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Synthesis and properties of bitumen from the residues of 'charcoal oil'

Z. Kairbekov*, N. Smagulova, E. Aubakirov and J. Myltykbaeva

For the first time, the liquid road bitumen is obtained from the residues formed after hydrogenation of charcoal of 'Karazhyra' mine field. According to the values of physical–mechanical indicators, obtained bitumen corresponds to the bitumen of mark MG70/130. Chemical composition of obtained bitumen: 64% mass, paraffin–naphthene hydrocarbons; 13·48% mass, asphaltenes; 21·75% mass, resins. The viscous road oil bitumen is obtained by oxidation of liquid road bitumen, corresponding to bitumen of mark BND130/200 in terms of physical–mechanical indicators.

Keywords: Bitumen, Residues of 'charcoal oil', Coal

Introduction

Republic of Kazakhstan is abundant in deposits of hydrocarbon flammable raw materials sources. While the deposits of oil are concentrated primarily in the western regions, mining sites of solid hydrocarbon sources are found in various regions of the Republic of Kazakhstan and are intensively developed.

The preparation from charcoal of various chemical products is of great practical importance. At present, the topical problem in Kazakhstan is that the bitumen is produced only at Pavlodar oil chemical plant that uses raw materials from Russia. Besides, processing of wastes is in urgent need with its widely application in numerous branches of bitumen industry. In this regards, scientific-research works carried out by synthesising this valuable product from the wastes of hydrocarbon raw materials processing are of great value.

Experimental procedure

The object of studying the paste-type waste of 'charcoal oil' was used, forming after vacuum stripping of the fractionated product of hydrogenation obtained by liquefication of charcoal of Karazhyra field.

The extraction of the organic part of 'charcoal oil' was carried out using the method of extraction. The experimental set-up used for the separation of organic mass by means of extraction is shown in Fig. 1. The mixture of alcohol–benzene in the proportion of 2 : 8 was used as a solvent. The diameter of extraction cartridge is equal to the diameter of the extraction column, and is prepared using several layers of filter paper. One end of the cartridge is closed with cotton and kept in the oven until the state of stabilisation of mass, which is followed by measurement.

The upper part of the column is connected to backflow condenser, and the lower part to the flask is filled with the solvent. The flask with the solvent is heated to the point of boiling temperature using the sand bath. Inside the condenser, the condensed vapour of solvent mixing with the residues of 'charcoal oil' leaves the mixture by separating and dissolving the hydrocarbons. After the extractor is filled, the solvent is collected by the siphon tube in the flask. The organic part is separated until the moment of discoloration of solvent collected in the extraction column. The cartridge, fully filled with organic part, is dried at the temperature of 50–60°C until the state of stabilisation of mass. The mass fraction of organic part within the composition of residues is computed using the formula

$$Q = \frac{(G_1 - G) - (G_2 - G)}{(G_1 - G)} \cdot 100\% \qquad (1)$$

where G_1 the mass of cartridge with the cotton and sampler before the extraction, g; G the mass of dried cartridge (with cotton), g; G_2 the cotton after the extraction, the mass of the cartridge with mineral part, g.

Results and discussion

The bitumen is obtained from the organic part of 'charcoal oil'. The structure and composition of bitumen from the organic part of 'charcoal oil' are compared with that from ordinary oil. To determine the corresponded marks of the road bitumen, the physical–mechanical indicators of obtained bitumen were determined (Table 1).

As can be seen from Table 1, physical–mechanical indicators of obtained bitumen are in accordance with the requirements of the standard. Consequently, it can be considered as the liquid road bitumen of mark MG70/130. The group composition of bitumen was determined

