ANALYSIS OF SULFUR IMPACT ON THE OXIDATION OF PETROLEUM RESIDUES

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Abstract

This study investigates the effect of introducing elemental sulfur into the oxidation feedstock during the production of oxidized petroleum bitumen. Vacuum residue from fuel oil distillation and granular sulfur were used as the base materials. Oxidation experiments were carried out at 230 °C with controlled air flow, varying the sulfur concentration from 0 % to 5 %. The results showed that introducing sulfur in optimal amounts (up to 2 %) significantly improves the physical and mechanical properties of the resulting sulfur–bitumen binders — increasing penetration and ductility and lowering brittleness temperature — compared to conventional oxidized bitumen. Higher sulfur concentrations (> 5 %) lead to process inefficiency and deterioration of binder properties. The findings confirm that sulfur additives can be effectively used to intensify the oxidation process, enhance product quality, and optimize production parameters for bitumen manufacturing.

Keywords

oil bitumen, sulfur, needle penetration, tar, oxidation process, softening point

1. Introduction

The existing technology for the production of oxidized bitumen, due to the often changing composition of petroleum feedstock for processing and the unstable quality of the feedstock for the oxidation process, causes difficulties in obtaining bitumen of the required quality. Therefore, directional regulation of the properties of the prepared raw materials for the oxidation process is an urgent task.

Modern trends in the development of science and technology associate the solution of this problem with the development of effective methods for influencing the properties of the initial raw materials used in the production of commercial petroleum bitumen, optimizing the technological parameters of the process for their production and adjusting the properties of oxidized bitumen in various ways [1]. In the production of oxidized bitumen, an effective way of such exposure is to control the properties of the oxidation feedstock using various additives.

We have studied elemental sulfur as such an additive, which is available in huge quantities at oil refineries and gas refineries as by-products. Her choice is because the use of elemental sulfur as a modifier to oil bitumen is currently expanding in the world in order to improve their physical and mechanical properties [2]. The role of elemental sulfur is to change the structure of petroleum bitumen due to reaction reactions with unsaturated components and compounds of petroleum bitumen with the formation of sulfur-containing compounds and supramolecular structures [3]. This circumstance should certainly affect the results of the oxidation of raw materials with the addition of sulfur.

2. Methodology

The vacuum distillation tar of fuel oil of the Ferghana Oil Refinery was chosen as the object of study, the main physicochemical properties of which are presented in *Table 1*. Granular sulfur was used as elemental sulfur, obtained as a by-product in a process unit for hydrodesulfurization of a fraction of diesel fuel (*Table 2*).

Samples of tar with the addition of sulfur in an amount of up to 5% to the tar were prepared as raw materials.

The prepared tar and sulfur samples were oxidized in a 5-liter laboratory unit equipped with a source for air circulation, a thermometer, and a refrigerator for cooling condensate vapor. The charge of oxidation feed was 2 kg.

Oxidation was carried out at a temperature of 230 °C with constant air circulation in the amount of 3 l/min per 1 kg of raw material until the softening point was reached to values that meet the requirements of the current standard.

Table 1. Basic physical and chemical properties of tar

№	Properties	Values
1.	Density , kg/m^3	984
2.	Conventional viscosity at 80°C, sec	16
3.	Flash point, °C	250
4.	Sulfur content,% wt.	2,77
5.	Softening temperature, °C	21
6.	Coking ability , %	7,83
7.	The composition,% wt.	
	oils, including:	60,6
	paraffin-naphthenic hydrocarbons	22,2
	aromatic hydrocarbons	32,7
	resin	37,5
	asphaltenes	6,7

Table 2. Main characteristics of technical sulfur

№	Properties	Temperature °C	
		20	150
1.	Density , kg/m^3	2050	1760
2.	Color	yellow	yellow
3.	Compressive strength, MPa	12 - 22	-
4.	Melting point, °C	119	-
5.	Viscosity, Pa·s	-	0,1
6.	Boiling point, °C	444,8	-
7.	Heat capacity, kJ / kg	0,7	1,84
8.	The degree of purity, %	99,9	

The properties of petroleum bitumen were determined according to the methods adopted for testing viscous road bitumen. The main indicators of the process and physico-mechanical properties of the obtained oxidized bitumen are presented in *Table 3*.

3. Result

It can be seen from the table that the addition of sulfur to the oxidation feedstock, the tar of vacuum distillation of fuel oil, leads to a change in the basic properties of the obtained oxidized bitumen. The resulting oxidized bitumen undergoes mixed changes. At certain optimal sulfur concentrations in the oxidation feedstock, the obtained bitumen possesses higher physical-mechanical and rheological properties compared to bitumen obtained by oxidation of tar only.

