Production of petroleum bitumen by oxidation of heavy oil residue with sulfur

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Abstract. In this paper production of bitumen adding elemental sulfur at oxidation of oil residue are investigated. The objects of research were distilled residue of Karazhanbas crude oil and elemental sulfur. These oil residue characterized by a low output of easy fractions and the high content of tar-asphaltene substances, therefore is the most comprehensible feedstock for producing bitumen. The sulfur is one of the oil product collected in oil extraction regions. Oxidation process of hydrocarbons carried out at temperatures from 180 up to 210 °C without addition of sulfur and with the addition of sulfur (5-10 wt.% ) for 4 hours. At 200 °C oxidation of hydrocarbons with 5, 7 and 10 wt.% sulfur within 3-4 h allows receiving paving bitumen on the mark BND 200/300, BND 130/200, BN 90/130 and BN 70/30. Physical and mechanical characteristics of oxidation products with the addition of 5-7 wt. % sulfur corresponds to grade of paving bitumen BND 40/60. At the given temperature oxidized for 2.5-3 h, addition of 10 wt. % sulfur gave the products of oxidation describing on parameters of construction grades of bitumen (BN 90/10).

1. Introduction

Bitumen is a complex combination of organic liquids that is viscous, black and sticky. It is a complex mixture of high boiling point range of compounds and molecules with a relatively low hydrogen-to-carbon ratio. In the United States the terms asphalt and bitumen are synonymous, while in other areas, e.g. in Europe and Asia, both terms have different meanings [1-4].

According to European Standard EN 12597 definition that the bitumen is a virtually in volatile, adhesive and water proofing material derived from crude petroleum, or present in natural asphalt, which is completely or nearly completely soluble in toluene, and very viscous or nearly solid at ambient temperature, whereas asphalt is defined as a mixture of mineral aggregates and bituminous binder. It is not known to present any safety, health or environmental hazard. Meanwhile, the American Society for Testing and Materials (ASTM) defines bitumen as a generic class of amorphous, natural or manufactured, dark colored, cementitious substances composed principally of high molecular mass hydrocarbons, soluble in carbon disulfide. Asphalt also is defined as a cementitious material in which the predominating constituents are bitumens. The terms bituminous and asphaltic then refer to materials that contain or are treated with bitumen or asphalt [2, 5-7].

A plenty of sulfur is taken during development of oil, gas and gas-condensate fields of Kazakhstan. The collected sulfur in oil extraction regions affect to the environment and health of the population.
Solid elemental sulfur is harmless, but there is an allocation in air more than half of hydrogen sulfide dissolved in liquid sulfur during flood of sulfur in sulfuric cards. The sulfuric dust formed at destruction of sulfur, also renders harmful influence and represents the biggest risk. In this connection there was a problem of utilization of sulfur as its open storage renders negative influence on an environment because of interaction with it. Sulfur is bread of chemical industry, a valued commodity in its own right that’s used in some 30000 products. So it’s should be use other economic roads, similar the oil-gas, cool and metals. One of perspective directions of use of elemental sulfur is road construction - extremely material-intensive branch of the construction industry. Here sulfur can be applied as the modifier of paving bitumen to giving of the improved operational characteristics. Also the sulfur estimated cheapness raw material. The USA spends industrial tests of sulfuric knitting sulfeks (60-70 % of sulfur with hydrocarbons and polymers) from 1979. Sulfur with hydrocarbons, can completely replace asphalt in asphalt concrete [8, 9].

Kazakhstan is the ninth largest country in the world, covering an area of 2717300 km² and government programs have been agreed for the improvement of infrastructure and road construction across the country [10, 11]. Regarding these reason the bitumen consumption is year by year increasing. The main problem with road building is the poor quality of bitumen used in asphalt-concrete pavements.