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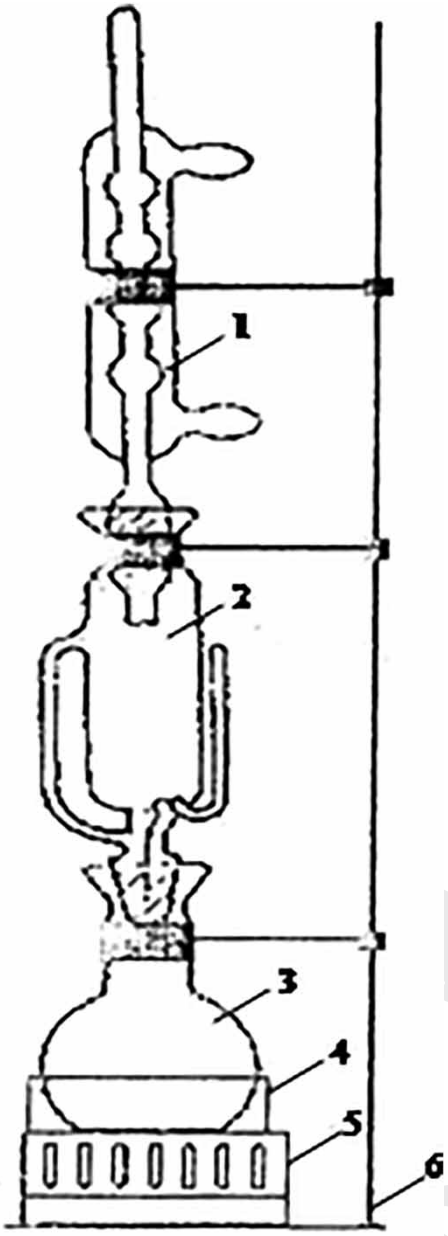


1 Laboratory set-up prepared for the extraction of the organic part from the residues of 'charcoal oil'

by using adsorption-chromatographic method of Marcusson. Results are shown in Table 2.

Increased content of resins (21·75 mass.%), asphaltene (13·48 mass.%) in bitumen, the total quantity of hydrocarbons (62·64 mass.%), including paraffin–naphthene hydrocarbons (29·33 mass.%) lead to decrease of viscosity of bitumen and produces the negative effect on its physical–mechanical indicators. Content of carbene and carbonic materials is 2·13 mass.%. Increased content of paraffin–naphthene hydrocarbons in the composition of bitumen is supported by the presence in its IR-spectra of intensive absorption bands. These band corresponds to vibrations of methyl groups $-CH_3$ (2926·8, 2947, 2917·8, 2903·2 $см^{-1}$ and of methylene groups $-CH_2$ (2858·8, 720·5 $см^{-1}$; Fig. 2).

Bitumen is composed of asphaltene (13·48% mass.), resins (21·75% mass.) and hydrocarbons (62·64% mass.). Consequently, it is different from the bitumen of oil

Table 1 Physical–mechanical indicators of bitumen

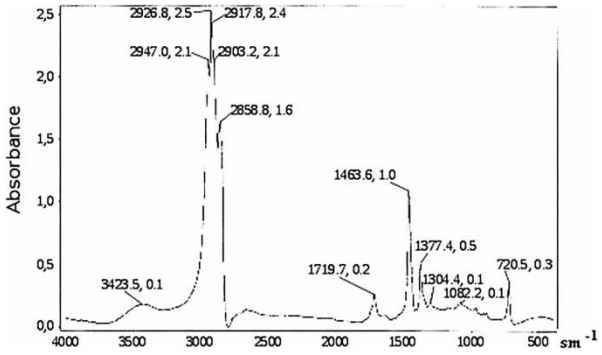
Indicators	Bitumen from 'charcoal oil '	Bitumen of mark MG70/130	Methods of testing
Relative viscosity with the diameter of a hole of 5 mm at 60°C, c	82	71–130	GOST 11503
Quantity of evaporated liquefier with bitumen temperature in thermostat (110°C, 5 h.), % mass, no less	6·7	7	GOST 11504
Temperature of softening of the residue after determination of the quantity of evaporated liquefier, °C no lower	24	29	GOST 11506

origin by the quantity of the main structure-forming components (Table 3). Such indicators, A/A + C and A/Y + C, have low values. Consequently, obtained bitumen does not refer to structural type of road bitumen.[1,2]

Process of oxidation of residues of oil is widely used in the production of high-quality road, and construction bitumen possessing special rheological and functional properties. The oxidation of residues of 'charcoal oil' was carried out by means of passing through 1 kg of