Table 3. Key indicators of tar oxidation with the addition of elemental sulfur

№	Indicators	GOST 22245-90 for BND 60/90	Tar sulfur content				
			0	0,5	1	2	5
1.	Needle penetration depth, 0,1 mm: at 25°C at 0°C	61-90 no less 20	81 23	83 24	88 25	84 20	78 18
2.	Elongation, sm: at 25 °C at 0 °C	no less 55 no less 3,5	58 4,2	62 4,5	64 4,3	59 3,8	51 3,4
3.	Softening point, °C	no less 47	49	49,5	49	49	49,5
4.	Fragility temperature, °C	not higher -15	-17	-20	-21	-17	-14
5.	Ductility interval, °C	-	66	69,5	70	66	63,5
6.	Structure coefficient	-	1,14	1,12	1,09	1,12	1,24
7.	Change in softening temperature after heating, °C	no more than 5	3	2	2	2	3
8.	Sulfur content,%wt.	-	2,2	2,7	3,2	4,2	6,9
9.	Oxidation time, hour	-	10	8	8	8	9
10.	The sum of gases and losses, %	-	2,8	2,5	2,3	3,1	3,8

A study of the basic standard properties of oxidized sulfur-bitumen binders showed that the addition of sulfur to the oxidation feedstock within 1% determines the production of bitumen with improved characteristics. The elongation of bitumen increases from 58 to 64 cm, the penetration of oxidized bitumen increases to 88 units, then drops to 78, that is, the hardness of bitumen increases. The brittleness temperature of oxidized bitumen showed an extreme change in the amount of sulfur - first the temperature decreases, and then when the sulfur content is more than 2% it rises to minus 14 ° C.

When the sulfur concentration in the tar is 5% or more, such indicators of bitumen as penetration, ductility, and the brittleness temperature of the oxidized product do not meet the requirements of the current standard.

In addition, at a sulfur concentration of more than 5%, coke is formed on the walls of the reactor, which indicates a decrease in the efficiency of the process. Obviously, the use of sulfur as an additive to oxidation feedstock leads to an increase in the degree of aromaticity of reaction products, an increase in the number of resins and asphaltenes in the reaction mixture, the subsequent interaction of which with sulfur leads to the formation of carbonaceous formations on the walls of the reactor.

The softening point after warming, which characterizes the heat resistance of oxidized bitumen from the addition of sulfur, decreases slightly. This can be explained by the oxidizing effect of sulfur, which, when entering into a dehydrogenation reaction with hydrocarbons, replaces hydrogen atoms and promotes the growth of molecular weight. Dehydrogenated chains undergo cyclization, resulting in an increase in the number of structure-forming complexes such as asphaltenes and other high molecular weight compounds. This, in turn, is accompanied by a change in the group composition of tar: the content of resins and asphaltenes increases, while the content of paraffin-naphthenic hydrocarbons decreases.

It should be noted that the introduction of technical sulfur in the oxidation tar in an amount of up to 2% wt. allowed to significantly intensify the process of its oxidation. At the same time, the duration of tar oxidation at an optimum sulfur content is reduced by 20%. This is important in the direction of reducing the economic constraints of bitumen producing enterprises and increasing the resources of the initial raw materials for the production of oil bitumen with controlled quality characteristics.

4. Conclusion

Thus, the involvement of sulfur in the composition of the oxidation feedstock in the production of oxidized bitumen can be considered one of the most effective technological approaches to intensifying the oxidation process. The introduction of elemental sulfur at optimal concentrations not only accelerates the reaction and improves process efficiency but also leads to the formation of sulfur–bitumen binders with enhanced physical and mechanical characteristics compared to conventional oxidized bitumen obtained from petroleum residues without additives. These improvements include increased ductility and penetration, better structural stability, and a lower brittleness temperature, which are critical for ensuring the operational reliability of bituminous materials in road construction.

Furthermore, this method of feedstock activation contributes to reducing the duration of the oxidation stage and increasing the yield of high-quality product, thereby optimizing resource utilization at refineries. In addition to technological advantages, the use of elemental sulfur — a widely available by-product of oil and gas processing — provides an economically viable and environmentally beneficial solution. Consequently, sulfur modification of oxidation feedstock represents a promising direction for expanding production capacity, improving product quality, and supporting sustainable development in the bitumen industry.

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