The Austrian Journal of Technical and Natural Sciences, No 9–10
ISSN 2310-5607

PREMIER Publishing
ppublishing.org

Section 1. Chemistry

DOI:10.29013/AJT-25-9.10-3-7

OXIDATION OF OIL SULFIDES OF THE EAST TASHLA FIELDS WITH HYDROGEN PEROXIDE IN THE PRESENCE OF SULFURIC ACID

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Cite: *Davranova G. T., Safarova M. A., Mamatova Sh. B., Kurbanov M. J., Salayev M. (2025). Oxidation of Oil Sulfides of the East Tashla Fields With Hydrogen Peroxide in The Presence of Sulfuric Acid. Austrian Journal of Technical and Natural Sciences 2025, No. 9–10.* https://doi.org/10.29013/AJT-25-9.10-3-7

Abstract

In this article, sulfuric acid extraction of sulfide organic compounds from the fuel oil fraction of the Tashlinsky field was carried out. The reaction and conditions of hydrogen peroxide on sulfide compounds from the fuel oil fraction of oil were studied. Organic sulfur compounds in the resulting sulfide concentrate were converted into the corresponding sulfoxides by a 30% peroxide solution.

Keywords: *sulfur, sulfoxide, organosulfur compounds, bitumen, high-sulfur oil, hydrogen peroxide, extract, distillate, refined*

Introduction

Domestic and foreign oil industry suppressed the amount of oil produced – sulfurous and high-sulfur, which are one of the main natural raw materials sources of organosulfur compounds. In this regard, synthetically similar compounds are very important not only as reference preparations for the purposes of identification, but also for a comprehensive study of their physicochemical, chemical, physiological, anti-corrosion and other specific properties, which will greatly facilitate the search for new areas of application of organosulfur compounds of oil.

Cyclic organic sulfur compounds attract more and more attention every year for their theoretical and practical significance. It should be noted that on the basis of organic sulfur compounds, new organic reactions and new effective reagents are discovered, which are successfully used in modern organic synthesis (Rakhmatova G. B., Kurbanov M.Zh., Atakulova D., 2020; Rakhmatova G. B., Kurbanov M.Zh., Ruziboev M. T., 2019; Rakhmatova G. B., Kurbanov M.Zh., Ruziboev M. T., 2020; Vyacheslav Y. Sosnovskikh. 2016). Successes in this direction to a certain extent complement the methods of fine organic synthesis and theoretical organic chemistry. The development of synthetic work in this direction is also dictated by the need of the national economy for substances with clearly expressed highly effective anti-corrosion and biological activity, which is inherent in many classes of sulfur compounds (Sharaf Demirayak, Leyla Yurttas, Nalan Gundogdu-Karaburun, Ahmet Cagri Karaburun, Ismail Kayagil. 2017; Ya-Li Song, Fan Vu, Chao-Chao Chjan, Guo-Chao Liang, Guan Chjou, Jiao-Jiao Yu., 2015; Henok H. Kurfe, Paseka T. Moshapo, Felix L. Makolo, David W. Gammon, Martin Ehlers, Carsten Schmuck. 2014).

Experimental part

Oxidation to the bituminous broad fraction of high-sulfur oil is carried out as follows: to the bitumen wide fraction of high-sulfur oil in the amount of 200 g, loaded into a three-necked flask with a capacity of 0.5 liters, equipped with a mechanical mixer, a thermometer and a drip funnel. 0.4 g of the emulsifier OS-20 (0.3% to the reaction mixture) was added to this amount of fraction. containing concentrated sulfuric acid in the amount of 0.85 g. Oxidizing mixture is prepared by adding portions of concentrated sulfuric acid to a 30% hydrogen peroxide solution cooled to 0 °C. The addition of the oxidizer was introduced at such a rate that the temperature of the mixture did not exceed 25 °C. After adding hydrogen peroxide, the mixture was stirred for another 2 hours, and then poured into three times the volume of water. They were shaken vigorously and left overnight. The organic layer was separated and dried with calcined calcium chloride.

