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Deep Purification of Vacuum Gas Oil by the Method of Oxidative Desulfurization

A. V. Akopyan[a], *, D. A. Plotnikov[a], P. D. Polikarpova[a], A. A. Kedalo[a], S. V. Egazar'yants[a], A. V. Anisimov[a], and E. A. Karakhanov[a]

[a] *Faculty of Chemistry, Moscow State University, Moscow, 119991 Russia*
**e-mail: arvchem@yandex.ru*

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Abstract—The possibility of using of the catalytic system based on formic acid and a transition metal salt in the presence of hydrogen peroxide for desulfurization of nonhydrotreated vacuum gas oil has been explored. Conditions for effective oxidation of organic sulfur compounds and maximal extraction of oxidized compounds from the feedstock have been selected. It has been shown that the catalysts based on tungsten salts are the most effective those for oxidative desulfurization of heavy feedstock. Under optimum conditions, the degree of desulfurization of vacuum gas oil was 89%.

Keywords: oxidative desulfurization, hydrogen peroxide, vacuum gas oil, extraction

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In the modern world, requirement to the quality of refinery feedstock are being permanently toughened and environmental standards are imposed on produced fuels [1, 2]; at the same time, the concentration of organic sulfur compounds in recovered organic minerals permanently increases, thereby leading to worsening their quality. To decrease the emission of sulfur oxides due to combustion of sulfur compounds into the atmosphere and neutralize the poisoning effect of sulfur on catalysts of refinery processes, it is necessary to remove sulfur compounds from hydrocarbon feedstock [3, 4]. In this connection, the desulfurization of both light and heavy petroleum fractions is a demanding problem.

Currently, there are a number of processes for the removal of sulfur compounds from heavy fractions: hydrotreating, biodesulfurization, extraction methods, aquathermolysis, and oxidative desulfurization [5–9]. One of the most widespread processes is catalytic hydrotreating when sulfur compounds are destroyed to form hydrogen sulfide and a hydrocarbon portion that is retained in target liquid products [10, 11]. The use of hydrotreating to desulfurize heavy petroleum fractions requires high hydrogen consumption and severe conditions, leading to rise in the process cost [12]. Alternative available methods to remove organic sulfur compounds are oxidative desulfurization, adsorption, extraction, and biodesulfurization [6, 13, 14].

The most effective process for hydrogen-free desulfurization of heavy petroleum fractions includes oxidation of sulfur compounds followed by their removal by extraction or adsorption methods [5, 15]. Hydrogen peroxide is most often used as an oxidant because it is environmentally friendly [16]. salts of transition metals, such as molybdenum and tungsten, proved to be effective catalysts for oxidative desulfurization, because in the presence of hydrogen peroxide they are capable of producing peroxo complexes active in oxidation of sulfur compounds [17, 18].

EXPERIMENTAL

The materials used were vacuum gas oil (VGO), manufactured by the Moscow refinery, as the feedstock with total sulfur content of 14800 ppm and the following chemicals: $(NH_4)_2MoO_4$ (analytical grade, Prime Chemicals Group), hydrogen peroxide (37%, Prime Chemicals Group), $(NH_4)_2WO_4$ (analytical grade, Prime Chemicals Group), $VOSO_4$ (analytical grade, Prime Chemicals Group), concentrated formic acid of a 1.22 g/cm^3 density (reagent grade), acetone (chemically pure grade, Komponent-Reaktiv), Neonol AF 9–6 (Nizhnekamskneftekhim), tetrabutylammonium bromide (TBAB, Sigma Aldrich), dimethylformamide (reagent grade, Komponent-Reaktiv), acetonitrile (reagent grade, Komponent-Reaktiv), *N*-methylpyrrolidone (reagent grade, Komponent-Reaktiv), and distilled water (GOST 6709).

