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Peroxide Oxidative Desulfurization of Crude Petroleum in the presence of fatty acids

Abstract. Oxidative desulfurization of crude petroleum with hydrogen peroxide in the presence of fatty acids has been studied. A procedure for the recovery of oxidized sulfur-containing compounds from the petroleum by extracting the oxidation products with acetone has been selected. The influence of fatty acid on the residual sulfur content and oil viscosity was determined. As a result of oxidative desulfurization, up to 45% of total sulfur is recovered from petroleum, with the viscosity decreasing of crude oil.

Key words: petroleum, oxidative desulfurization, hydrogen peroxide, viscosity, fatty acids.

Introduction

Due to constant growth in the consumption of petroleum refinery products, the sulfur content in oil is subject to strict limitation. Nowadays is essential the search for costefficient technologies for decreasing the total sulfur content in refinery products and viscosity of crude oil [1]. Sulfur-containing compounds have a negative influence on many performance characteristics of petroleum products: stability and response to additives of motor gasolines decrease and their sooting tendency and corrosion activity increase; the service life of oil-refining equipment and transportation pipes decreases [2-4].

In the process of oxidative desulfurization with hydrogen peroxide, sulfur-containing compounds are oxidized first to sulfoxides and then to sulfones. This method allows to achieve low levels of sulfur in crude oil with a very simple technological design process [5] with the removal of chemically inactive benzothiophene derivatives and dibenzothiophene [6-8]. Currently, hydrogen peroxide is one of the most suitable oxidizing agents for the process of oxidative desulfurization. This is due to the fact that it has the highest percentage of active oxygen (47.1%), in addition, it has such technological and economic advantages as relatively low cost, environmental friendliness and commercial availability [9,10]. As additives to hydrogen peroxide, carboxyl compounds are effectively used, which significantly accelerate the oxidation of organic sulfur compounds and increase the degree of desulfurization of the feedstock [11, 12]. The combination of hydrogen peroxide with complexes of various metals also provides a high degree of petroleum fractions organic sulfur compounds oxidation[13–15]. Removing of oxidized sulfur-containing compounds from raw materials is carried out by extraction from oxidized oil fractions with polar solvents.

The reduction of viscosity is especially important for the transportation of oils with increased viscosity, since the process of pumping them requires an increase in the power of pumping units. The processing of such oil requires the improvement of technological schemes at all stages, which leads to an increase in the cost not only of its transportation, but also of production and refining [16]. The main characteristics that determine the technological processes associated with the oil processing with high viscosity are structural and mechanical properties, which are particularly influenced by the content in the oil of high-molecular compounds, including asphaltenes. In low-paraffinic oils, the important reason for high viscosity of oil is the presence of asphaltenes [17, 18]. To improve the rheological characteristics of viscous and highly viscous oils and increase their stability against delamination, synthetic surfactants, such as fatty acids, as well as specialized technological processes, such as aquatermolysis, are used [19]. The aim of this work was to develop a method for transferring oil from the medium-sour class to the low-sour class, without affecting the basic physicochemical parameters, such as viscosity and density, applying the principles of oxidative desulfurization.

Materials and Methods

Crude oil from the Moscow refinery with a sulfur content of 1.24% was used in the study. This oil belongs to the medium and low-viscosity. The main physicochemical parameters are presented in table 1.

Table 1 – Physicochemical parameters of the crude oil

Parameter	Initial oil
Density, kg/m^3	872.7
Kinematic viscosity, cSt	2.623
Dynamic viscosity, mPa•s	2.3
Total sulfur, ppm	12400
Mercaptan sulfur, ppm	8
Asphaltenes, wt %	2.5
Water, vol %	0.1

