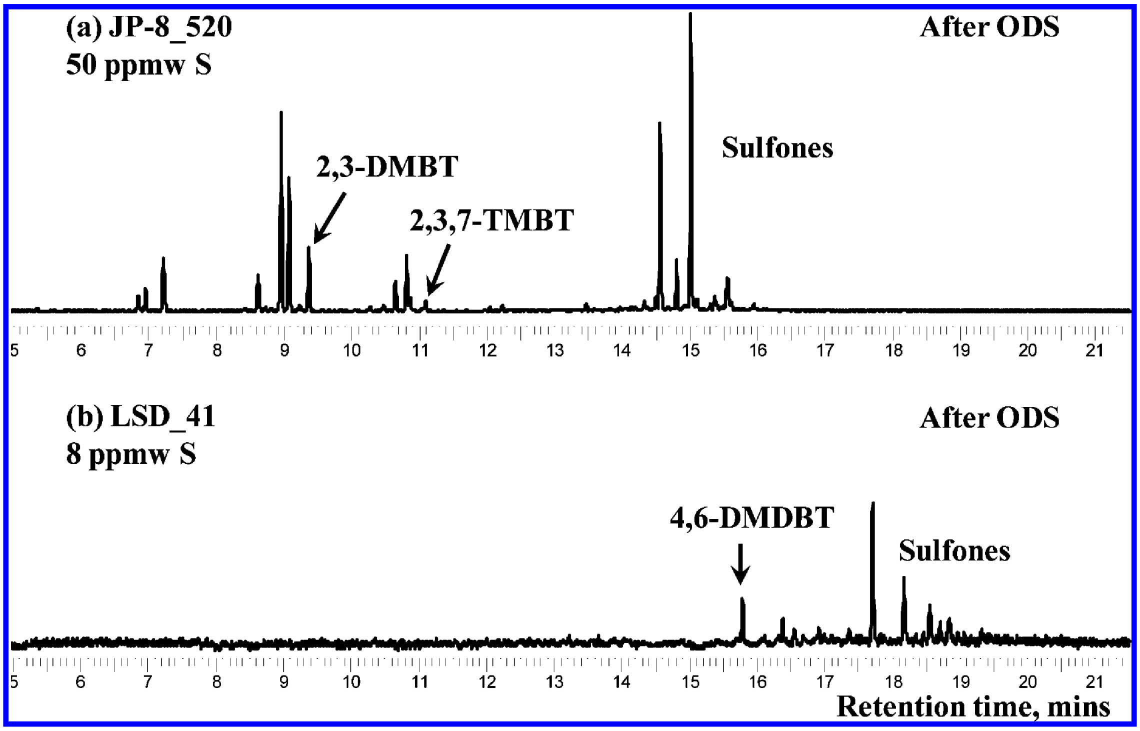

**Figure 10.** PFPD chromatogram of (a) JP-8-520 after ODS and (b) LSD-41 after ODS. (ODS, two step oxidation coupled with adsorption). Sulfur concentration in parts a and b represent the final sulfur concentration of the treated JP-8-520 and LSD-41, respectively.Parts a and d are the magnified versions of Figures 8d and 9d, respectively.

compounds present in the fuel in the presence of $SiO_2$-supported $MoO_3$ at 85 °C without air bubbling. At the end of the reaction, most of the sulfur compounds present in JP-8-520 were oxidized to their corresponding sulfones, which can be seen from the PFPD chromatogram (Figure 8c). This shows that the hydroperoxides which were generated in situ were effective in oxidizing the sulfur compounds that were present in JP-8-520. In the third step, the oxidized sulfur compounds contained in JP-8-520 were adsorbed using beta zeolite adsorbent at 85 °C and most of the sulfones produced by the two-step oxidation were removed by adsorption as shown in the PFPD chromatogram (Figure 8d). The total sulfur concentration of JP-8-520 after the two step oxidation procedure and adsorption was reduced to 50 ppmw S.