Total sulfur in hydrocarbon fractions was determined using a Spectroscan SL X-ray fluorescence sulfur analyzer with a relative error of 3% in the range of detectable concentrations from 7 to 5000 ppm according to ASTM D4294-10 [19]. The principle of operation of the instrument is based on the method of energy dispersive analysis, which is a reference method for determining the

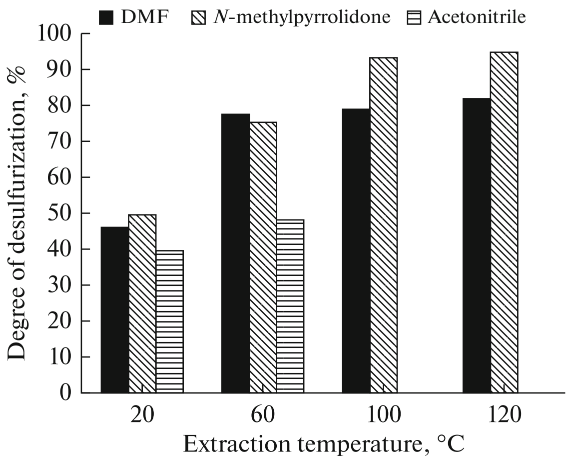

Fig. 1. Effects of extractant nature and extraction temperature on the degree of desulfurization of vacuum gas oil. Conditions: H_2O_2 : S = 20 : 1; HCOOH : S = 10 : 1 (by mole); total 6 h, including: 1 h at 40°C, 5 h at 60°C.

mass fraction of sulfur in diesel fuel and is acceptable for determining the same in unleaded gasoline.

Preparation of Catalytic Mixture

A transition metal salt ($(NH_4)_2MoO_4$, $(NH_4)_2WO_4$, or $VOSO_4$) (0.0018 mol) was dissolved in distilled water (1.3 mL), the solution was stirred for 5 min, formic acid (6.5 mL) was added, and the mixture was stirred for another 3 min. Then 0.2 g of Neonol AF 9-6 and 0.1 g of TBAB were added and stirring was continued for 20 min.

Desulfurization of Vacuum Gas Oil

A reactor equipped with a magnetic stirrer was charged with 20 mL of vacuum gas oil and the necessary amount of 37% hydrogen peroxide solution and the catalytic mixture were added to have the H_2O_2 : S molar ratio from 2 : 1 to 10 : 1 and the HCOOH : S molar ratio of 1 : 1 or 10 : 1. The reaction was carried out at 40–80°C for 2–12 h. After completion of oxidation, the reaction mixture was washed with 20 mL of distilled water to remove residues of the oxidizing system. Then oxidized vacuum gas oil was extracted with 20 mL of a polar solvent (dimethylformamide, *N*-methylpyrrolidone, acetonitrile) at 20–120°C. The gas oil freed of sulfur compounds was analyzed for the sulfur content.

RESULTS AND DISCUSSION

Nonhydrotreated vacuum gas oil with the initial sulfur content of 14800 ppm was used as the object of investigation.

Because vacuum gas oil is heavy feedstock and contains a great deal of aromatic compounds hindering the adsorption process, oxidized sulfur compounds were removed by extraction with a polar solvent. As extractants of oxidized sulfur compounds, diethylene glycol, ethanol, dimethylformamide, acetonitrile, *N*-methylpyrrolidone, and furfural are mostly frequently used [20]. Since heavy petroleum fractions have high viscosity at room temperature and it is necessary to carry out the extraction at an increased temperature, extractants with high boiling point were selected: DMFA (153°C), *N*-methylpyrrolidone (202°C), and acetonitrile (82°C).

Effects of Extractant Nature and Extraction Temperature

The effects of the extractant nature and extraction temperature on the degree of desulfurization were studied using the sample of vacuum gas oil oxidized in an excess of the catalytic oxidizing system. In ensure the full completion of the reaction, oxidation was carried out at a high excess of hydrogen peroxide and formic acid using stepwise heating (1 h at 40°C and 5 h at 60°C). The results are shown in Fig. 1.

As seen from Fig. 1, the maximal removal of sulfur compounds was attained at an extraction temperature of 120°C. The best results in extraction were obtained with *N*-methylpyrrolidone. In this connection, *N*-methylpyrrolidone was taken as the extractant in further experiments.

