

Oxidative Desulfurization of Straight-Run Diesel Fraction

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Abstract—Oxidative desulfurization of straight-run nonhydrotreated diesel fraction with hydrogen peroxide in the presence of Na₂MoO₄ or Na₂WO₄, dibenzyl peroxide, and potassium permanganate; by air bubbling; and in the presence of ionic liquids has been studied. The oxidation products have been recovered from the oxidized diesel fraction using alumina, silica gel, or activated charcoal or via extraction with acetonitrile, *N,N*-dimethylformamide, or acetone. The best results of the diesel desulfurization have been achieved in the case of dibenzyl peroxide as an oxidizing agent in the presence of Na₂MoO₄.

Keywords: oxidative desulfurization, hydrogen peroxide, diesel fraction, adsorbent, extraction

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An increasing demand for various types of motor fuels and toughening of their quality requirements makes the improvement of the existing desulfurization processes and development of new process solutions increasingly important. An alternative to hydrotreating, which does not always allow completely removing condensed sulfur-containing derivatives of benzothio- phene and dibenzothio- phene, can be various hydro- gen-free desulfurization methods, of which oxidative processes performed under much milder conditions in comparison with hydrotreating appear to be the most promising [1–4]. The use of such methods, especially in combination with adsorption and extraction techniques for the removal of oxidized sulfur compounds from the hydrocarbon fraction [5, 6], can have a per- spective in the cases when the use of hydrogenation processes is impossible due to the process and eco- nomic reasons. In many cases, the application of oxi- dative methods to the desulfurization of various petro- leum fractions, crude petroleum, and mixtures mod- eling them offers a possibility to substantially decrease the total sulfur content in the hydrocarbon feedstock. For this, both methods of direct action of various oxi- dizing agents on petroleum fractions and an increase in the efficiency of their action with the use of organic acids, transition metal complexes, and other sub- stances and reagents were used [7, 8]. In this work, the oxidative desulfurization of a straight run nonhydro- treated diesel fraction under different conditions was studied in order to find the most suitable oxidizing sys- tems which would have made it possible to perform the preliminary decrease in the sulfur content in the frac- tion, which is important for decreasing the expendi-

tures during the more energy-intensive hydrotreating step.

EXPERIMENTAL

The object of study was the straight-run nonhydro- treated diesel fraction (DF) from the Ryazan refinery with a total sulfur content of 10190 ppm. The required chemicals, hydrogen peroxide (Prime Chemicals Group), Na₂MoO₄ · 2H₂O, Na₂WO₄ · 2H₂O (Aldrich Chemical), ionic liquids 1-butyl-3-methylimidaz- o- lium tetrafluoroborate and 1-butyl-3-methylimidaz- o- lium hexafluorophosphate, dibenzyl peroxide, SiO₂ of the ASKG brand (activated granular coarse-pore silica gel), Al₂O₃, KMnO₄, and extracting agents *N,N*- dimethylformamide (reagent grade) and acetonitrile (reagent grade) were purchased from commercial sources. The sulfur content in the samples before and after desulfurization was determined on an ASE-2 X-ray energy dispersive sulfur analyzer (NPP Burevestnik) with a relative error of no more than 5%; the concentration detection range was 50 to 50000 ppm.

The gas chromatographic–mass spectrometric (GC–MS) analysis of the initial and desulfurized die- sel fractions was performed on a Thermo Focus DSQ II instrument (a VF-5ms capillary column (Varian) with a length of 15 m, an internal diameter of 0.25 mm, and a film thickness of 0.25 μm; the carrier gas was helium; the operating mode was as follows: the injector tem- perature of 300°C and initial column oven tempera- ture of 45°C followed by isothermal holding for

20 min; the mass spectrometer was operated at an ionization energy of 70 eV, an ion source temperature of 250°C, and a scanning rate of 1.5 scan/s in the range of 10–800 Da with unit resolution throughout the mass range). Reference mass spectra presented in a NIST/EPA/NIH 14 database were used for the identification of the components.