**3.6. ODS of LSD-41.** ODS of LSD-41 was carried out by a two step oxidation coupled with adsorption as shown in Figure 1. LSD-41 was air oxidized in the presence of unsupported CuO catalyst, and the peroxide number at the end of the reaction was 1028 ppmw (peroxide number after 15 min of reaction in Figure 1). As shown in Figure 9a, most of the sulfur compounds in LSD-41 are the substituted dibenzothiophenes, which have a very low relative reactivity when compared with benzothiophene and the thiophene type sulfur compounds for HDS. After the first step oxidation, we did not see any significant formation of oxidized sulfur compounds, which is in contrast to JP-8-520 (Figure 9b). Diesel containing 1028 ppmw of hydroperoxide was then treated in the presence of $SiO_2$-supported $MoO_3$ catalyst at 85 °C for 60 min. GC-PFPD analysis in Figure 9c revealed that most of the refractory sulfur compounds that were present in LSD-41 were converted to their corresponding sulfones. The sulfones present in LSD-41 were then removed by adsorption using a beta zeolite at 85 °C and the total sulfur concentration of LSD-41 was reduced to 8 ppmw S, and from Figure 9d, it can be seen that the adsorbent was effective in removing the sulfones in LSD-41.

**3.7. PFPD Analysis of Treated JP-8-520 and LSD-41.** JP-8-520 after ODS contained 50 ppmw S and gas chromatography-pulsed flame photometric detector (GC-PFPD) analysis revealed that most of the compounds that were left after adsorption were the sulfones. Also from the PFPD chromatogram in Figure 10a, it can be seen that substituted benzothiophenes, such as 2,3,5-trimethyl benzothiophene + 2,3,6-trimethyl benzothiophene, 2,3,7-trimethyl benzothiophene (2,3,5-TMBT + 2,3,6-TMBT, 2,3,7-TMBT), showed high activity for oxidation. The nonconverted sulfur compounds were mostly the nonhindered sulfur compounds that were present in JP-8-520. Thus, oxidation is very effective in removing the hindered sulfur compounds, such as 2,3,7-TMBT, which usually have a very low adsorption capacity with the Ni-based adsorbent, which effective in removing the nonhindered sulfur compounds present in jet fuel.[28]

Also from the GC-PFPD chromatogram in Figure 10b, the majority of the sulfur compounds are the oxidized sulfur compounds in LSD-41 after ODS. The total sulfur concentration of LSD-41 after ODS was 8 ppmw S, and the recalcitrant sulfur compounds were oxidized in high conversion. Oxidation was effective in converting both the substituted benzothiophene and dibenzothiophene compounds that were present in JP-8-520 and LSD-41, respectively.

## 4. Conclusions

In this work, oxidative desulfurization of a JP-8 jet fuel and a low sulfur diesel fuel was carried out effectively using air as an oxidant. Unsupported CuO catalyst showed substantial activity for liquid phase oxidation of the fuels to form hydroperoxides in situ in the presence of air. It was observed that the concentration of the hydroperoxide during oxidation of JP-8 jet fuel decreases in the order of 120 °C > 140 °C ≫ 100 °C but the oxidation rate for formation of hydroperoxides decreases in the order of 140 °C > 120 °C ≫ 100 °C. The hydroperoxides generated in situ were effective in oxidizing the alkyl substituted benzothiophene and dibenzothiophene present in jet and diesel fuels, respectively, to their corresponding sulfones which were then removed by adsorption on a beta zeolite. This study demonstrates an effective way of carrying out oxidative desulfurization using air, thus eliminating the need for use, storage, and handling of liquid peroxide oxidants or other sacrificial agents reported in prior literature. Also, by development and a single catalyst tailored which can perform all of the three steps, viz, air oxidation to form hydroperoxides, oxidation of sulfur compounds using in situ generated hydroperoxides, and adsorption of sulfones in the ODS process discussed, can further simplify the process from a three stage ODS process based on air and can pave the way for a single stage ODS process using air as an oxidant for producing ultralow sulfur fuels.

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