Effects of Transition Metal Nature and Reaction Temperature

The oxidation reaction of organic sulfur compounds of vacuum gas oil with hydrogen peroxide occurs at the interface between the aqueous and hydrocarbon phases, thereby creating diffusion limitations on the reaction. A phase-transfer agent is added to the reaction mixture to reduce diffusion limitations, and a surfactant is introduced to improve emulsification of the aqueous phase. In this work, Neonol AF 9-6 and tetraethylammonium bromide were used as the surfactant and the phase-transfer agent, respectively. It is known that an acid medium promotes oxidation of sulfur compounds [14]; therefore, formic acid was selected for the purpose as it had been successfully used in oxidation of light petroleum fractions [13].

The effect of temperature on the degree of VGO desulfurization was investigated using as a catalyst transition metal salts that are capable of producing peroxo complexes in the presence of hydrogen peroxide (molybdenum, tungsten, vanadium). The temperature was varied in the range of 40–80°C, with programmed heating (oxidation for 1 h at 40°C, then heating up to preset temperature) being used. The use of gradual heating of the reaction mixture is due to fact that hydrogen peroxide can decompose at a high temperature. At 40°C, oxidation of light sulfur compounds occurs and hydrogen peroxide is partially consumed; the further temperature rise promotes the oxidation of hardly oxidizable organic sulfur compounds. It is evident from results given in Fig. 2 that the most effective catalyst is

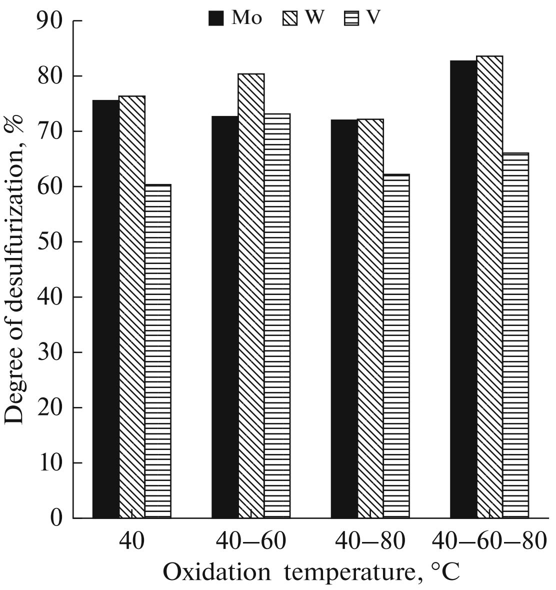

Fig. 2. Effect of transition metal nature and reaction temperature on the degree of desulfurization of vacuum gas oil. Conditions: H_2O_2 : S = 4 : 1; HCOOH : S = 1 : 1 (by mole), 6 h.

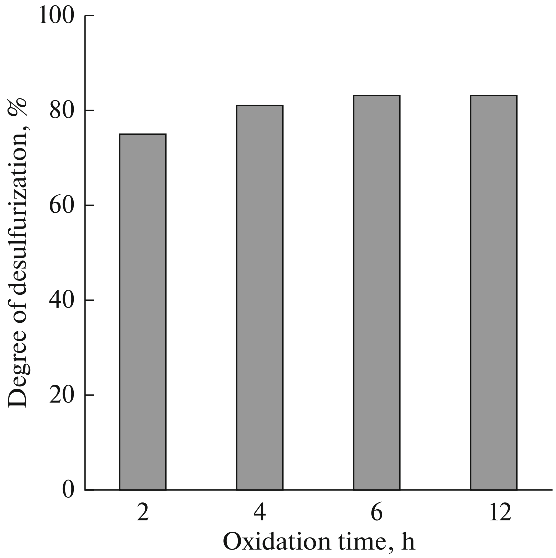

Fig. 3. Effect of oxidation time on the degree of desulfurization of vacuum gasoil on catalyst $(NH_4)_2WO_4$. Conditions: H_2O_2 : S = 4 : 1; HCOOH : S = 1 : 1 (in moles), total 6 h, including: 1 h at 40°C, 1 h at 60°C, 4 h at 80°C.

