Production of Improved Oil Bitumen of European Quality

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Abstract. The possibility of obtaining bitumen of improved quality from oil mixtures of the newly developed Vankor and West Siberian fields of variable composition was described in the article. The optimal hydrocarbon composition of raw materials was formed and the technological parameters of the oxidation process were selected to obtain improved bitumen of sonochemical activation, which provided high plasticity and thermal stability of bitumen while maintaining low-temperature properties. The group hydrocarbon composition of tars was determined by the method of liquid-adsorption chromatography with gradient displacement. The fuel oil sample obtained during the processing of given oils and oil residues of different oil fractions sampling depth was used for carrying out the research. The obtained cubic residues were oxidized at a laboratory unit for production of oxidized petroleum bitumen under conditions of sonochemical activation simulating the technology of obtaining oxidized bitumen under industrial conditions. The loading of the laboratory cube for oxidation was 2.8 kg of tar, experiments were carried out under the following conditions: temperature 250±2 °C, air flow 4.0±0.1 l*min/kg with periodic sampling for monitor the quality of the oxidized product at the softening temperature.

1. Introduction

Almost every oil produces a heavy residue when heated and separated, from which bitumen can be obtained. However, the structure and properties of the bitumen, depending on the nature of the feedstock and the installed production process, will be different, as different percentage of the heavy oil residue outcome from the total amount of processed oil. So, for example, bitumen of foreign producers, obtained by vacuum distillation technology from the most favorable for bitumen production of heavy high-tar oils, differ in terms of the complex properties from most bitumen of Russian production obtained by oxidation of heavy residues of oil mixtures, characterized as light, low-sulfur, low-tar. In addition, the experience of using road bitumen of foreign production in Russia such as, for example, Ninas, Neste, showed that the operational reliability of asphalt concrete is much higher when using bitumen of foreign firms. Due to the fact that the task of import substitution is now a priority in the oil refining industry, the development of technologies for the production of bitumen binders, on the complex of physical, chemical and rheological properties as close as possible to foreign road bitumen is the most relevant.

It is known that the properties of bitumens, produced in different oxidizing devices, can vary [1]. Previously, we found that the use of ultrasound [2-9] promotes acceleration and intensification of physical and chemical processes in liquids and improves the rheological properties of road construction materials [10-17]. It is known that the properties of bitumens can also be influenced by
another way — increasing the selection of the distillate in the preparation of tar for oxidation or involving various components in the oxidation raw material [18].

The possibility of obtaining bitumen of improved quality from oil mixtures of the newly developed Vankor and West Siberian fields of variable composition, not previously mentioned. The content of Vankor oil in the oil mixture ranges from 20-25 % wt., West Siberian oil is mainly included in the remaining part. Oil mixture refers to paraffin, resinous, low-sulfur oils. The amount of asphaltenes and tars in oil mixtures is not more than 9-10% wt, the content of paraffins is 3.5-5% wt., sulfur 0.5-0.6% wt. The extensibility of the bitumen produced from these oils is within the lower limits of the standards due to the low resin content at a relatively high content of paraffin-naphthene hydrocarbons (including paraffins), which is accompanied by a deterioration of bitumen adhesion to mineral coatings. The low sulfur content of oil facilitates the production of high-quality fuel distillates, but negatively affects the properties of oxidized bitumen, slowing the formation of asphaltenes [19].

2. Experimental part
The purpose of this work is to form the optimal hydrocarbon composition of raw materials and technological parameters of the oxidation process to obtain improved bitumen, taking into account the nature of the processed oil mixture. Studies carried out earlier [20, 21] have shown that a decrease in the content of paraffin-naphthenic hydrocarbons and an increase in aromatic hydrocarbons in the oxidation raw material leads to an increase extensibility and thermo-oxidative stability of oxidized bitumen. At the same time, there is a deterioration of the low-temperature properties of oxidized bitumen with a decrease in the share of paraffin-naphthenic hydrocarbons. This implies the need to optimize the hydrocarbon composition of the raw material, which will provide high plasticity and thermal stability of bitumen with preservation low-temperature properties.

The fuel oil sample obtained from the processing of these oils as well as oil residues of different oil fractions depths obtained on its basis were used as basic samples for research. The oil fractions were selected by vacuum distillation according to ASTM D 5236 using a Fischer apparatus. The obtained heavy bottoms were oxidized in a laboratory unit for production of oxidized petroleum bitumen under conditions of sonochemical activation, simulating the technology of obtaining oxidized bitumen in industrial conditions. All laboratory experiments were carried out under the same conditions: the temperature of 250 ± 2°C, the air flow rate of 4.0 ± 0.1 lpm/kg with periodic (every hour) sampling to control the quality of the oxidized product at the softening temperature. The loading of the laboratory cube for oxidation in all cases was 2.8 kg of tar. The group hydrocarbon composition of tar was determined by liquid-adsorption chromatography with gradient displacement on the “Gradient-M chromatograph” [22].