Oxidative Desulfurization with Hydrogen Peroxide in the Presence of Metal Compounds

The oxidative desulfurization of the diesel fraction was performed in a thermostated reactor equipped with a magnetic stirrer and a reflux condenser. The oxidizing mixture was prepared by adding a weighed amount of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ or $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ to a calculated amount of 50% H_2O_2 at reactants molar ratios of metal : sulfur = 1 : 100 and H_2O_2 : sulfur = 4 : 1. A calculated amount of the oxidizing catalytic system was added to 20 mL of the diesel fraction and stirred at 40–60°C for 6 h. The reaction mixture containing the oxidized diesel fraction was first washed with water (6 mL \times 2) to remove the oxidizing system and then treated with an adsorbent (2 g \times 9 mL of fuel) or an extracting agent (9 \times 9 mL of fuel); after the extraction, it was washed with water (6 mL \times 1) to remove the residual extractant, dried, and analyzed for total sulfur.

Oxidative Desulfurization in the Presence of Ionic Liquids

A 0.25-g portion of an ionic liquid was added to 20 mL of the diesel fraction, the mixture was heated up to 40°C, 0.02 g of Na_2MoO_4 in the form of an aqueous solution and 0.02 mL of 37% H_2O_2 were added under stirring, and then the mixture was stirred while keeping the set temperature for 6 h. Upon the completion of the oxidation, 5 mL of water was added to the mixture and it was washed with water (6 mL \times 2) to remove the oxidizing system; the organic phase was separated from the aqueous phase, treated with an extracting agent (10 \times 20 mL of the fuel), dried over anhydrous CaCl_2 , and analyzed for total sulfur.

Oxidative Desulfurization with Dibenzyl Peroxide in the Presence of Na_2MoO_4

The process was carried out at 60°C for 6 h in the presence of Na_2MoO_4 similarly to the oxidation by the action of H_2O_2 at the ratios of metal : sulfur = 1 : 100 and dibenzyl peroxide : sulfur = 2 : 1.

Oxidative Desulfurization in the Presence of Potassium Permanganate

The diesel fraction in an amount of 20 mL and a calculated amount of the oxidizing system at the stoi-

chiometric ratio of KMnO_4 : sulfur = 3 : 1 and four drops of a cocatalyst (sulfuric or phosphoric acid) were added to a reactor equipped with a magnetic stirrer. The mixture was stirred for 6 h at room temperature. Then, the mixture was allowed to stay for 15 min until a clear interphase boundary appeared. The upper phase containing the oxidized fuel was washed with water (5 mL \times 2); a half of the sample was passed through a glass column filled with 2 g of ASKG silica gel, and the second half was extracted with acetone (9 \times 9 mL of fuel). The obtained purified fuel was analyzed for total sulfur.

Oxidative Desulfurization by Air Bubbling

An aqueous solution of 0.02 g of Na_2MoO_4 was added to 20 mL of the diesel fraction, and an atmospheric air flow was passed then at a flow rate of 300 mL/min through the mixture for 6 h. Upon the completion of bubbling, the diesel fraction was washed with water, treated with an adsorbent or an extracting agent, dried over anhydrous CaCl_2 , and analyzed for total sulfur.

RESULTS AND DISCUSSION

The preliminary assessment of the efficiency of the adsorbents and extractants in the recovery of sulfur compounds from a hydrocarbon mixture was performed using the unoxidized nonhydrotreated diesel fraction (Table 1). The choice of the adsorbents was determined by the purpose to reveal finding the effect of their surface properties on the adsorption capacity for the oxidation products of diesel sulfur compounds.

The results obtained show that silica gel possesses better adsorption properties regarding the degree of removal of unoxidized sulfur compounds from the diesel fraction in comparison with the other adsorbents, while the acidity of alumina has almost no effect on the degree of recovery of unoxidized sulfur compounds. Of the extracting agents used for the same purpose, *N,N*-dimethylformamide and acetone showed the best results according to the presented data on the extraction of unoxidized sulfur compounds. It is DMF and acetone that were further used for the removal of the oxidized forms of sulfur compounds from the diesel fraction subjected to the oxidative treatment.

