Determining the conditions for oxidative desulphurization of oils

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Abstract. The paper studies oxidative desulphurization of oils with an initial sulphur content of 1.98 wt% by hydrogen peroxide on a carbon-black (CB) catalyst coated by a combination of cobalt and nickel. The results demonstrate the effects of temperature and duration of the process, amount of the catalyst and the nature of the selected extractant on the removal efficiency of oxidized sulphur compounds. The extractant was represented by a solution of dimethylformamide (DMF) with water (10 vol%). The maximum removal degree of sulphur exceeded 70% and was achieved in 90 minutes with an amount of the catalyst of 1.0–1.3 wt.% and a temperature of 50 °C.

1. Introduction
The issues of heavy oil transformation into low-sulphur petroleum products are becoming increasingly high on the agenda. This is mainly due to the depletion of low-sulphur oil fields, which necessitates developing oil fields with moderate and high content of sulphur. Therefore, the share of high-sulphur petroleum products increases [1]. The presence of sulphur compounds in oil gives rise to corrosion and rapid destruction of equipment used in oil extraction and processing [2]. Increasing sulphur content in Russian oil is one of the major reasons for its declining competitiveness. The cost of oil depends on its processing depth. Oil extracted from different fields differs in chemical composition and may have considerably variant quality. Crude oil which incurs minimal processing costs has the highest value. High-quality benchmark crudes contain approximately 0.5% of sulphur. Oil quality can be improved by processing and removing the sulphur.

High-quality oil products are expensive and cover the processing costs. This justifies the development and implementation of advanced oil refining technologies, namely the extraction of sulphur products and the development of high-quality petroleum products.
One of the ways to reduce the sulphur content in oil and petroleum products is desulphurization which significantly improves the commercial and consumer appeal of oil and its products, reduces the environmental footprint, and increases the life of oil processing equipment.

Oil and its residues can be desulphurized—without decomposition of sulphur compounds—by oxidative desulphurization which modifies the functional groups of sulphur compounds to be removed.

Due to its simplicity, the method has been actively used in oil refining for decades to separate oxidized sulphur compounds from hydrocarbons.

The most technologically favorable oxidizer is hydrogen peroxide ($\text{H}_2\text{O}_2$), a commercial product that is often used in industry. It is considered to be a green solvent, because its decay products include water [3]. Effective use of hydrogen peroxide in desulphurization of crude oil feedstock requires catalysts. Selective oxidation of sulphur compounds involves such metals as Ti, V, W, Mo, Co/Mn, Ag, Au, and Re and their oxides that serve as heterogeneous catalysts [4–7]. Alternatively, hydrocarbon-based systems are deemed to be attractive from the perspective of catalysis, due to specific physical and chemical properties, first of all extended surface and chemical inertness [8, 9]. The numerous research works—along with traditional carbon carriers, like active coals—also scrutinize other carbon-based materials, such as carbon nanotubes, graphitized nanofibers, carbon black (CB), fullerenes and various composite carbon-carbon materials [8–10].

Carbon materials are also used in petrochemistry to catalyze oxidation of sulphur compounds residing in heavy fractions of oil processing products [11–13].

The work was aimed at experimentally studying oil oxidative desulphurization using hydrogen peroxide in the presence of a CB-based catalyst coated by transition metals.

2. Experimental part

The object of the study was Usinsk oil field. The physical and chemical properties of its oil are shown in Table 1.

| Characteristic                        | Value   |
|--------------------------------------|---------|
| Density (kg/m$^3$)                   | 966.7   |
| Kinematic viscosity at 20 °C (mm$^2$/s) | 3852.39 |
| Molecular weight (AMU)               | 365     |
| Elemental composition (wt%):         |         |
| • carbon                             | 84.94   |
| • hydrogen                           | 11.98   |
| • oxygen                             | 0.47    |
| • **sulphur**                        | **1.64**|
| • nitrogen                           | 0.63    |
| • N/A                                | 1.68    |
| Content (wt%)                        |         |
| • Paraffin wax                       | 1.24    |
| • N-alkanes                          | 1.29    |
| • chlorides (mg/dm$^3$)              | 36.92   |
| Component composition (wt%):         |         |
| • resins                             | 18.3    |
| • asphaltenes                        | 8.1     |
| • oils                               | 73.9    |
| Pour point (°C)                      | -22.5   |