Table 1 presents the results of the study of physicochemical properties and the group hydrocarbon composition of heavy oil residues derived from fuel oil.

3. Results and discussion
A comparative analysis of the data in Table 1 shows that with an increase in the selection of oil fractions from fuel oil from 480 °C to 560 °C, the nominal viscosity (NV₈₅) of tar increased from 22 to 170 s. In the group hydrocarbon composition, as the tar grows heavier, paraffin-naphthenic hydrocarbons are reduced from 27 to 10% by weight, tars accumulate, and a slight increase in aromatic hydrocarbons (from 44 to 47% by weight) is observed. The most noticeable increase in the proportion of aromatic hydrocarbons in the region of heavy aromatics is observed in residues with a sampling depth of> 520 °C and higher. The authors of [23] showed that the packing density of tar and bitumen in their complex structural units (micelles) is higher and, accordingly, the bitumens obtained on such tars will be distinguished by increased thermostability when polycycloarenes predominate among the aromatic hydrocarbons included in the oils (heavy aromatic hydrocarbons). It is specially noted that to obtain a thermostable bitumen, a certain ratio between oils, tars and asphaltenes is required. As the ratio of asphaltenes to tars (A/T) and asphaltenes to oils (A/O) increases, the strength
of the colloidal bitumen structure increases in the raw material, the thermal stability of bitumen increases.

**Table 1.** Results of the study of physicochemical properties and the group hydrocarbon composition of heavy oil residues derived from fuel oil.

| Indicators | Heavy Oil Residues, Fraction |  >480 °C | >500 °C | >520 °C | >540 °C | >560 °C |
|------------|-------------------------------|---------|---------|---------|---------|---------|
| Nominal Viscosity at 80 °C, s | | 22,0 | 38,1 | 67,9 | 84,9 | 170,2 |
| Kinematic Viscosity at 80 °C, mm²/s | | 466,9 | 882,2 | 1381 | 1785 | 3680 |
| Density, g/cm³ | | 0.952 | 0.957 | 0.973 | 0.979 | 0.987 |
| Needle Penetration Depth at 25 °C, 0,1mm | | >500 | >500 | >500 | >500 | 308 |
| Ring-and-Ball Softening Point, °C | | 24,0 | 24,7 | 26,3 | 28,6 | 33,3 |

**Group Hydrocarbon Composition, % wt.**

| Oils, including.: (O) | 70,5 | 67,7 | 64,4 | 61,3 | 56,7 |
| Paraffin-Naphthene Hydrocarbons (PNH) | 26,7 | 22,5 | 18,3 | 14,9 | 9,8 |
| Aromatic Hydrocarbons (AH) | 43,8 | 45,2 | 46,1 | 46,4 | 46,9 |
| Light Aromatic Hydrocarbons (LAH) | 9,1 | 8,2 | 6,7 | 5,1 | 4,4 |
| Medium Aromatic Hydrocarbons (MAH) | 10,0 | 6,4 | 5,1 | 4,2 | 3,6 |
| Heavy Aromatic Hydrocarbons (HAH) | 24,7 | 26,3 | 34,3 | 37,1 | 38,9 |
| Tars (T) | 24,7 | 27,3 | 28,2 | 28,5 | 29,5 |
| Asphaltenes (A) | 4,8 | 5,0 | 7,4 | 10,2 | 13,8 |

Table 2 presents the results of the study of physicochemical properties of bitumen samples obtained by oxidation of heavy oil residues under conditions of sonochemical activation.

**Table 2.** Results of the study of physicochemical properties of bitumen samples obtained by oxidation of heavy oil residues under conditions of sonochemical activation.

| Indicators | Standard for bitumen | Sample №1 | Sample №2 |
|------------|----------------------|------------|------------|
| Number of samples | 50/70 | | |
| 1. Needle Penetration Depth, 0,1 mm | | | |
| at 25 °C | 50-70 | 63 | 66 |
| at 0 °C | no standards are applicable | 24 | 23 |
| 2. Ring-and-Ball Softening Point, °C | 46-54 | 52,9 | 51,0 |
| 3. Expansibility, cm | no standards are applicable | 95 | 143 |
| at 25 °C | no standards are applicable | 3,6 | 3,7 |
| at 0 °C | not less than 230 | >300 | >300 |
| 4. Flash Point | not less than 145 | 482 | 384 |
| 5. Dynamic Viscosity at 60 °C, Pa·s | not less than 295 | 506,9 | 466,1 |
| 6. Kinematic Viscosity at 135 °C, mm²/s | not higher than -8 | -23 | -23 |
| 7. Brittleness Temperature, °C | from -1,5 to + 0,7 | 40,2 | -0,6 |
| 8. Penetration Index | not more than 9 | 4,6 | 5,0 |
| 9. Change in Softening Temperature, °C, after heating in accordance with State Standard 18180 | not less than 99,0 | 99,9 | 99,9 |
| 10. Dissolvability, % | no standards are applicable | 0,03 | 0,06 |
| 11. Mass Change, % | not more than 0,5 | 71 | 68 |
| 12. Needle Penetration Depth at 25 °C, % from the original value | not less than 50 | | |
| 13. Expansibility, at 25 °C, cm | no standards are applicable | 28,0 | 41,3 |
| 14. Dynamic Viscosity at 60 °C, Pa·s | no standards are applicable | 1343 | 1108 |
| 15. Dynamic Viscosity Increasing Coefficient | no standards are applicable | 2,8 | 2,9 |
The extensibility of oxidized bitumens changes intensively in the process of thermal oxidative aging, determined after heating in a thin film by the RTFOT method under the influence of air oxygen at a temperature of 163 °C. This indicator is most important for bitumens obtained by oxidation of raw materials from paraffin oils with low tar content. To determine the relations between the physical and chemical properties of oxidized bitumens (at the same softening temperature of 51 °C) and the ratios of A/T and A/O in tar of different viscosities presented in Figure 1.