Aqueous solutions of hydrogen peroxide (Prime Chemicals Group) were used as an oxidizing agents; formic acid (88% aqueous solution, analytical grade, Component-reagent), oleic (reagent grade, Reachim), stearic (97 %, Acros Organics) and lauric acid (reagent grade, Mas Albion). The following metal salts were used: $Na_2MO_4 \cdot 2H_2O$, $Na_2WO_4 \cdot 2H_2O$ (Aldrich Chemical), $(NH_4)_2MoO_4$ (AMX Line), $C_{10}H_{14}MoO_6$ (molybdenum acetylacetonate, DALHIM), $Mo(CO)_6$ (reagent grade, Reachim). Extractants served as solvents: acetone (analytical grade), methanol (reagent grade), N, N-dimethylformamide (reagent grade), acetonitrile (reagent grade), methyl ethyl ketone, dimethyl sulfoxide (reagent grade), N, N- dimethylacetamide (reagent grade). N-hexane (analytical grade, Ecos-1) was used as a solvent for determining the mass fraction of asphaltenes.

The sulfur content in the samples before and after desulfurization was determined on an ASE-2 X-ray energy dispersive sulfur analyzer (Burevestnik) with the relative error of no more than 5% and concentration range from 50 to 50000 ppm.

Crude oil desulfurization was carried out according to the following scheme: the required volume of the oxidizing system was added to a 10 ml sample of crude oil based on the molar ratios S: H_2O_2: acid: Me from 1: 1: 0: 0 to 1: 4: 1: 0.02. The reaction was carried out with constant stirring at 20 ° C for 2 to 6 hours. 10 mL of the oxidized petroleum were rinsed with 10 mL of water, extracted with 12 mL of the extracting agent with 20 vol % water, and the extracting agent and petroleum were separated by centrifugation. The operation was repeated twice, after which petroleum was rinsed with 10 mL of water, and the petroleum after extraction was analyzed for sulfur.

Determination of kinematic and dynamic of crude oil viscosity was carried out according to the method GOST 33-2016 using a glass viscometer at room temperature.

Fractional composition was determined by distillation according to GOST 2177-99.

Asphaltenes determination in the initial and oxidized crude oil was carried out according to the following procedure: 5 – 10 g of the sample were dissolved in 40-fold amount of n-hexane and left in the darkness for 18 – 20 h to precipitate asphaltenes. The solution was filtered, the precipitate was washed with hexane until the oil stains on the filter disappeared and until the flowing hexane wascompletely transparent. After that, the filter cake was dissolved in hot benzene and placed in a suspended flask, and benzene was distilled off to obtain a constant mass of the flask with an error of 0.01% [20]. The content of asphaltenes was found by the formula:

$$\text{Asphaltenes} = 100 * (a / A), \text{ wt. \%}$$

a – weight of the obtained sediment, A – weight of the sample.

Results and discussion

The process of oxidative desulfurization of hydrocarbon feedstock generally includes two steps: (1) oxidation of sulfur compounds present in the fraction and (2) the recovery of oxidation products from the fraction. Adsorption, extraction, or thermal methods are used to selectively remove oxidation products of sulfur compounds [21]. Previous studies have shown that the most effective method for extracting oxidized sulfur-containing compounds is extraction with polar solvents [5]. At the initial stage of work, the evaluation of extractants of various chemical nature was carried out.

The data obtained (Fig. 1) show that acetone and N, N-DMF most oxidized sulfur-containing compounds are extracted from oil, which is most likely due to the high polarity of the extracted compounds. Due to the simplicity of its regeneration and the best result on the residual sulfur content, acetone was used as extractation agent for oxidative products.