Table 2 Elementary and group composition of bitumen

Indicators	MG70/130	Refractive coefficient	
	g	mass. %	
Bitumen sample	3·0	100	
Elementary composition, mass.%			
C		89·40	
H		9·83	
S		0·21	
N		1·22	
Hydrocarbons:	1·6698	62·64	
Paraffin–naphthenes hydrocarbons	0·7818	29·33	<1·49
Monocycloaromatic hydrocarbons	0·5091	19·10	1·49–1·53
Condensed bicycloaromatic hydrocarbons	0·2652	9·95	1·53–1·59
Condensed polycyclicaromatic hydrocarbons	0·1137	4·26	>1·59
Resins:	0·5797	21·75	
Petroleum–benzene resins	0·3136	11·76	
Benzene resins	0·0908	3·41	
Alcohol–benzene resins	0·1753	6·58	
Asphaltenes	0·3594	13·48	
Carbene, carboid, mechanical admixture	0·3913	2·13	
Total	3·0	100	



2 IR spectra of liquid road bitumen of mark MG70/130

sources of 1·4 m^3 of air on the laboratory set-up in periodic regime at 220°C for 5 hours (Fig. 3).

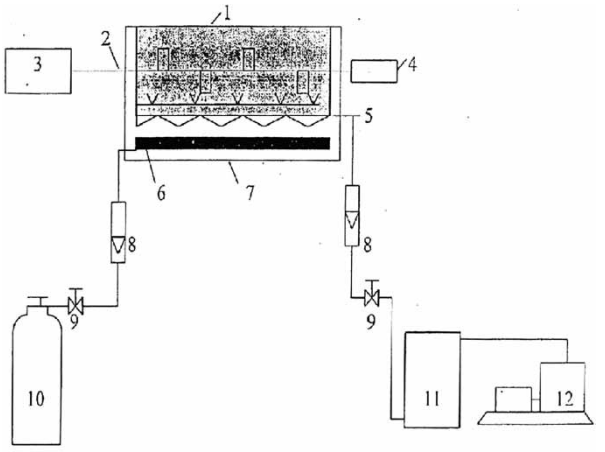
Physical–mechanical indicators of bitumen are shown in Table 4.

As can be seen from Table 4, the values of physical–mechanical indicators of obtained bitumen correspond to the requirements of the standard. Consequently, it can be considered to be the viscous road oil bitumen of mark BND130/200. In accordance with the values of penetration index (+2·1), it is the bitumen of group III, rheological state of which corresponds to bitumen of type gel.[3]

Interval of stretching of bitumen is wide (76–55·3°C), consequently, its deformation ability is high. The chemical group composition of bitumen was determined (Table 5).

As can be seen from Table 5, the concentration of resins, hydrocarbons, asphaltenes, carbene, carbonic materials in the composition of bitumen is equally corresponding to 38·0%, 38·5%, 22·3%, 1·2% mass. Increased concentration of condensed polycycloaromatic hydrocarbons, benzene resins increase dispersion degree of bitumen. The quantity of asphaltene in viscous road oil bitumen of mark BND130/200 was increased from 13·48 to 22·3% mass. In chemical group composition of liquid road bitumen of mark MG70/130, the concentration of paraffin–naphthene hydrocarbons is high (29·33% mass.). Consequently, in the course of the oxidation process, the amount of these hydrocarbons decreases owing to the formation of asphaltenes and resins. This may be explained with the help of the scheme, showing the direction of formation of asphaltenes in the course of oxidation of residues of oil (Scheme 1).

The data of IR-spectral analysis confirm the increase of the quantity of structure-forming components: resins, asphaltene and the presence of intensive absorption bands. The data correspond to the vibrations of aromatic groups 910–650 sm^{-1}, C–O–C– groups of ethers



3 Experimental set-up for oxidation of residues of 'charcoal oil' 1, reactor; 2, bubbler; 3, drive; 4, enforcing set-up; 5, air transfer tube; 6, heater; 7, external closing; 8, rotameter; 9, valve regulator; 10, container (baloon) with propane–butane mixture; 11, receiver; 12, compressor

Table 4 Physical–chemical indicators of bitumen

Indicators	Bitumen	Bitumen of mark BND 130/20	Methods of testing
Penetration at 25°C, 0·1 mm	190	131–200	GOST11501
Temperature of softening according to K and Sh, °C	46	40	GOST11506
Temperature of fragility (according to Fraas), °C	−30	−18	GOST11507
Penetration index	+2·1	46–190	GOST22245
Interval of plasticity	55·3–76°C	46–190	GOST22245

1200–1000 sm^{-1}, having in all carbonyl compounds of groups C=O, т.е 1900–1580 sm^{-1} (Fig. 4).