The oxidized petroleum distillate (organic layer) was loaded into a dividing funnel equipped with an agitator. To this fraction was added 34 g of 60% sulfuric acid, taken at the rate of three equivalents per equivalent of sulphoxide sulfur in solution. The contents of the unit were vigorously stirred for 15 minutes and then left for two hours to stratify. After stratification, the bottom layer (a solution of sulphoxide sulfates in dilute sulfuric acid) was separated from the refined sugar. The acid extract was washed with petroleum ether from the impurity of non-oxidized sulfur and hydrocarbon compounds, and sulfoxides were isolated from the washed sulfuric acid layer when the complex was destroyed by dilution with water up to 15% of the acid concentration. At the same time, the sulfoxides floated and were extracted with ethyl ether. The resulting ether extracts of sulfoxides were washed with water to a neutral reaction ($pH = 7$), dried with freshly calcined calcium chloride, filtered from the dryer and distilled the solvent. As a result of two treatments of the oxidized broad fraction of oil with 60% sulfuric acid, we obtained 14 g of sulfoxide.

The isolated sulfoxides are dark brown oil, insoluble in water. It is poorly distilled in vacuum, when heated above 110 °C, it darkens. In terms of chemical composition – CnH2nSO, CnH2n-2SO, which correspond to saturated thiocyclanes. Refined, obtained according to both schemes, after purification with 92–93% sulfuric acid, can be used as a component of kerosene – diesel fuel.

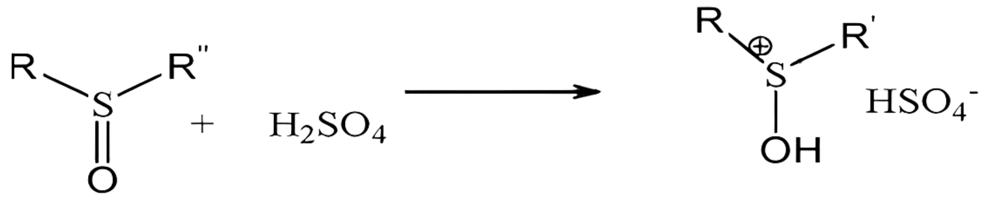
Discussion of the results

Sulphide concentrates up to a bituminous wide fraction of high-sulfur oil, released by sulfuric acid, are of considerable interest for the production of petroleum sulfoxides. However, there are various publications in the literature devoted to the study of the oxidation of sulfide oil concentrates. In this regard, we conducted a study of the oxidation of sulphide concentrate isolated from the pre-bitumen wide fraction of the East Tashly deposit with sulfuric acid. High-sulfur oil produced in the south of Uzbekistan does not receive enough qualified use for processing into valuable products. Therefore, the purpose of this work is to develop a technology for desulfurization to a bituminous broad fraction of high-sulfur oil (BCH) by selective oxidation of sulfides, directly in oil distillates, and to isolate the resulting sulfoxides from oxidized distillates by a cheap and safe sulfuric acid method. The sulfuric acid method includes two stages:

1) Oxidation of sulfides contained in the straight-run kerosene-solar fraction of high-sulfur oil by heterogeneous-emulsion method to sulfoxides with 30% hydrogen peroxide with catalytic additives of sulfuric acid.

2) Release of sulfoxides by a dilute solution of sulfuric acid.

In all the experiments carried out, the oxidation temperature was about 80 °C. The amount of hydrogen peroxide consumption was 1.2 g/mol per 1 g/atom of sulfide sulfur oil. It has been established that the oxidation of VSN sulfides in a foam-emulsion reactor has a higher reaction rate than in a reactor with a mechanical agitator due to the greater dispersion of the heterogeneous system. Sulfides separated from spent 60% sulfuric acid oxidize at a higher rate. The separation of sulfoxides from the oxidized fraction of oil is based on the peculiarities of the electronic structure of organosulfur compounds. Sulfoxides, when dissolved in a dilute 60% solution of sulfuric acid, are protonized, giving sulphoxide sulfoxides according to the scheme:



Sulfoxides, forming a complex, pass into a solution of sulfuric acid and, during the stratification of phases, are separated from hydrocarbons and the non-oxidized part of organosulfur compounds. When the sulfuric acid layer is diluted to a 15% concentration of H_2SO_4, the complex is destroyed and the sulfoxides float to the top, and the dilute solution of sulfuric acid remains at the bottom.

