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Study of Pyrolysis Products-Oil-Bitumene Rocks Western Kazakhstan

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Abstract

The investigations of the pyrolysis products oil-bitumene rocks (OBR) of different fields in Western Kazakhstan by gas-liquid chromatography (flame ionization detector) and IR spectroscopy. It was found that pyrolysis products comprise mainly masut 370-500 and diesel 200-370.

Keywords: Oil and bitumen rocks, pyrolysis, IR-spectroscopy, the mechanism of thermical destruction, depolymerization

Introduction

Currently, the following questions are particularly acute environmental improvements oil-producing regions, as contaminated soil, spills and accidental releases of oil, barn oil, sediments remaining after oil extraction or waste sewage occupy vast areas and harmful to the environment because they are not processed and this problem becomes more threatening. [1]. Kazakhstan has huge reserves oil-bitumene rocks (OBR) (950-1000 million tons), containing in the structure of natural bitumen [1]. The Republic of Kazakhstan pays great attention to the construction of modern highways that meet international standards, but for long term use in the spring and summer and especially in autumn and winter periods in multiple alternating temperature changes from -40 ° C to + 40 ° C and in heating Road cover 90-100 ° C, roads wear out quickly, which requires annual renewal of the top layer - the asphalt. Earlier thermomechanical studies have shown that the bitumen softens at 0 ° C, becomes viscous-fluid state at 20 ° C and 100% degradation is reached at 40 ° C, the area of rubbery deformation is absent [2].
Oil-bitumene rocks, and especially isolated from their natural bitumens are used as binders for the production of modified road-building materials, sporting and flooring, sealants, mastics, etc. In the industry of building materials bitumen is widely used for construction and repair of road and airfield pavements and foundations, floors, industrial buildings, soil stabilization, protection against corrosion of metal and concrete, the manufacture of roofing, hydro, thermal and vapor barrier, materials and products, the protection of radioactive radiation, in the manufacture of paints [3-8].

Experiment

The objects of study were the various oil-bitumene rocks of western Kazakhstan. Samples of various OBR after pyrolysis without air:
F-1, a dark brown solid residue; № 2, a dark solid residue;
F-3, the bottom layer - the thin, transparent, F-3, the upper layer - a dark oily liquid.
F-4 - a clear liquid.
F-5, the bottom layer - the thin, transparent, F-5, the top layer - a dark oily liquid.
OBR No. 4 - 1st distillation, the bottom layer - brown liquid;
OBR No. 4 - 1st distillation upper layer - light-brown oil.

Gas-liquid chromatography. Currently, of particular interest is the study of the qualitative and quantitative composition of the products of pyrolysis oil-bitumene rocks modern rapid methods, including gas-liquid chromatography. The investigations of the pyrolysis products *oil-bitumene* species by gas-liquid

chromatography (flame ionization detector). In this work, we used a gas chromatograph "Crystal Suite 4000" production (Yoshkar-Ola, Mari-El). Assay conditions: packed column, length 1 m Sorbent - "Chromaton NDMCS» c 5% OV-101; Carrier gas - helium gas flow rate of 30 ml / min hydrogen - 30 ml / min air - 300 ml / min; flame ionization detector (FID). Temperatures Detector - about 270; Evaporator - about 270; Column - initial temperature of 40, and 2 minutes in the isothermal mode, and then heating the 4 o / min to 260 of Volume of the sample injection - 3 l. The calculation was performed by the method of simulation of distillation ASTM-89.

IR spectroscopy. For information about the processes by mixing oil-bitumene rocks with polymeric binders were held infrared spectroscopic studies of the respective samples. Infrared absorption spectra of bitumen, OBR and polymer compositions were obtained on an automatic dual-beam spectrometer UR-20 in the absorption interval of 400-4000 cm^{-1}.

Pyrolysis held various fields neftebituminoznyh rocks of western Kazakhstan and the method of gas-liquid chromatography investigated liquid and solid products of decomposition. Previously there have been studied methods modified OBR electron paramagnetic resonance (PMR) [5]. The pyrolysis process comprises heating OBR without access of air, which leads not only to *oil-bitumene* distillation fraction to flow but of complex chemical reactions at high temperature pyrolysis at 580-600 0C. As a result, the pyrolysis gas produced (not caught) liquids and solids are removed, and almost all of the volatile products. To carry out distillation was used iron retort. Liquid and solid pyrolysis products OBR was dissolved in benzene.

