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Characteristics Evaluation of Modern Bituminous Binders in Group Hydrocarbon Composition and Their Application in Construction

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Abstract

The article is the result of theoretical and experimental studies aimed at determining the structural groups of modern bituminous materials in order to assess the raw materials, production technology, rational directions for their use in construction, the road industry and waterproofing. Commercial oil bitumen, raw tars and heavy oil residues (semi-finished products) of oil refineries aimed at meeting large-tonnage needs have been studied. The assessment was carried out according to the group hydrocarbon composition, by liquid chromatography using model compounds. Comparative analysis showed a general trend for all studied samples of petroleum bitumen: low content of asphaltenes (from 3.9 to 23.9 wt.%), low content of resins (from 11 to 19.07 wt%), insufficient for the formation of stable structuring layers, and a significant content of aromatic hydrocarbons, including heavy aromatic compounds (more than 20 wt.%). An assumption was made about the influence of the origin and the structure obtained during the processing of asphaltenes and resins on the transition from one type of bituminous structure to another based on the lyophility of high-molecular group components. A comparative structural characteristic of heavy oil residues from gasoline and oil production is considered in comparison with bitumens of various viscosities. Recommendations are given on the technology of processing petroleum feedstock and the use of heavy oils in order to obtain a given bitumen structure for the production of rational bitumen products for construction and waterproofing.

Keywords

Bitumen, Tar, Construction, Waterproofing, Oil Refining, Group Hydrocarbon Composition, Viscosity, Asphaltenes

1. Modern Specifics of Bitumen Binders

Bitumen as an accessible raw material formed as a result of the natural course of oil refining into light oil products is an outdated definition that does not correspond to modern realities. Modern bitumen is a residual product of oil refining, as a rule, not a target product in terms of hydrocarbon composition, the technical characteristics of which are "finished" by oxidation with atmospheric oxygen at 220˚C - 250˚C and/or compounding.

Today, with the commissioning of large-scale delayed coking units for heavy oil residues (DCU HOR) at oil refineries of the fuel profile, there is a narrowing of the range and physical mass of available hydrocarbon feedstock for the production of bitumen. That is, since the depth of processing for light (marginal) oil products is 97% - 98%, there is no quality raw material in the required quantity for the production of bitumen.

Large-tonnage production of modern bitumen is carried out according to the following scheme. Straight-run tar or fuel oil (a highly demanded raw material that is directly processed into gasoline and diesel fuel using thermal and catalytic destructive processes), to obtain bituminous materials, must be separated and removed from the technological chain for the production of marginal (light) types of petroleum products. At the same time, the customer of bitumen in its price, as it were, pays for the cost of diesel fuel and gasoline, which would be produced from a given volume of raw materials (tar) necessary for the production of bitumen at his request. In the context of rising fuel prices, the cost of bitumen is steadily growing, and its quality is steadily declining due to the narrowing of the raw material base. In this situation and in a rather monopolized oil industry, the regulatory possibilities for resolving this issue (for example, by the state) are reduced.

A rational direction could be the processing of heavy oils [1] [2], with the yield of light oils up to 10% - 15%, processed using a technology similar to NYNAS. The experience of its application since 1990 and studies of the USSR period [3] indicate the prospects for processing heavy oils and bituminous rocks into building, insulating, and road bitumen materials.

A rational way out of the emerging trend in oil refining can be the search for alternative sources of bitumen raw materials that most fully meet the technology of bitumen production and the quality of the finished bitumen material [4]. Let us further consider a comparative characteristic of the group hydrocarbon composition of modern petroleum road bitumen (BND), heavy oil residue (HOR), heavy tar and products of its processing.

2. Methods for Studying the Composition of Bituminous Binders

It is known that bitumens with similar rheology, viscosity-temperature characteristics (Viscosity *η*; Softening point T_s R&B; Penetration, P_{25}) may have different physicochemical and operational properties. This is due to the different origin, raw material composition and method of obtaining a particular bitumen. Modern methods, such as RTFOT and PAV, are designed only to cut off the volume from the total batch of bitumen, which will potentially give a guaranteed reject at the process temperature and on the coating. The scientifically substantiated choice of raw materials, production methods and resulting internal properties of bitumen remains their structural analysis, determined on the basis of group hydrocarbon composition (HCC) data.

The study of bitumen HCC is a rigorous scientific, time-consuming, complex analytical test and is carried out through solid-phase selective analysis [5] [6] [7], solid-liquid and liquid chromatography [8] [9] [10], solubility method [11] and the "Yatroscan" method [12]. Methods for studying the HCC of bituminous materials, as a rule, take significant periods of time, require instrumentation, highly qualified specialists, and cannot be used in general construction laboratories specializing in incoming and operational control. However, the study of HCC is of considerable interest in scientific research and in determining the raw material base of refineries, bitumen production, choosing one or another oil refining scheme, and obtaining bitumen materials of a given quality.

