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Studying the Influence of Sulfur on the Oxidation Process of Oil Residues

Saydakhmedov Elyorbek Egamberdiyevich

Phd HEAD OF OIL REFINING, PETROCHEMISTRY AND ALTERNATIVE FUELS DEPARTMENT
JSC «O'ZLITINEFTGAZ», TASHKENT, UZBEKISTAN

ABSTRACT:The results of the involvement of sulfur in the composition of the oxidation feedstock of processes for the production of oxidized bitumen were showed. The addition of sulfur to the oxidation feedstock in the optimal amount allows obtaining sulfur-bitumen binders with improved physical and mechanical properties compared to oxidized bitumen obtained from oil residues without adding sulfur.

KEY WORDS: Oil bitumen, sulfur, needle penetration, tar, oxidation process, softening point

I.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.

II. 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.

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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.

III. EXPERIMENTAL RESULTS

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.

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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
5	Change in softening temperature after heating, °C	no more than 5	3	2	2	2	3
6.	Sulfur content,%wt.	-	2,2	2,7	3,2	4,2	6,9
8.	Oxidation time, hour	-	10	8	8	8	9
9.	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

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producing enterprises and increasing the resources of the initial raw materials for the production of oil bitumen with controlled quality characteristics.

IV.CONCLUSION AND FUTURE WORK

Thus, the involvement of sulfur in the composition of the oxidation feedstock of processes for the production of oxidized bitumen can serve as one of the effective directions of its application in order to intensify the oxidation process. At the same time, the addition of sulfur to the oxidation feedstock in the optimal amount allows obtaining sulfur-bitumen binders with improved physical and mechanical properties compared to oxidized bitumen obtained from oil residues without adding sulfur. Moreover, the method of activating the feedstock of oxidation with elemental sulfur, along with improving the important properties of bitumen, will provide additional resources for the production of road oil bitumen.

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