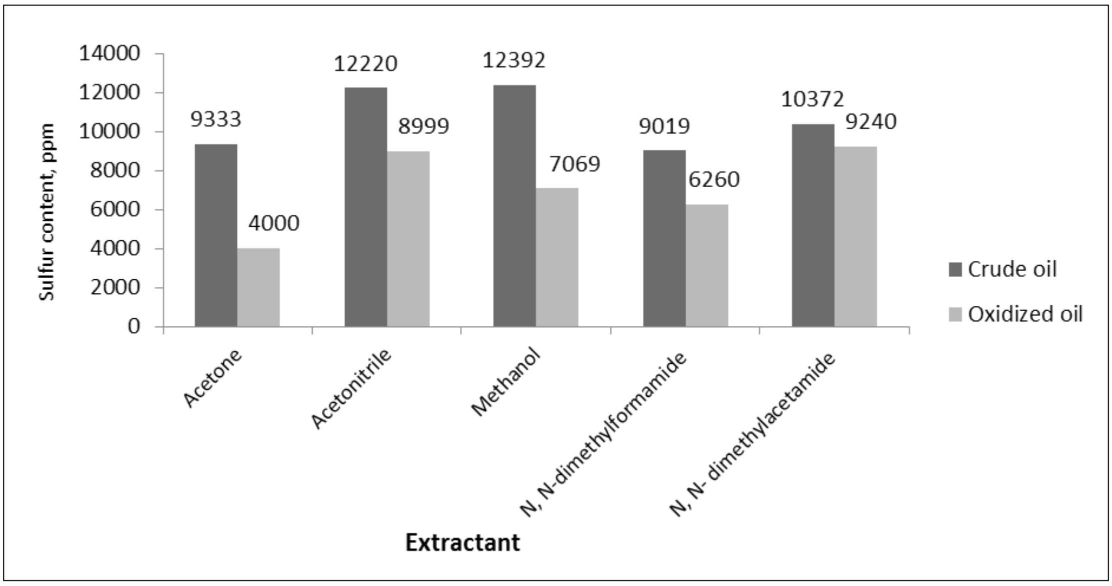

Figure 1 – Dependence of residual sulfur content on the nature of the extractant. (Conditions: S: H_2O_2 (50%): HCOOH = 1: 10: 6 (mol.), 20 ° C, 6 hours)

Aqueous solutions of hydrogen peroxide were used as oxidizing agents. To ensure optimal desulfurization conditions, the effect of the amount and concentration of hydrogen peroxide on the residual sulfur content was studied.

According to the data obtained (Table 2), 5 and 10% aqueous solutions of hydrogen peroxide are advisable to use in a molar ratio of 1: 1 for 10% hydrogen peroxide and 4: 1 and 2: 1 for 5% hydrogen peroxide. These solutions in combination with 88% formic acid and subsequent extraction can reduce the residual sulfur content in the oil to 5500 ppm. This is most likely due to the fact that at high concentrations of hydrogen peroxide, the mainly oxidized compounds which are difficult to extract.

Table 2 – The dependence of the residual sulfur content on the concentration and amount of hydrogen peroxide. (Conditions: S: HCOOH = 1: 1 (mol.), 20 ° C, 2 hours)

Molar ratio H_2O_2 : S	Residual sulfur content, ppm				
	Hydrogen peroxide concentration, vol %				
	50	37	24	10	5
4 : 1	9000	8400	7800	8000	5500
2 : 1	8700	8700	7700	7600	6000
1 : 1	8000	8700	7800	7000	7700

It is known from the published data [11,12] that desulfurization in an acidic medium provides positive results on the residual sulfur content in the feedstock, and the use of fatty acids has a positive effect on the viscosity of oil. During the work, the effect of carboxylic acids on the residual content of oxidized sulfur-containing compounds, the mass fraction of asphaltenes and the viscosity of oil were investigated.

The data obtained indicate that the use of fatty acids can reduce the viscosity of oil, but does not provide oxidation of sulfur-containing compounds of oil compared with formic acid. The increase in the mass fraction of asphaltenes in oxidized oil is most likely due to the increase in the proportion of the fraction of insoluble asphaltenes.

The published data suggest that salts of transition metals forming peroxo complexes with H_2O_2

contribute to the reduction of the content of sulfur-containing compounds in the feedstock [22]. Sodium molybdate and sodium tungstate were used as salts containing transition metals.

Based on the data obtained, the use of sodium molybdate in the oxidative system in combination with oleic acid can reduce the residual sulfur content to 6000 ppm as compared with tungstates.