The oxidation of the diesel fraction was performed with various oxidizing agents, first of all, hydrogen peroxide, in a two-phase system using sodium molybdate or tungstate in the presence of tetrabutylammonium chloride (TBAC) as the surfactant. Earlier, this approach turned out to be productive for decreasing the sulfur content in various petroleum fractions and model mixtures [9]. The oxidized sulfur compounds were removed from the hydrocarbon mixture using ASKG silica gel or extractants that demonstrated high

Table 1. Efficiency of adsorbents and extractants in the recovery of sulfur compounds from the unoxidized diesel fraction (20°C, total sulfur content of 10190 ppm, 6 h)

Total sulfur content in unoxidized diesel fraction after recovery of sulfur compounds, ppm								
adsorbents						extracting agents		
ASKG silica gel	Al ₂ O ₃ neutral	Al ₂ O ₃ acidic	Al ₂ O ₃ basic	activated charcoal	sulfonated charcoal	<i>N,N</i> -DMF	acetonitrile	acetone
8575	10080	10060	9970	9920	10160	8450	9530	8850

Table 2. Oxidative desulfurization of the diesel fraction at different temperatures (H₂O₂ : S = 4 : 1, Me : S = 1 : 100, TBAC, 6 h, the initial sulfur content is 10190 ppm)

Temperature, °C	Metal compound	Total sulfur content, ppm			
		<i>N,N</i> -dimethylformamide	acetone	silica gel	Al ₂ O ₃ acidic
40	Na ₂ MoO ₄	8840	8450	7620	9120
	Na ₂ WO ₄	6580	9320	7640	9130
60	Na ₂ MoO ₄	6300	4170	5680	8010
	Na ₂ WO ₄	7280	6400	7450	8450

efficiency in the removal of unoxidized sulfur compounds, namely, *N,N*-dimethylformamide and acetone.

It is seen from the data presented in Table 2 that up to 35% sulfur compounds was removed from the diesel fraction oxidized at 40°C (W : S = 1 : 100) in the case of extraction with DMF. Among the adsorbents, the best results were shown by silica gel, and the degree of sulfur removal was almost the same in the presence of sodium molybdate or tungstate, not exceeding 25%.

The degree of oxidation of sulfur compounds including oxidation-resistant dibenzothiophene derivatives increases with an increase in the oxidation temperature to 60°C [10]; however, the further increase in temperature does not lead to improvement in the desulfurization parameters [11], the lack of progress being due to the growth in the contribution of the hydrogen peroxide decomposition process. As is seen from Table 2, the best result in the desulfurization of the diesel fraction oxidized at 60°C with hydrogen peroxide in the presence of sodium molybdate was achieved in the case of further extraction of the oxidized products with acetone. As a result of the purification, it turned out to be possible to recover 60% total sulfur, whereas the degree of sulfur removal was as low as 44% in the case of the purification of the same sample with silica gel. Comparing the data on the recovery of sulfur compounds from the unoxidized and oxidized diesel fractions (Tables 1 and 2) shows that of the adsorbents used, silica gel provides high results in both cases, the highest degree of recovery of sulfur com-

pounds by extraction after the oxidation is achieved in the case of the use of *N,N*-dimethylformamide and acetone. A higher degree of recovery of sulfur compounds from the hydrocarbon fraction with silica gel in comparison with other adsorbents can be explained by the joint action of its surface hydroxyl and silanol groups, of which the latter are absent from the alumina surface [12]. The difference in the yields by extraction with DMF or acetone at 40 and 60°C can be explained by the fact that the oxidation at 40°C does not proceed as deep as at 60°C and oxidized sulfur compounds, rather than all of them, are mainly extracted. At 60°C, the oxidation is more intense and acetone as a more polar solvent extracts a larger amount of sulfur compounds.