In our country the satisfaction of need for a bitumen material occurs due to its import Russia and Iran. Characteristics of imported bitumen completely mismatch climatic conditions of our country, i.e. do not maintain sharp differences of temperatures from -40 up to +40 °C. And also with a view of preservation of quality and technological properties, bitumen is not recommended to be transported on greater distances. In this connection, production of bitumen in various marks on the basis of domestic raw material is an actual problem [12]. In this work is proposed use of sulfur collected in oil extraction regions for production of bitumen.

2. Experimental section
The objects of research were distilled residue of Karazhanbas crude oil and elemental sulfur. Crude oil of Karazhanbas oil field is characterized by a low output of easy fractions and the high content of tar-asphaltene substances, therefore is the most comprehensible feedstock among Kazakhstan crudes for production of bitumen. The sulfur is one of the oil product collected in oil extraction regions.

Oxidation process of hydrocarbons carried out at 3 L of cylindrical reactor made by stainless steel. At process, the heated air blowing given to the raw material from compressor. Oxidation of oil residue carried out at temperatures from 180 up to 210 °C without the addition of sulfur and with the addition of sulfur in quantity from 5 up to 10 wt. %. Through the certain time intervals (2; 2,5; 3; 3,5; 4 h) were selected tests of oxidation product.

Penetration involves the determination of the extent to which a standard needle penetrates a properly prepared sample of bitumen under specified conditions of temperature, load, and time. The unit of penetration is 0.1 mm, which is generally omitted in favor of reporting just the measured number. It was determined by a apparatus Penetrometer PNB-03 in accordance with standard 11501-78. Softening temperature – the temperature at which the bitumen of a relatively solid state in to the liquid state. The softening point was determined by the method of "ring and ball" according to standard 11506-73. The penetration index characterizes the degree of penetration of colloidal bitumen or rejection of his status from a purely viscous. It is determined by the empirical formula.

3. Results and discussion
Modification of oil feedstock by elemental sulfur allows making sulfur-bitumen binders with the improved characteristics under soft conditions of experiment [13]. In this connection, in the given work the opportunity of bitumen production by oxidation of oil residue of Karazhanbas oil field with the addition of elemental sulfur. At first, oxidation process tested at low temperature (at 180 °C) and 5-10 weight percentage of sulfur were added into bitumen. But, results of analyses showed that the almost samples on the physical and mechanical characteristics were poor indicator. At 180 °C
necessary values of softening point and penetration under requirements of the standard are reached only at the addition of sulfur in quantity 10 wt. % and time of oxidation 4 h. Therefore, the oxidation temperatures were increased to 200 and 210 ºC and results were shown in the below tables.

Table 1. Physical and mechanical characteristics of the oxidation products of Karazhanbas oil residue with the addition of sulfur at 200 ºC.

| Amount of sulfur added to oil oxidation, mas. % | 0  | 5  | 7  | 10 |
|-----------------------------------------------|----|----|----|----|
| Oxidation time, hour                          | 3  | 3,5| 4  | 3  |
| The depth of penetration of the needle into the bitumen at 25 ºC, 0.1mm: | 295| 205|156|206|
| Softening point, ºC, not less:                | 40 | 42 |44 |41 |
| Brittleness temperature, ºC, max:             | -  | -21| -23| -25|
| Penetration index                             | 2,3| 0,9| 0,4| 0,5|
| Standard accordance                           | BND| BND| BND| BND|

Table 2. Physical and mechanical characteristics of the oxidation products of oil residue at the temperature 210 ºC with sulfur.