In connection with obtaining a positive effect from the use of molybdenum as a catalyst for the oxidation of sulfur compounds of oil, various molybdenum salts were used in the work.

Table 3 – Effect of carboxylic acids on the residual sulfur content and oil viscosity. (Conditions: S: H_2O_2 (10%): acid = 1: 1: 1 (mol.), 20 ° C, 2 h, * – conditions: S: H_2O_2 (10%): mixture of acids = 1: 1: 2 (mol .), 20oC, 2 hours)

Acidd	Residual sulfur content, ppm	Kinematic viscosity, cSt	Asphaltenes, wt %
Formic	7300	2.76	6.17
Acetic	8300	2.64	5.3
Stearic	9066	2.23	4.16
Oleic	9500	2.30	4.38
Lauric	11000	2.34	4.46
Stearic + formic*	9700	2.05	5.9
Oleic + formic*	8800	2.13	5.34
Lauric + formic*	9400	2.21	6.23

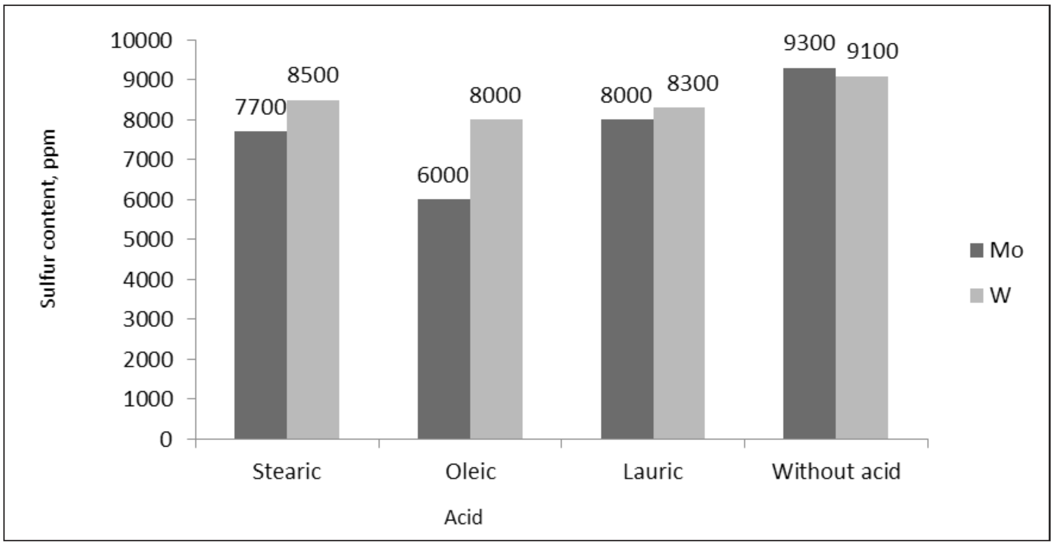

Figure 2 – The effect of transition metal salts and fatty acids on the residual sulfur content. (Conditions: S: H2O2 (10%): acid: Me = 1: 1: 1: 0.02 (mole), 20 ° C, 2 hours)

Based on the data obtained (Fig. 3), the use of sodium molybdate in a molar ratio of sulfur to 1: 200 is preferable compared with other salts of molybdenum and sodium molybdate in a molar ratio of 1: 100.

The work also determined the fractional composition of the original oil, oil after oxidation with an excess of hydrogen peroxide and formic acid, as well as oil after its oxidation. The oxidizing system in the presence of oleic acid and sodium molybdate was used, followed by extraction of sulfur-containing compounds of oxidation products, as well as the of total sulfur content in each of the oil fractions was determined (Table 4).

