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Peroxide Oxidative Desulfurization of a Mixture of Nonhydrotreated Vacuum Gas Oil and Diesel Fraction

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Abstract—Oxidative desulfurization of a model mixture on the basis of vacuum gas oil and diesel fuel by hydrogen peroxide in the presence of formic acid has been studied. A technology of a two-phase system with a phase-transfer catalyst has been employed for the desulfurization. The optimum reaction time is 6 h and the hydrogen peroxide : sulfur molar ratio is 4 : 1. As a result of successive triple oxidative desulfurization, 90% of total sulfur is removed from the model mixture.

Keywords: vacuum gas oil, diesel fraction, oxidative desulfurization

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Disposal of high-sulfur heavy petroleum fractions and their processing into quality motor fuels is one of the most important problems in petroleum refining [1–3]. The leading role in solving this problem is assigned to catalytic hydrogenation processes, which are characterized by high quality of the resulting products but require severe conditions, sophisticated equipment, and availability of cheap hydrogen sources for conducting the process [4].

The processing of high-boiling petroleum fractions by catalytic cracking is characterized by catalyst deactivation due to their high carbon residue value [3]. This value is associated with the presence of polycyclic sulfur compounds, such as benzothiophene, dibenzothiophene, and naphthothiophene derivatives, in these fractions [3]. Preprocessing, in particular, peroxide oxidative desulfurization of high-sulfur heavy petroleum fractions [5–8], can promote the enhancement of the yield and quality of the products of catalytic cracking.

The aim of this work is to develop conditions for the desulfurization of a model mixture based on nonhydrotreated vacuum gas oil (NHT VGO) (30 wt %) and Euro-5 diesel fuel (70 wt %). The model mixture was taken for the purpose of decreasing the feedstock viscosity for convenience of operation at room temperature and for improving the process of extraction of oxidized sulfur compounds with dimethylformamide (DMF) [9].

EXPERIMENTAL

A 50% hydrogen peroxide solution, *N,N*-dimethylformamide, and 88% formic acid were used in the study. The model mixture was prepared by mixing nonhydrotreated vacuum gas oil from TAIF-NK and commercial diesel fuel of the Euro-5 standard from a Lukoil filling station with the sulfur content below 10 ppm. Main physicochemical parameters of the vacuum gas oil and the Euro-5 diesel are presented in Table 1.

The sulfur content in the samples before and after desulfurization was measured on a Spektoskan S X-ray fluorescence energy-dispersive analyzer for determining sulfur in petroleum and petroleum products; the range of measured concentrations (two subranges) was from 7 to 1000 ppm and from 1000 to 50000 ppm, the limit of detection over 100 s was 5 ppm.

Desulfurization in this study was performed using the method of phase-transfer catalysis at 50–60°C with a 50% hydrogen peroxide aqueous solution in the presence of a phase-transfer catalyst. The model mixture with formic acid was desulfurized using a 50% aqueous solution of hydrogen peroxide at 60°C and constant stirring. A 20-g portion of the model mixture with total sulfur content of 6300 ppm was placed into a reactor, and 0.184 g (4 mmol) of formic acid and 0.272 g (4 mmol) of 50% hydrogen peroxide were successively added with continuous stirring. After completion of the reaction, the hydrocarbon phase was washed with water (3 × 10 mL) or DMF (3 × 10 mL) to remove oxidized sulfur compounds. In the case of

Table 1. Physicochemical parameters of vacuum gas oil and diesel fuel

Parameter	Vacuum gas oil	Euro-5 diesel fuel
1. Fractional composition, distilled at a temperature of, °C		
—IBP	333	200
—10%	380	250
—38%	437	355
—50%	535	96
—FBP	0.9	
—to 350°C, vol %	2.9	
— to 360°C, vol %		
2. Mass fraction of sulfur, ppm	21000	9
3. Density at 20°C, kg/m^3	910.0	823.2
4. Carbon residue, %	0.16	0.02

multistep oxidative desulfurization, this procedure was repeated several times, after which the hydrocarbon phase was analyzed for total sulfur.

RESULTS AND DISCUSSION

The results of the oxidative desulfurization of the model mixture having the total sulfur content of 6300 ppm (solution of 30 wt % nonhydrotreated vacuum gas oil) with 50% hydrogen peroxide and formic acid are presented in the figure.

In the study, the effect of various parameters in the process of oxidative desulfurization of the NHT VGO and diesel mixture on the decrease in the total sulfur content in it was examined. The use of DMF for extraction makes it possible to extract up to 40% sulfur compounds, while the extraction with water is inefficient because of the low solubility of the oxidation products (dibenzothiophene sulfones and naphthothiophene sulfones); the degree of desulfurization did not exceed 3% in the case of its use. The optimum reaction time is 6 h.

An increase in the hydrogen peroxide : total sulfur molar ratio to 4 : 1 in combination with the extraction method for the recovery of oxidation products makes it possible to achieve more complete desulfurization of the model mixture, reaching the degree of desulfurization of 74%, which may be associated with the involvement in the oxidation process of sulfur compounds with a higher molecular mass as compared to benzothiophenes and dibenzothiophenes (Table 2).

To increase the cleaning efficiency, stepwise oxidative desulfurization was performed: the fuel treated at the first step was subjected to repeated cleaning under the same conditions (amounts of hydrogen peroxide and formic acid were taken as calculated for the total sulfur content in the fraction purified at the first step) and the third cleaning step was performed in a similar

Table 2. Effect of the amount of hydrogen peroxide on the oxidative desulfurization of the model mixture (30% NHT VGO in Euro diesel; total sulfur content, 6300 ppm)

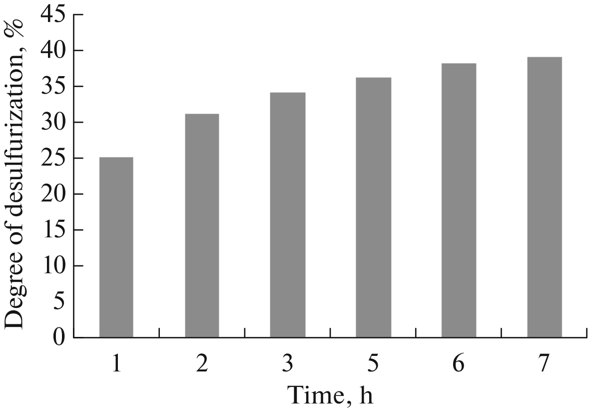
S : H_2O_2	Residual S content, ppm	Degree of desulfurization,%
1 : 1	2830	55
1 : 2	2010	68
1 : 3	1830	71
1 : 4	1640	74

Reaction conditions: 60°C, 6 h; molar ratio S : HCOOH = 1 : 1; extractant, DMF.

Table 3. Stepwise oxidative desulfurization of the model mixture (30% NHT VGO in Euro diesel; total sulfur content, 6300 ppm)

Step no.	Initial S content of feed mixture, ppm	Residual S content, ppm	Total degree of desulfurization, %
1	6300	1790	72
2	1790	860	86
3	860	620	90

Reaction conditions: 60°C, 6 h; molar ratio H_2O_2 : S : HCOOH = 4 : 1 : 1; extractant, DMF.



The effect of time on the oxidative desulfurization of the model mixture (30% nonhydrotreated VGO in Euro diesel)at 50°C, an S : HCOOH molar ratio of 1 : 1, and sulfur content in the initial model mixture of 6300 ppm.

manner. As a result of the three-step purification, we managed to remove 90% total sulfur (Table 3).

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