Results and discussion

Therefore, the actual problem has both theoretical and practical interest is the modification of bitumen with various polymers, which give the set of physico-mechanical and operational parameters, as well as durability. By infrared spectroscopy (IR) was used as the primary method of genetic-typing typical oilbitumene rocks and assess qualitative and quantitative relations of their component hydrocarbon and heteroatomic components. Of particular concern is the problem of creating highly flexible organic corrosion inhibitors of road-building materials, roofing systems, sealants, and other products based on natural bitumen by modifying their various additives and analysis of the products of pyrolysis. The additives used polymeric binders, rubber, waste production, and polyesters. Polyester was prepared from phthalic anhydride and glycerol. Degree of polycondensation of synthetic resin glyptal determined by acid value and saponification number. For information about the processes occurring in mixing *oil-bitumene rocks* with polymer binders were held infrared spectroscopic studies of relevant samples. The research methods of pyrolysis products NBP gas-liquid chromatography (flame ionization detector). Figures 1 and 2, respectively, are the IR spectra of natural bitumen extracted from the NBP and the modified polyester synthesized by us from phthalic anhydride and glycerol. Very intense pp at 1375-1376,3 and 1453,9-1457,7, 1486.4 cm^{-1} in the oil fractions are stretching and bending vibrations of the CH2 and CH3 groups in paraffin and tsikloparafinovyh hydrocarbons. In the spectra of all the components is clearly visible pp at 726.8 cm^{-1}, which corresponds to the bending vibrations of CH 2 groups in free paraffinic chains. The presence of polyester characterized by the appearance of the absorption band is much more intense in the 1721.5 cm^{-1} (Fig. 2), indicating the presence of oxygen-containing compounds. Simultaneously observed in the modified bitumen low intensity pp at 1453.9 and 1282.6 cm^{-1}, which disappear in the original bitumen. The modified bitumen reduced intensity pp at 1125.6 and 1070.1, as well as 776.4 and 705 cm^{-1}.

Pyrolysis of various deposits held oil-bitumene rocks (OBR) in Western Kazakhstan and by gas-liquid chromatography investigated liquid and solid products of decomposition. It was found that the pyrolysis products contain mainly masut 370-500 and diesel 200-370.

Fig. 1 and 2 show the chromatograms and the content of the pyrolysis products OBR number 4 of the lower and upper layers, respectively. From Figure 1 it follows that in the products of pyrolysis gasoline fraction and no tar. The pyrolysis products are diesel and fuel oil fraction. Diesel 200-370 is present in an amount of 65.18%, and oil 370-500 - in an amount of 34.82%.

From Fig. 2 shows that the top of the content of the gasoline fraction pyrolysate minor - 0.12%, diesel fuel - 41.75% oil - 58.13%. From a comparison of data content of diesel fuel and fuel oil NBP number 4 in the top and bottom fractions (Fig. 1 and Fig. Two, respectively) that during the transition from the bottom to the top of the diesel fuel fraction falls to 23.43%, and amount of fuel oil increased by 23.31%. Apparently, the depolymerization reactions occur and degradation oil-bitumene rocks.

Of particular interest are the IR spectroscopic studies of the OBR.

Figures 3 and 4 respectively shows the IR spectra of natural bitumen derived from OBR modified polyester synthesized Center of phthalic anhydride and glycerin. A comparison of the IR spectra show that the samples of

bitumen in the 400-2200 cm-1 absorption band (pp) are observed at 425 and 426.9, 471.2 and 485.3, 537.5 and 559.5 , 618.9 and 646.8, 705 and 726.8, 882, 911.8 and 925.7, 986.1, 1032.3 and 1042.2, 1070.1, 113.5 and 1125.6, 1218 , 8, 1236, 1282.6 and 1376.3 1375, 1453.9 and 1457.7, 1486.4, 1557.9, 1581.7, 1598.3, 1641.6, 1699.3, 1721.5, 1958.1, 2108.2 and 2149.6 cm^{-1}. Very intense pp at 1375-1376,3 and 1453,9-1457,7, 1486.4 cm^{-1} in the oil fractions are stretching and bending vibrations of the CH2 and CH3 groups in paraffinic hydrocarbons and cycloparaffinic. In the spectra of all the components is clearly visible pp at 726.8 cm^{-1}, which corresponds to the bending vibrations of CH2 groups in free paraffinic chains. The presence of polyester characterized by the appearance of the absorption band considerably higher intensity of 1721.5 cm^{-1} (Fig. 4), indicating the presence of oxygenated compounds. At the same time in a modified bitumen there is less intensity pp at 1453.9 and 1282.6 cm^{-1}, which disappear in the original bitumen. Slightly less than in the modified bitumen intensity pp at 1125.6 and 1070.1, and at 776.4 and 705 cm^{-1}. In the 2200-4000 cm-1 are absorption bands at 2726.9, 2860.1 and 2860.6, 2923.7, and 2924, 2950.7 and 2951, 3071.9, 3434.7 and 3434.9 cm^{-1}. It is known [8], which is low in intensity and broad 3434.7 and 3434.9 cm^{-1} may pertain to stretching vibrations of OH and CH. The strongest in the medium-wave part of the spectrum ap 1453,9-1457,7 cm^{-1}, she, like pp 3071 cm^{-1} belongs to the methylene groups. In the initial bitumen missing pp at 3071.9 cm^{-1}. Changing polymer content of the resulting composition results in compositions of various consistencies, from mastic to a solid material.