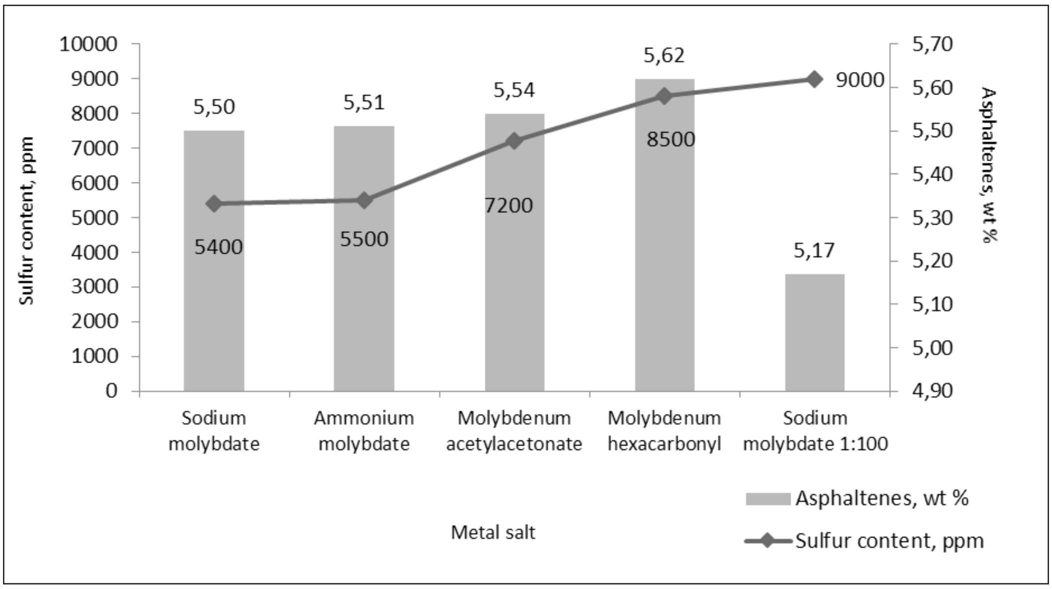

Figure 3 – The effect of molybdenum salts on the residual sulfur content and asphaltene content. (Conditions: S: H2O2 (10%): oleic acid: Me = 1: 1: 1: 0.02 (mole.), 20 ° C, 2 h, * – S: H2O2 (10%): oleic acid: Me = 1: 1: 1: 0.01 (mole), 20 ° C, 2 hours)

Table 4 – Fractional composition of the original and oxidized oil. (Conditions: 1) S: H_2O_2 (50%): HCOOH = 1: 10: 6 (mole), 20 ° C, 6 h; 2) S: H_2O_2 (10%): oleic acid: Me = 1: 1: 1: 0.02 (mole), 20 ° C, 2 hours)

Fraction	Initial crude oil		Oxidized oil (Conditions 1)		Oxidized oil (Conditions 2)	
	Volume, ml	Sulfur content, ppm	Volume, ml	Sulfur content, ppm	Volume, ml	Sulfur content, ppm
Petrol (38°C – 180°C)	9	600	7.6	220	9	350
Diesel (180°C – 360°C)	16.5	6690	14.5	158	15	3200
Residue	24	19400	27	9800	25	12800
Oil	50	12400	50	4000	50	4500

The data obtained from table 4 indicate that the oxidation composition in an excess of hydrogen peroxide and formic acid changes the oil fractional composition. The decrease in the residual content of oil sulfur-containing compounds and in each of the fractions was also observed. When using a 10% solution of hydrogen peroxide, oleic acid and sodium molybdate, the residual sulfur content in the fractions is higher than when using an excess amount of hydrogen peroxide and formic acid.

Conclusion

The use of fatty acids in oxidizing systems allows to reduce the viscosity of oil by 10 – 15%, but not in all cases it allows to reduce the sulfur content to acceptable parameters specified when using the oxidizing system with hydrogen peroxide (10%): formic acid (88%) 1: 1. The oxidative system with hydrogen peroxide (10%): oleic acid: sodium molybdate in a molar ratio of 1: 1: 0.02 able to transfer oil from medium-sulfur to low-sulfur and reduce kinematic viscosity by 12%.

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