According to the results of IR-spectral analysis in the composition of bitumen obtained by oxidation, the concentration was increased of paraffinic hydrocarbons. The concentration leading to the increase of density of aromatic hydrocarbons and oxygen-containing compounds was decreased. Obtained viscous road oil bitumen of mark BND 130/200 may be used in the quality of road covering for light-weight automobiles in road-climate zones II and III during cold times at the average monthly temperature from −10 to −20°C.

Table 3 Structural types of road bitumen

Nature of bitumen	Structural type	Amount of structure-forming components			A/A+C	A/Y+C
Oil bitumen	I	>25·0	50·0	<24·0	0·5	0·35
Bitumen of 'charcoal oil'	II	<18·0	<48·0	>36·0	0·34	0·22
	III	21·0–23·0	45·0–49·0	30·0–34·0	0·39–0·44	0·25–0·30
	…	13·48	62·64	21·75	0·38	0·16

A, asphaltene, Y, hydrocarbon, C, resins

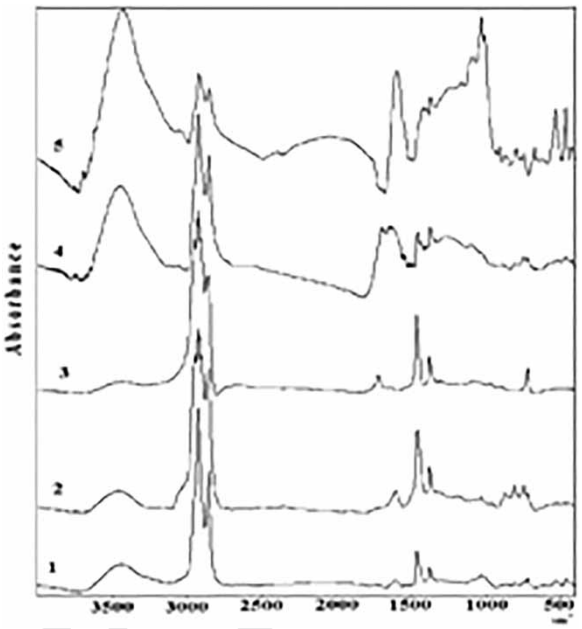
Table 5 Elementary and group composition of bitumen

Indicators	BND 130/200		Refraction coefficient
	g	mass. %	
Bitumen sample	5·0	100	
Elementary composition, mass.%			
C		91·61	
H		7·02	
S		0·51	
N		0·86	
Hydrocarbons:	1·9215	38·5	
Paraffin–naphthene hydrocarbons	0·3896	7·8	<1·49
Monocycloaromatic hydrocarbons	0·4095	8·2	1·49–1·53
Condensed bicycloaromatic hydrocarbons	0·4694	9·4	1·53–1·59
Condensed polycycloaromatic hydrocarbons	0·6530	13·1	>1·59
Resins	1·9000	38·0	
Petroleum–benzene resins	0·7900	15·8	
Benzene resins	0·8900	17·8	
Alcohol–benzene resins	0·2200	4·4	
asphaltene	1·1138	22·3	
Carbene, carboid, mechanical admixture	0·0647	1·2	
total	5·0	100	

Scheme 1 Direction of changes, occurring in the course of the oxidation process

Conclusions

For the first time, to the best our knowledge, the liquid road bitumen is obtained from the residues formed after hydrogenation of charcoal of 'Karazhyra' field. According to the values of physical–mechanical indicators, obtained bitumen corresponds to the bitumen of mark MG70/130. Chemical composition of obtained bitumen: 64% mass. Paraffin–naphthene hydrocarbons, 13·48% mass. Asphaltenes, 21·75% mass resins. The viscous road oil bitumen is obtained by oxidation of liquid road bitumen, corresponding to bitumen of mark BND130/200 in terms of physical–mechanical indicators. In the course of oxidation of general content of hydrocarbons, it decreased to 38·5%. mass, and the concentration of asphaltenes and resins increased to 22·3% mass and 38·0% mass correspondingly. The decrease of the general content of hydrocarbons in bitumen can be explained by their reaction with the formation of resins and asphaltenes. The scheme of formation is proposed of the main component of bitumen– asphaltene.



4 IR spectra of viscous road bitumen of mark BND130/200 1, benzene-alcohol resin; 2, petroleum–benzene resin; 3, asphalthene; 4, benzene resin; 5, bitumen

Acknowledgements

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