[Figure 1. Dependence of the physical and chemical properties of oxidized bitumens on the ratios A/T, A/O in tar of different viscosities.]

The most intensive increase in A/T and A/O ratios (twice as much as the initial values) is observed in the transition to tar with a sampling depth of >520 °C, which corresponds to NV₈₀ for more than 68 s. The thermal stability of bitumens obtained by oxidizing tars with a viscosity of more than 68 s (fractions > 520 -> 560°C) is higher compared to bitumens obtained on light tar (22-38 s). The high thermal stability is indicated by an extensibility increase of more than two times after heating of the bitumens obtained by oxidation of tar NV₈₀ for more than 68 s (fractions> 520 -> 560°C). However, in the viscosity range 85 - 170 s, the most intense increase in the brittleness temperature of oxidized bitumens occurs (from -22°C to -12°C). Consequently, an increase in the depth of selection is possible up to a fraction of not more than 540°C, which corresponds to NV₈₀ not more than 85 s. The stretchability of bitumen after heating in a thin film by the RTFOT method obtained on the NV₈₀ tar is 85 s that corresponds to indicators for improved bitumen (45 cm) [23].

All tar samples with different depths of selection and viscosity were analyzed for Conradson carbon residue with a percentage of outcome reflected in terms of fuel oil (Figure 2).

A sharp rise in the tar carbon residue is observed in the region of increase in the tar viscosity from 85 to 170 s (Fig. 2). Naturally, with an increase in the selection of oil fractions in the temperature range from 540 to 560°C, the conversion of tar (by 7% wt) is maximally reduced, which ultimately will affect the reduction of the raw material base of the bituminous block.

The results of laboratory tests indicate that the optimum raw material for obtaining improved bitumen is the residue with a viscosity of 70-80 s. These residues were used to obtain bitumen samples on a laboratory plant for the production of oxidized petroleum bitumen under conditions of sonochemical activation.
Samples of bitumen taken during the tests at the laboratory plant for the production of oxidized petroleum bitumen under conditions of sonochemical activation preserve the necessary margin of quality after the aging test. Dynamic viscosity at 60 °C, characterizing the deformation resistance of bitumen, and together with the penetration depth and kinematic viscosity at 135 °C - the thermal sensitivity of bitumen, are positioning at a high level. According to these indicators a preliminary assessment of the durability of road surfaces can be predicted [23, 24]. Thus, the resulting bitumen samples have a high quality margin at the softening point and dynamic viscosity and can be used as a bituminous basis for compounding.

The results of carried out tests (Table 2) showed that the quality of the produced bitumen samples fully complies with the European norms for road bitumen, and by a number of indicators it considerably exceeds the requirements of the European Standard. The reduced brittleness temperature and high dynamic viscosity characterize the resulting bitumen as the most suitable for roads laying in a climate similar to Russian Federation's climate, characterized by significant temperature changes in summer and winter.

4. Conclusion
This paper shows the potential for the production of European quality improved bitumen. The optimal hydrocarbon composition of the raw material was formed to obtain improved bitumen under conditions of sonochemical activation. In order to reduce coke formation and improve the thermal stability of oxidized bitumens, the temperature of the oxidation process was reduced by 30°C from the standard process mode. The change did not affect the process, cause tar with NV<sub>80</sub> 70-80 s contains 1.5 to 2 times more asphaltenes and heavy polycyclic aromatic compounds, the formation of which requires a high temperature in the oxidation of low-viscosity tar.

These technological measures to increase the viscosity of tar lead both to a reduction in energy costs and provide a higher content of aromatic hydrocarbons, since they are most active (usually with a conversion of up to 60%) enter into an oxidation reaction. The fact that aromatic hydrocarbons are contained in sufficient amount in the oxidized tar makes it possible to exclude the stage of appending highly flavored products into oxidized bitumen and, thereby, substantially simplify the process.

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Acknowledgments
The research was supported by the Ministry of Education and Science of the Russian Federation within the framework of the agreement 14.577.21.0209, the unique identifier of the agreement – RFMEFI57716X0209.