HCC of Bitumen Binders

Due to the complexity of the structure, it is rather difficult to isolate any individual compounds from the composition of bitumen, with the exception of paraffins. Therefore, bitumen is divided into groups of components that differ in their solubility [2] [10] [11]. The main groups of compounds in bitumen, which differ in molecular weight and solubility in certain hydrocarbon solvents, are: oils (hydrocarbons), resins, and asphaltenes (high molecular weight non-hydrocarbon compounds [11]). The oils are released [10]: paraffin-naphthenic hydrocarbons; light, medium, heavy, aromatic. Resins are divided into benzene, alcohol-benzene. Asphaltenes are the highest molecular weight branched products of resin compaction.

The results of the physicochemical analysis of the series of the studied samples of bitumen and heavy oil residues are presented in **Table 1**.

Resins and oils are usually combined under the general name of maltenes. From the point of view of adhesive and structuring (strength) properties of binders, the ratio of resinous-asphaltenic substances (RAS) is important for bitumen.

The nature and origin of the molecules of individual groups (resins and asphaltenes) plays a significant role in adhesion, cohesion, and physicochemical stability. However, it does not cancel the established patterns of bitumen structure. And, on the contrary, it illustrates them well if they are obtained in various

Table 1. Physical and chemical analysis and group hydrocarbon composition of oil bitumen, raw materials and HOR[a].

Indicator		Bitumen binders				
	GOST/ASTM	Tar AVT2	APD 36/30	VCCR	BND 70/100	BN 70/30
T_s, ˚C, R&B	11506-73	38	42	45	47	70
Density, kg/m^3	3900-85	1008	1010	1012	1022	1024
Sulfur total, %	4294-03	2.74	2.34	1.25	-	-
Viscosity η 120˚C, mPa·sec	2919	358.0	367.5	380.2	452.7	495.3
Crystalline paraffin, %	17789-72	1.62	0.86	-	-	-
Group hydrocarbon composition (HCC) data, wt.%						
Paraffin-naphthenic	GrozNII	11.76	6.94	8.6	12.3	12.9
Monoaromatic (light)		14.87	15.09	8.7	11.2	5.1
Bicyclic (medium)		19.87	23.57	11.6	8.6	9.5
Polycyclic (heavy)		38.42	34.97	42.3	35.4	20.2
Benzene resins		14.85	19.08	1.9	10.3	9.5
Alcohol-benzene resins		-	-	14.0	13.0	18.9
Asphaltenes	BashNII	8.93	5.85	3.9	9.2	23.9

[a]HOR—heavy oil residues of refineries. Tar AVT 2—straight-run tar, accumulating at the base of the installation of atmospheric vacuum tubing (AVT); APD 36/30—propane deasphalting asphalt of oil block tar deasphalting unit (process name 36/30); VCCR—vacuum residue of the thermal cracking unit; BND 70/100—Refinery road bitumen grade 70/100 (P_{25} = 70 - 100, 0.1 mm); BN 70/30—Refinery building bitumen grade 70/30 (T_s R&B 70˚C - 80˚C/P_{25} 21 - 40, 0.1 mm). Samples of oil binders were taken at the production (refinery): Perm, Nizhny Novgorod, Ufa, Omsk and tested for the period 2018-2023.

ways and characterized according to the criteria of the indicated structures during the transition from one structure to another [13]. The quantitative ratio of RAS and their properties determine the structure of the bituminous substance as a dispersed system [5] [13].

3. Bitumen Structure

Traxler Ralph N. [14] for the first time divided bituminous materials according to the group composition and the degree of peptization of asphaltenes into gel, sol, and sol-gel.

Subsequently, bitumens of equal penetration, but of different categories, were assigned to different rheological types. A.S. Kolbanovskaya and V.V. Mikhailov proposed [5] to divide bitumen into three types according to their dispersed structure. This idea formed the basis for the division of bitumen into construction, road and insulating bitumen—which is still used today. At present, the bitumen structure is presented as a dispersed system with a dispersed phase of asphaltenes and a dispersion medium of resins and hydrocarbons [3] [4].

Figure 1 shows the classification of the structural types of bitumen, which clearly shows the ratio of resin oils and asphaltenes in relation to the conditional groups gel (I), sol (II) and sol-gel (III).

Type I structure (Gel) is a coagulation network—a framework of asphaltenes in a dispersion medium weakly structured by resins, which consists of a mixture of paraffin-naphthenic and aromatic hydrocarbons. Bitumens of the gel group are characterized by an increased softening point and a lower brittleness temperature. At the same time, they are able to exfoliate, are characterized by a high aging rate, and have low extensibility.