The metal-carbon composite was made from P354 CB synthesized at the Institute of Hydrocarbon Processing Problems of the Siberian Branch of the Russian Academy of Sciences (Omsk, Russia). The CB specimen contained 96.4% of C, 2.5% of O, 0.5% of S, and 0.3% of N and H each [14]. The surface
of the CB specimen was coated by nanoparticles of transition metals (nickel and cobalt) by chemical reduction of the metals from solutions of their salts using sodium hypophosphite (Ni–Co–CB). This method is widely used for chemical deposition of nickel on small metal products [15]. The advantages are final fineness of the coating and the uniformity of metal deposition on the substrate.

Oxidative desulphurization of oil was carried out in a 500-ml KGP-3-1-500-29/32-14/23-14/23 three-neck flask with a mechanical stirrer, a TL-2 N2 laboratory mercury in-glass thermometer and KhSh-1-400-29/32 ball reflux condenser. The flask was placed in a LOIP LB-140 water bath for thermal conditioning at temperatures of 35–95 °C. Thirty grams of crude oil feedstock were heated in the flask up to the necessary temperature after which a portion of the catalyst and 40 ml of oxidant were simultaneously added to the solution. The amount of the catalyst varied from 0.16 to 1.65 wt%. The oxidant was a 15-percent aqueous solution of hydrogen peroxide derived by dilution from a high-purity 30% solution (Yugtekhhkom Company, Russia). The moment of the oxidant contacting with the feedstock was considered as the beginning of the reaction. The durations of sulphur compound oxidation were 30, 60, 90, 120 and 150 minutes.

After the reaction ceasing, the layer of hydrocarbons was separated from the aqueous phase in the separating funnel. To extract oxidized sulphur compounds, a solvent was added to the hydrocarbon layer; the solution was stirred for 10 minutes and kept under a layer of extractant for 60 minutes at a temperature of 35–40 °C. The mass ratio of the feedstock to the extractant was 1:2. Chemically pure acetonitrile (AN) or N,N-dimethylformamide (DMF) (EKOS-1 Company, Russia) with 10 vol.% of water were used as the solvent to extract oxidized sulphur compounds.

Total sulphur content in the feedstock and desulphurized product was determined by the method of burning in a lamp in the presence of oxygen (GOST 19121-73) [16]. The method entails burning an oil sample in a platinum sample carrier mounted on a stopper of a Schoniger combustion flask containing an oxygen-saturated absorption solution. After the combustion ceasing, the absorption solution was titrated by a barium nitrate solution in the presence of an indicator until reaching stable color. A blank experiment (without oil sample) was carried out under the same conditions. Using the results obtained, total sulphur content in the oil sample was calculated.

3. Results and discussion
The experiments on the oxidative desulphurization of oil allowed studying the influence of temperature and duration of the process on the sulphur removal degree (Table 2). The amount of the catalyst was 1 wt%; the molar ratio of sulphur in the feedstock to oxidant was 1:4. The extractant was DMF with 10 vol.% of water.

| Oxidation time (min) | Temperature (°C) | Sulphur residue (%) |
|----------------------|------------------|---------------------|
| 30                   | 35               | 0.75                |
| 60                   | 35               | 0.61                |
| 90                   | 35               | 0.52                |
| 120                  | 35               | 0.50                |
| 150                  | 35               | 0.53                |
| 30                   | 50               | 0.70                |
| 60                   | 50               | 0.60                |
| **90**               | **50**           | **0.50**            |
| 120                  | 50               | 0.55                |
| 150                  | 50               | 0.49                |
| 30                   | 95               | 0.90                |
| 60                   | 95               | 0.80                |
| 90                   | 95               | 0.72                |
| 120                  | 95               | 0.70                |
| 150                  | 95               | 0.71                |
According to Table 2, the minimum amount of sulphur in oil remains after 90-minute oxidation at a temperature of 50 °C.