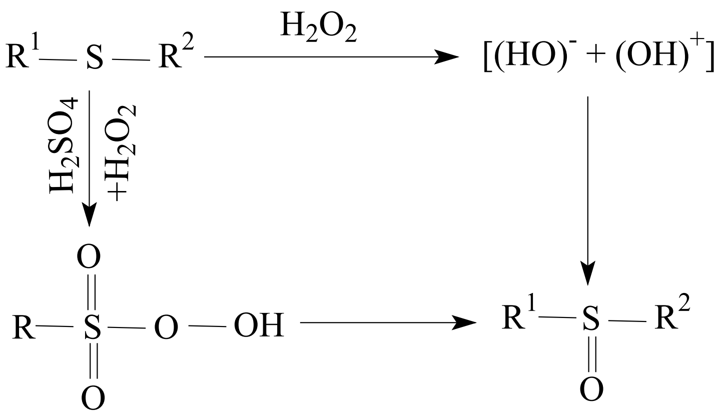
$$R-SO-R-H_2SO_4+H_2O\rightarrow$$
$$R-SO-R+H_2O\cdot H_2SO_4$$

To find out the reasons for the different reactivity of sulfide concentrates in the oxidation reaction, their structural and group composition, as well as the nature of the main impurities were studied by mass spectrometry using UV and IR spectroscopy data. It was found that the structural-group composition of both concentrates is quite close and is represented mainly by thiamonocycloalkanes. The characteristics of the resulting sulfoxides are given in Table 1.

Table 1. *Characteristics of oxidized concentrates of organosulfur compounds isolated from the oxidized to bituminous broad fraction of high-sulfur oil from the East Tashly fields*

Name Products	**Exit**		**d204**	**N20D**	**Mr (cp)**	**Sob, %**		**Sulfoxide, %**		**S=O, %**
	in the year	**in %**				**in a tail-coat**	**to ex.**	**in a tail-coat**	**to ex.**	**in a tail-coat**
Oxidized BCH	201.3	100	0.85256	1.4903	194.0	2.42	100	0.82	100	1.12
Extract (sulfoc seeds)	14.1	6.75	0.99187	1.5405	204.0	13.3	44	–	–	13.1
Cube	184.5	92.3	–	–	–	1.36	54	0.75	93.2	0.021
Petroleum ether leachable product from extract	2.34	1.12	–	–	–	1.78	0.8	–	–	1.15

One of the important points for understanding the mechanism of oxidation of sulfides into sulfoxides using hydrogen peroxide is the diagram below, which assumes the presence of hemolytic and heterolytic reactions.



Depending on the nature of the acid and the temperature of the reactions, the proportion of each of these reactions can range from 1 to 100% of the total rate of hydrogen peroxide decay. Closely related to the question of which decomposition predominates under the action of a hemolytic or heterolytic catalyst is the question of the selectivity of sulfide oxidation. In the presence of sulfuric acid, which causes an incomparably faster breakdown of hydrogen peroxide into radicals, the selectivity of oxidation is low. Thus, the question of the catalytic effect of inorganic acids on the mechanism of oxidation of petroleum sulfides is quite complex. In addition, during the oxidation of petroleum sulfides, along with the decomposition of hydrogen peroxide by heterolytic and homolytic mechanisms, the formation of pyroacids takes place. As is known, the products of the reaction of pyroacids with sulfides are the corresponding sulfoxides. Depending on the conditions of oxidation, the concentration of hydrogen peroxide and the nature of the activating additives, the proportion of pyroacids formed under these conditions varies widely.

Based on this, it can be concluded that the specific nature of oxidation of the sulfide concentrate isolated by spent sulfuric acid with hydrogen peroxide forms pyroacids, which are superior to hydrogen peroxide in oxidizing capacity. Even with a lack of oxidant (65% of the stoichiometry), the amount of sulfonic acids in the reaction mixture reaches 0.5% by weight in three minutes. Sulfones appear in oxidation products only when an excessive amount of hydrogen peroxide is used, and they are formed after the conversion of most of the sulfides into sulfoxides. Thus, sulfones are formed from sulfoxides. With an increase in the concentration of hydrogen peroxide, the formation of sulfones occurs more intensively. In the above-described method of obtaining sulfoxides by oxidation of sulfuric acid extracts of sulfides, the yield of the sulfoxide concentrate based on the initial raw material is about 4.7%. In order to increase the rate of conversion of sulfides into sulfoxides, the oxidation process should be carried out in a foam-emulsion apparatus.

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submitted 08.10.2025;
accepted for publication 22.10.2025;
published 26.11.2025

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