The structure of type II (Sol) is an extremely stabilized dilute suspension of asphaltenes in a dispersion medium highly structured by resins. Asphaltenes, not connected and not interacting with each other, adsorb resins, transforming them into a film state with increased viscosity and strength.

Bitumens of structural type III (Sol-gel) have intermediate properties and are recommended for use on roads, especially high technical categories.

The structure of the forming dependence is the maximum concentration of asphaltenes when passing through which the properties of bitumen change abruptly. At the same time, the properties within the specified ranges of influence are stable, are in good agreement with the method of application of this bitumen, fully meet the quality criteria (atmospheric, fatigue, temperature resistance) that apply to construction, road and insulating bitumens.

An important circumstance is the lyophilicity of asphaltenes. Asphaltenes isolated from thermal cracking residues are the most lyophobic, and the critical concentration occurs much faster. For asphaltenes of residual, weakly oxidized, and oxidized bitumens with similar degrees of lyophilicity, the critical concentration for the formation of a coagulation skeleton is approximately the same, which indicates close values of the effective sizes of solvate shells. This is consistent with the positive experience of using natural bitumen and oxidized bitumen with a similar group hydrocarbon composition.

4. Evaluation of the Structure Modern Bituminous Binders

Unfortunately, the data on the group hydrocarbon composition of bitumen produced by large manufacturers indicate that it is impossible to attribute them to a certain structure, Figure 2. Along with commercial bitumen, heavy oil residues and components are shown in order to represent the current trend and the raw material picture that accounts for to deal with when drawing up a plan for their production.

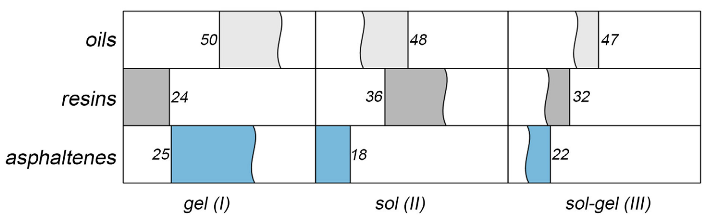
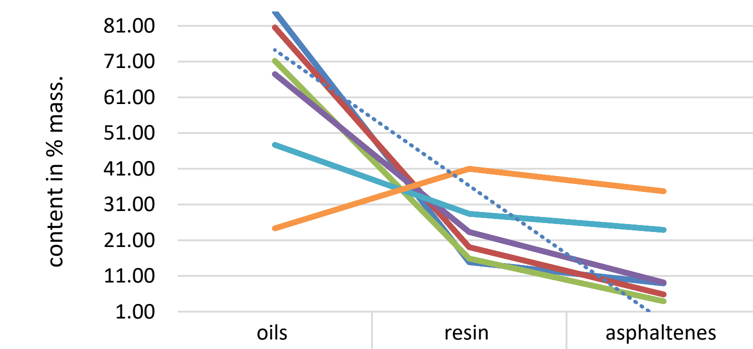


Figure 1. Distribution of the ratio of group hydrocarbon components in road, construction and insulating bitumens according to Kolbanovskaya A.S. [5].



	oils	resin	asphaltenes
straight-run tar	84.92	14.85	8.93
deasphalting asphalt	80.57	19.08	5.85
vacuum cracking residue	71.20	15.90	3.90
road bitumen	67.50	23.30	9.20
soft construction bit.	47.70	28.40	23.90
solid construction bit.	24.30	41.00	34.70

Figure 2. Structural analysis of large-tonnage oil binders: raw materials, commercial bitumen and heavy oil residues (HOR)—summary oils, resins and asphaltenes.

The nature of the trend (dotted line) for oil binders of the same degree of asphaltene peptization is similar, with the exception of deeply oxidized construction grades of bitumen. They are given for a visual understanding of the relationship and differences in the structural analysis of oil bitumen with different rheological characteristics.

All oil binders are characterized by an extremely low asphaltene content. When considered as the second structural group (II), they are characterized by a too high oil content and at least two times lower resin content. Obviously, from the point of view of production, we are dealing with a technological chain that is not oriented towards the production of high-quality bitumen. When each subsequent refinery process selects hydrocarbons of interest to it in order to maximize profitability, without regard to what quality the residue will be transferred to the next technological process.

And since it is known that our common path still ends in a delayed coking unit (DCU) with the production of additional fractions of diesel fuel, gasoline and petroleum semi-coke, we do not need bitumen production.