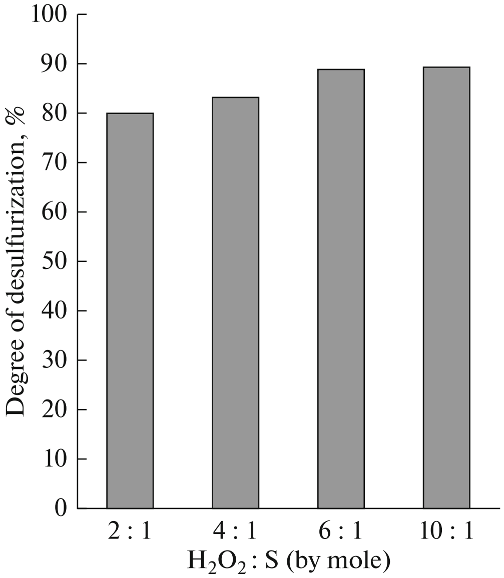

Fig. 4. Effect of hydrogen peroxide amount on the degree of desulfurization of vacuum gas oil on catalyst $(NH_4)_2WO_4$. Conditions: HCOOH : S = 1 : 1 (by mole), total 6 h, including: 1 h at 40°C, 1 h at 60°C, 4 h at 80°C.

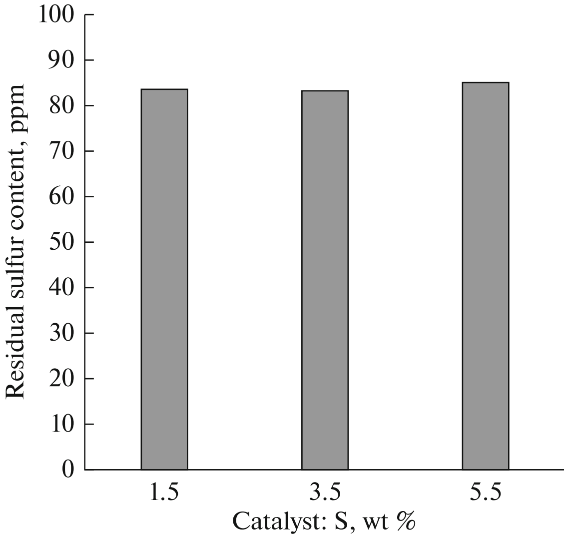

Fig. 5. Effect of the catalyst amount on the degree of desulfurization of vacuum gas oil. Conditions: H_2O_2 : S = 6 : 1 (by mole), 1 h at 40°C, 1 h at 60°C, 4 h at 80°C; catalyst $(NH_4)_2WO_4$.

ammonium tungstate under the temperature conditions of 40–60–80°C (1 h at 40°C, 1 h at 60°C, 4 h at 80°C).

Influence of Reaction Time

The oxidation time was varied in the range of 2–12 h. The results obtained are given in Fig. 3. According to these data, the oxidation of VGO sulfur compounds proceeds to the maximal extent for 6 h. Further oxidation does not lead to increase in the degree of desulfurization.

Influence of the Amount of Oxidant

The effect of the amount of hydrogen peroxide on the degree of desulfurization was investigated using it in the molar ratio of H_2O_2 : S ranging from 2 : 1 to 10 : 1. The need in the excess of the oxidant is due to fact that the partial decomposition of hydrogen peroxide is possible during the reaction.

As seen from Fig. 4, an increase in the excess of hydrogen peroxide with respect to sulfur from 6 : 1 to

Table 1. Physicochemical parameters of vacuum gas oil

Vacuum gas oil	Density, g/cm^3	Kinematic viscosity, cSt	Sulfur content, wt %	Fraction composition			
				IBP, °C	10%, °C	50%, °C	FBP, °C
Prior to oxidation	0.904	7.1	1.48	346	390	442	532
After oxidation	0.910	7.2	0.13	342	387	440	536

10 : 1 does not lead to significant improvement of the degree of desulfurization. To minimize the hydrogen peroxide consumption, the sixfold excess of oxidant was used in further work.