| Amount of sulfur added to oil oxidation, mas. % | 0  | 10 |
|-----------------------------------------------|----|----|
| Oxidation time, hour                          | 2  | 10 |
| The depth of penetration of the needle into the bitumen at 25 ºC, 0.1mm: | 255| 225|155|105|
| Softening point ring and ball, ºC, not less: | 16 | 23 |31 |36 |
| Standard accordance                           | -  | -  |BN |BN |
| Amount of sulfur added to oil oxidation, mas. % | 5  | 7  |
| Oxidation time, hour                          | 2  | 10 |
| The depth of penetration of the needle into the bitumen at 25 ºC, 0.1mm: | 27 | 6  |202|123|
| Softening point ring and ball, ºC, not less: | 32 | 37 |40 |46 |
| Brittleness temperature, ºC, max:             | -  | -  |18 |18 |
| Penetration index                             | -1,4| -1,9| -1 |-0,2|
| Standard accordance                           | BND| 40/60|BND|40/60|
Apparently from the table 1, the values of softening point and penetration of oxidation products without the addition of sulfur at all investigated temperatures mismatch requirements of the standard. At 200 °C oxidation of hydrocarbons with 5 and 7 wt.% sulfur within 3-4 h allows receiving paving bitumen on the mark BND 200/300, BND 130/200 and BN 90/130. At increase in the content of sulfur up to 10 wt. % physical and mechanical parameters sharply differ and come nearer to norms of construction bitumen (BN70/30).

The technical parameters of oxidation products, which formed at a temperature of 210 °C were significantly changed than the products obtained at a temperature of 200 °C. This occurs due to an increase the oxidation rate when increasing the temperature.

The data on compliance of physical and mechanical characteristics of oxidative products with the standard at the temperature 210 °C are given in table 2. As shown the tabulated dates, the oxidation products which without adding sulfur do not meet the standard on physical and mechanical properties. Physical and mechanical characteristics of oil residue oxidation products with the addition of 5-7 wt. % sulfur corresponds to grade of paving bitumen BND 40/60. At the given temperature oxidized for 2.5-3 h, addition of 10 wt. % sulfur gave the products of oxidation describing on parameters of construction grades of bitumen (BN 90/10).

Physical and mechanical characteristics of oxidized bitumen were compared. The road bitumen’s main characteristics are penetration and softening temperatures. They determine the consistency and application areas of bitumen. Dependence or changing of bitumen properties on the oxidation time at the 210 °C are showing in figure 1 and figure 2.

![Figure 1](image1.png)

**Figure 1.** Dependence of penetration on the oxidation time of products at the 210 °C.

![Figure 2](image2.png)

**Figure 2.** Dependence of softening point on the oxidation time of products at the 210 °C.

When oxidizing oil residue without adding sulfur, within 2 hours the product's softening temperature increased from 16 to 41 °C, ie the growth is 25 °C (figure 1). Meanwhile softening temperature sulfur of oxidation products with sulfur had higher. During this time, ST of bitumen adding 5 wt. % of sulfur increased from 32 to 53 °C and adding 7 wt. % of sulfur increased from 44 to 62 °C. As seen from figure 2, with increasing content of sulfur from 5 wt. % to 10 wt. % in these processes, the penetration of sulfur bitumen were decreased. Consequently, as the amount of sulfur in the mixture increases, the rate of oxidation of the oil is considerably reduced. The softening temperatures of the 10 % sulfur-added bitumen were increased by 26 °C in 2 hours (from 82 °C to 108 °C). In this case, the softening temperature increases rapidly, and the penetration decreases only slightly.
Thus the all results of oxidation process showed that the oxidation products exhibit elasticity, increased softening point, decreased penetration and enhanced strength. It means the sulfur influenced to oxidation of hydrocarbons as oxidizer.

4. Conclusion

Obtained data allow making the conclusion that the addition of elemental sulfur leads to reduction of time of process of oxidation and mitigation of regimes of process. The results of researches have shown, that oxidation of high-viscous oil residue with the addition of elemental sulfur (5-10 wt. %) at low temperatures (200 and 210 °C) for short time (3.5-4 hours) can receive bitumen of satisfactory quality. The resulting of oxidation process exhibit elasticity, increased softening point, decreased brittle point, and enhanced strength. These properties allow sulfur bitumen products to be used both as binders for asphalt concretes and as mastics for pavement repair. Also, it allows partially solving the problem of utilization of sulfur which collected in oil extraction regions.

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