According to the GC–MS data for the unoxidized diesel fraction and that oxidized in the presence of Na₂MoO₄ with the subsequent removal of the oxidized products with silica gel or acetone, the concentration of benzothiophene and dibenzothiophene in the oxidized diesel fraction is slightly lower (by ~20 rel %) than in the initial unoxidized sample and the concentration of methyl- and dimethyldibenzothiophenes remains almost unchanged. This finding is the evidence that benzothiophene and dibenzothiophenes can be oxidized under the conditions of the desulfurization process.

To evaluate the performance of different oxidizing agents in the liquid-phase desulfurization of the diesel fraction, dibenzyl peroxide, potassium permanganate, and bubbled atmospheric air were used along with

Table 3. Comparative efficiency of different oxidizing agents in the desulfurization of the diesel fraction (initial sulfur content is 10190 ppm)

No.	Oxidant, process conditions	Sulfur in purified fraction, ppm
1	H ₂ O ₂ , Na ₂ MoO ₄ , 40°C, acetone, 6 h	4170
2	KMnO ₄ , H ₃ PO ₄ , 40°C, acetone, 6 h	7920
3	KMnO ₄ , H ₂ SO ₄ , 40°C, acetone, 6 h	7140
4	Dibenzyl peroxide, 40°C, Na ₂ MoO ₄ , acetone, 6 h	5150
5	Air, Na ₂ MoO ₄ , 40°C, acetone, 6 h	7990
6	Air, Na ₂ MoO ₄ , 40°C, silica gel, 6 h	7320

Table 4. Comparative efficiency of different ionic liquids (ILs) in the desulfurization of the diesel fraction (Mo or W : sulfur = 1 : 100, initial sulfur content is 10190 ppm, 60°C, 6 h)

IL (metal compound)	Total sulfur in purified fraction, ppm		
	<i>N,N</i> -dimethylformamide	acetone	silica gel
1-Butyl-3-methylimidazolium tetrafluoroborate (Na ₂ MoO ₄)	5780	7470	4780
1-Butyl-3-methylimidazolium hexafluorophosphate (Na ₂ MoO ₄)	4700	6450	4020
1-Butyl-3-methylimidazolium tetrafluoroborate (Na ₂ WO ₄)	5230	7660	5710
1-Butyl-3-methylimidazolium hexafluorophosphate (Na ₂ WO ₄)	5640	7350	6130

hydrogen peroxide (Table 3). The experiments performed under comparable conditions involving the extraction of the oxidation products with acetone showed that hydrogen peroxide in the presence of sodium molybdate was the best oxidizing agent; dibenzyl peroxide was just a little inferior to hydrogen peroxide in the desulfurizing activity.

The earlier studies by different research groups on the oxidative desulfurization of model mixtures of different compositions in the presence of various ionic liquids (ILs) showed that the ILs can enhance the process, functioning as surfactants and selective solvents for the oxidized forms of sulfur compounds [1, 13, 14]. In this study, we performed desulfurization in the presence of ionic liquids, which can act as a surfactant and an extractant in this process as well, and showed that their presence gives no significant advantages (see Table 4).

Thus, the oxidative desulfurization of a nonhydro-treated diesel fraction with hydrogen peroxide is the most efficient in the presence of sodium molybdate with the subsequent recovery of the oxidation prod-

ucts of sulfur compounds with silica gel and extractants, such as acetone and *N,N*-dimethylformamide. The use of the adsorption purification of the diesel fraction after the oxidation makes it possible to decrease the total sulfur content in it by 44%. The combination of the oxidation of the nonhydro-treated diesel fraction with hydrogen peroxide with the subsequent extractive removal of the oxidized products results in the removal of up to 60% total sulfur. Silica gel, among the adsorbents, and acetone, among the extracting agents, provide a higher degree of desulfurization in comparison with other adsorbents and extracting agents.

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