At a lower temperature, the feedstock (oil) is relatively viscous, while the reagents (oxidant and catalyst) are unevenly distributed in the raw material. Therefore, the degree of sulphur compounds during the first 30 minutes is low. However, with increased duration of the process and a reaction time of 90–150 minutes, the residual sulphur content in the feedstock drops to 0.5–0.53 wt%.

Increased temperature to 95 °C reduces sulphur removal extent, probably due to the partial decomposition of hydrogen peroxide into oxygen and water, and consequently, fewer active -OH-particles. Even at short heating time (30 mins) the residual sulphur content (0.9 wt%) exceeds that reached at 35 and 50 °C at different processing times.

The O–O bond is fragile, which makes hydrogen peroxide (H₂O₂) an unstable compound that easily decomposes. This may be also caused by the presence of transition metals, such as cobalt and nickel which are a part of the catalyst.

The work also studied the effect of the catalyst content on the oxidation of oil sulphur compounds (Table 3) at 50 °C during 90 minutes. Oil sulphur compounds were extracted by DMF or AN diluted by 10 vol.% of water.

**Table 3. Influence of catalyst content in reaction mixture on residual sulphur content in oil.**

| Catalyst content (CB-Co-Ni) (wt%) | Residual sulphur (wt%) | Sulphur removal degree X (%) |
|----------------------------------|------------------------|-----------------------------|
|                                  | DMF        | AN    | DMF        | AN    |
| 0.16                             | 1.3        | 1.45  | 20.7       | 11.6  |
| 0.33                             | 1.15       | 1.28  | 29.9       | 22.0  |
| 0.48                             | 0.8        | 0.9   | 51.2       | 45.1  |
| 0.64                             | 0.65       | 0.7   | 60.4       | 57.3  |
| 1.0                              | 0.5        | 0.6   | 69.5       | 63.4  |
| 1.3                              | **0.48**   | 0.66  | **70.7**   | 59.8  |
| 1.65                             | 0.52       | 0.63  | 68.3       | 61.6  |

The degree of sulphur removal from the feedstock was calculated by eq. (1):

\[
X = \frac{(\omega_0 - \omega_k)}{\omega_0} \cdot 100\%,
\]

where X is the degree of sulphur removal (%); \(\omega_0\) is the initial sulphur content (wt%); \(\omega_k\) is the sulphur content in the feedstock after desulphurization (residual content) (wt%).

Evidently from Table 3, the residual sulphur content in oil steadily falls with increasing catalyst content, while the optimal value in the reaction system was 1–1.3 wt%.

At a lower catalyst content, the residual sulphur concentration under similar conditions is higher, which may be due to insufficient number of active sites on the catalyst surface. A catalyst content above 1–1.3 wt% demonstrates increased residual content of total sulphur in the processed feedstock, which may be caused by the shielding of the active sites on the catalyst surface by oxidation products.

The extraction efficiency of oxidized sulphur compounds by selected extractants is shown in Figure 1.
Figure 1. Influence of extractant type on the removal of oxidized sulphur compounds from oil.

Obviously, the most effective extractant is DMF with 10 vol.% of water. The residual sulphur content in oil achieved was 0.48 wt% at a process time of 90 minutes, temperature of 50 °C and catalyst concentration of 1.3 wt%.

Probably, the larger effectiveness of the DMF-water system v. AN-water system is conditioned by the formation of more sulphoxides than the sulphones during oxidative desulphurization, while the DMF-water system is more selective to sulphoxides then to sulphones. In the case of the AN-water system, sulphones are preferably extracted [17].