Effect of the Amount of the Formic Acid–Ammonium Tungstate Catalyst Mixture

The effect of the catalyst amount on the degree of VGO desulfurization was investigated using the catalyst : sulfur weight ratio in the range from 1.5 to 5.5 wt %. As seen from Fig. 5, a decrease in the amount of formic acid slightly affects the degree of desulfurization of vacuum gas oil.

To analyze the effect of oxidation on physicochemical parameters of vacuum gas oil, vacuum distillation was carried out and density and kinematic viscosity were measured. The results are given in Table 1.

As seen from Table 1, the oxidation of vacuum gas oil does not affect negatively its physicochemical parameters, suggesting that this method can be used for desulfurization of heavy fractions.

In summary, in this study we have determined optimum conditions for oxidative desulfurization of vacuum gas oil: the total reaction time of 6 h comprised of 1 h at 40°C, 1 h at 60°C, and 4 h at 80°C; $(NH_4)_2WO_4$; $H_2O_2 : S = 6 : 1$ (by mole); and $HCOOH : S = 1 : 2$ (by mole); extractant *N*-methylpyrrolidone; extraction temperature, 100°C.

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REFERENCES

1. *Technical Regulations No. 609 “On the Requirements to Polluting Exhaust Emissions by Motor Vehicles in the Russian Federation” of October 12, 2005* [in Russian].
2. E. V. Rudyakova, *Quality Assessment System for Fuels, Lubricating Oils, and Specialty Fluids* (Izd. Irkutskogo Gos. Tekhn. Univ., Irkutsk, 2013) [in Russian].
3. A. V. Anisimov and A. V. Tarakanova, Zh. Ross. Ob-va Imeni D.I. Mendeleeva **52** (4), 32 (2008).
4. J. K. Dunleavy, Platinum Met. Rev. **50**, 110 (2006).
5. R. Javadli and A. de Klerk, Appl. Petrochem. Res., No. 1, 3 (2012).
6. I. V. Babich and J. A. Moulijn, Fuel **82**, 607 (2003).
7. J. M. Campos-Martin, M. C. Capel-Sanchez, P. Perez-Presas, and J. L. G. Fierro, Chem. Technol. Biotechnol. **86**, 879 (2010).
8. J. Eber, P. Wasserscheid, and A. Jess, Green Chem. **6**, 316 (2004).
9. Q. Li, X. Wang, L. Yu, and J. Yang, Pet. Sci. **15**, 613 (2018).
10. K. A. Nadeina and O. V. Klimov, Catal. Today **271**, (2016).
11. E. Rodriguez, G. Felix, J. Ancheyta, and F. Trejo, Fuel **225**, 118 (2018).
12. M. Xiaoliang, S. Lu, and S. Chunshan, Catal. Today **77**, 107 (2002).
13. A. V. Akopyan, E. V. Ivanov, P. D. Polikarpova, et al., Pet. Chem. **55**, 571 (2015).
14. A. V. Akopyan, R. A. Fedorov, B. V. Andreev, et al., Russ. J. Appl. Chem. **91**, 529 (2018).
15. Z. Jiang, H. Lü, Y. Zhang, and C. Li, Chin. J. Catal. **32**, 707 (2011).
16. G. G. Zeelani, A. Ashrafi, A. Dhakad, et al., Int. Res. J. Eng. Technol. **3**, 331 (2015).
17. Z. Ismagilov, S. Yashnik, M. Kerzhentsev, et al., Catal. Rev.–Sci. Eng. **53**, 199 (2011).
18. J. A. Kadijani and E. Narimani, Pet. Coal **56**, 116 (2014).
19. *ASTM D4294-10. Standard test method for sulfur in petroleum and petroleum products by energy dispersive X-ray fluorescence spectrometry.*
20. M. F. Ali, A. Al-Malki, B. El-Ali, et al., Fuel **85**, 1354 (2006).

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