The directions of modern modification with polymers cannot have a significant effect on the structure of bitumen, since the types of polymers that are widely used do not increase the content of asphaltenes. Moreover, when modifying modern bitumen with polymers such as SBS, Elvaloy, Honeywell Titan, they often do not give the desired increment. Apparently, the indefinite—unstable structure of bitumen, planned for modification, ultimately plays its decisive role. Thus, we can conclude about the chosen path for the development of bitumen on the products of refineries of the fuel profile and technical regulation with a large-tonnage demand for bitumen.

5. Scientific and Technical Substantiation in Natural Bitumen and Heavy Oil Processing Products

Modern design requirements for the operation of a road surface in Russia using a polymer-bitumen binder and traditional bitumen range from 3 to 5 years. This norm is fully justified by the experience of overhaul periods and the actual operation of roads.

The use of natural bitumen is widely known in the art. The confirmed service life of road bitumen in coatings of various traffic intensity and climatic conditions ranges from 12 to 24 years [3] [7] [15]. Studies of the physicochemical properties of bitumen obtained from heavy oils, monitoring of asphalt concretes with their use [2] [3] [15], confirms the period of maintenance-free operation of 6 - 12 years.

Achieving the group hydrocarbon ratio of the bitumen components into the desired range of the bitumen structure can show an improved result when used in construction, road or insulation applications. On the other hand, the more native origin of asphaltenes of the bitumen under consideration, due to their greater lyophilicity, can have a structuring effect on the thickness solvate shells of asphaltene associates, and, as a result, a more correct transfer of the internal physical properties of the bitumen structure.

To confirm our reasoning, we plan to conduct additional studies with heavy tar from the Yaroslavl Pilot Petroleum and Oil Plant named after D.I. Mendeleev (OPNMZ, Yaroslavl). A comparison of traditional tars, OPNMZ tars and the recommended feedstock structure for bitumen production is shown in **Figure 3**.

The specificity of this raw material is not outstanding, the content of paraffin-naphthenic hydrocarbons is too high and the content of asphaltenes is low. However, we will consider the possibility of a shallow impact of processing technology on raw materials and modification additional additives into bitumen.

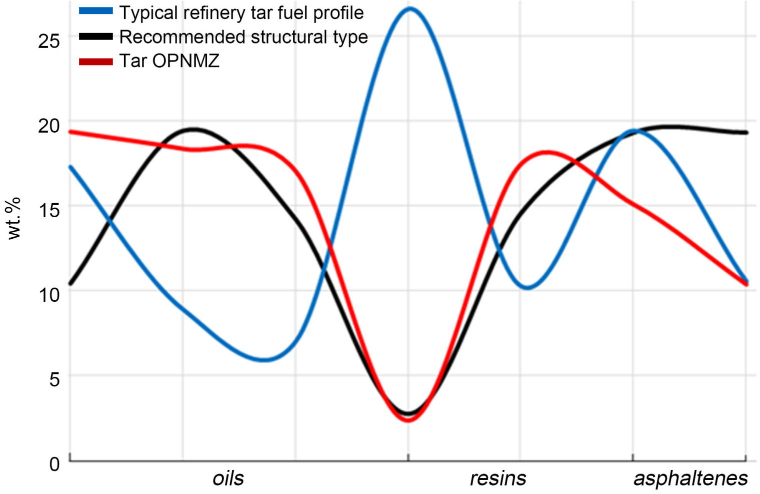


Figure 3. Comparison of traditional tars, OPNMZ tars and recommended feedstock structures for bitumen production—deterministic oils, resins and asphaltenes.

An intermediate determination of HCC phase transitions during the processing of this raw material is planned.

The program of experiments provides for the isolation of asphaltenes from this raw material in order to assess their lyophilic properties and compare with other large-capacity industrial products, and HOR. According to the modified solubility method of VNII NP for this task, the final step will be to check the compliance of the technical properties of these bitumen and asphalt concrete with modern test methods for waterproofing membranes, bituminous binders and asphalt concrete.

6. Conclusions

Petroleum bituminous materials are complex high-molecular colloidal systems, the structure of which is determined by the amount, ratio and structure of resins and asphaltenes. Group hydrocarbon composition data of raw materials and processed products makes it possible to obtain waterproofing and bituminous materials with specified performance properties, aging resistance and durability in building and road structures. An important issue for further research is the evaluation of the properties of asphaltenes isolated from raw materials of various origins.

In modern conditions of bitumen production at refineries operating on a fuel scheme, there is a negative trend in obtaining bituminous materials with a low content of asphalt-resinous substances (asphaltenes—less than 10 wt.%). It is necessary to apply compounding technology more widely, use asphalt-resin concentrates (heavy oils, asphaltites, HORs with a high RAS content) to obtain high-quality building and waterproofing materials with a stable and semi colloidal structure (gel, gel-sol). Asphaltene content at the final stage of production should be not less than 20 wt.%.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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