Thus, following the experimental data, oxidative desulphurization using carbon black coated by nickel and cobalt (CB-Co-Ni) is feasible under mild conditions: a temperature of 50 °C, the duration of the process is 90 minutes, the amount of catalyst is 1–1.3 wt%, and a molar ratio of sulphur-containing feedstock to oxidant of 1:4. The DMF-water system (with 10 vol.% of water) is more effective for the extraction of oxidized sulphur compounds from oil to a high degree of more than 70%.

4. Conclusion
The research has discovered that the carbon black-based catalyst coated by nickel and cobalt shows high catalytic activity in oxidative desulphurization of oil. At a temperature of 50 °C, the duration of the process is 90 minutes, the amount of catalyst is 1-1.3 wt% and the extraction degree of oxidized sulphur compounds by an aqueous solution of dimethylformamide can exceed 70%.

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References
[1] Schepalov A A 2012 Heavy oil, gas hydrates and other promising sources of hydrocarbon raw materials Teaching and methodical manual. - Nizhny Novgorod: UNN 93p
[2] Kundik A A 2017 Ensuring the reliability of pipeline systems. Method for diagnosing internal anticorrosion coating of pipelines // Oil. Professionally about oil. 1 74–76
[3] Campos-Martin J M , Blanco-Brieva, J M and Fierro J L G 2006 Hydrogen peroxide synthesis: An outlook beyond the anthraquinone process Angew. Chem. Int. Ed. 45 6962–84
[4] Kong L et al. 2006 Oxidative Desulphurisation of Organic Sulphur in Gasoline over Ag/TS-1 Energy & Fuels 20 (3) 896–902
[5] Xiaojuan Si S C et al. 2007 Oxidative Desulphurisation of Model Oil over Au/Ti-MWW Catalysis Letters 122 (3–4) 321–324

[6] Rakov E G, Baronin I V, Anoshkin I V 2008 Catalysis in industry. Special edition. pp 83–86

[7] Likholobov V A, Surovikin V F, Plaksin G V, Tsekhanovich M S, Surovikin Yu V, Baklanova O N 2008 Catalysis in industry. Special edition. pp 63–69

[8] Yang G W, Gao G Y, Wang C, Xu C L, Li H L 2008 Carbon. 46 747–752

[9] Kobotaeva N S, Skorokhodova T S, Ryabova N V 2015 Catalytic Systems of Cumol Oxidation Based on Multiwalled Carbon Nanotubes Russian Journal of Physical Chemistry 89 (3) 462–468

[10] Guoxian Yu, Shanxiang Lu, Hui Chen, Zhongnan Zhu. 2005 Diesel fuel desulphurisation with hydrogen peroxide promoted by formic acid and catalysed by activated carbon Carbon. 43 2285–94

[11] Guoxian Yu, Shanxiang Lu, Hui Chen, and Zhongnan Zhu 2005 Oxidative desulphurisation of diesel fuels with hydrogen peroxide in the presence of activated carbon and formic acid Energy & Fuels 19 447–452

[12] Jing Xiao, Luoming Wu, Ying Wu, Bing Liu, Lu Dai, Zhong Li, Qibin Xia, Hongxia Xi 2014 Effect of gasoline composition on oxidative desulphurisation using a phosphotungstic acid/activated carbon catalyst with hydrogen peroxide Applied Energy. 113 78–85

[13] Razdyakonova G I, Likholobov V A, Moiseevskaya G V, Petin A A, Karavayev M Yu 2014 Innovative dispersed carbon. From idea to technology: monograph Omsk: Omsk State Technical University Publishing House 312 244–245

[14] Rakov E G 2004 Journal of the Russian Chemical Society. DI. Mendeleev. 48 (5) 12–29

[15] Petrova T P 2011 Chemical coatings. // Soros Educational Journal. 6 (11) 57–62

[16] GOST RF 19121-73 Petroleum products. Determination of sulphur content by lamp method

[17] Zarifyanova M Z, Kozin V G 2007 Investigation of the selectivity of solvents in the separation of oil sulfoxides and sulphones from oxidates of oil fractions Bulletin of Kazan Technological University. 5 111–116