Conclusions

1. It is considered that the pyrolysis oil-bitumene rocks (OBR) without air accompanied by preferential formation of diesel fuel and fuel oil 200-370 370-500 that can be applied in the petrochemical industry.
2. It was showed that in rock oil-bitumene rocks (OBR) No. 4 in the upper part of pyrolysate gasoline - 0.12%, whereas in the lower part of the gasoline fraction is absent.
3. It was found that oil-bitumene breed F-5 in the upper part of pyrolysate gasoline - 0.03%, whereas in the lower part of the gasoline fraction is absent.
4. The possibility of using oil-bitumene rocks for diesel fuel and heating oil and gasoline in small quantities.

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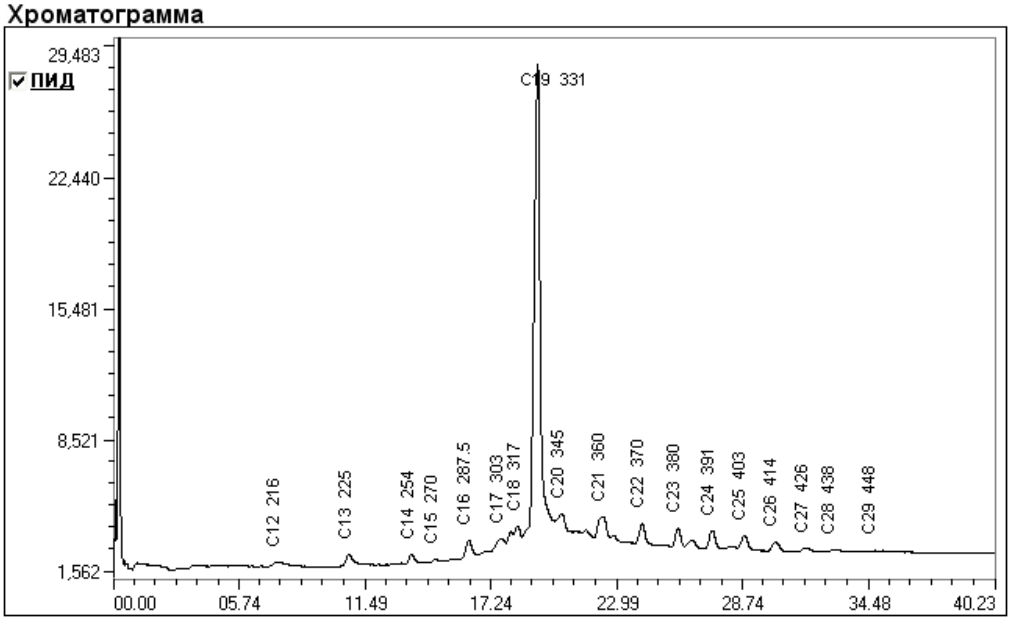

Пики

№	Время, мин	Компонент	Площадь,%
1	7,51	C12 216	0,5610
2	10,77	C13 225	1,0024
3	13,61	C14 254	0,4063
4	14,73	C15 270	0,3564
5	16,21	C16 287.5	1,8317
6	17,67	C17 303	2,9573
7	18,44	C18 317	4,7592
8	19,36	C19 331	34,3398
9	20,45	C20 345	9,6762
10	22,31	C21 360	9,6574
11	24,11	C22 370	9,2102
12	25,75	C23 380	6,8562
13	27,30	C24 391	6,8165
14	28,77	C25 403	4,8157
15	30,19	C26 414	2,7352
16	31,58	C27 426	1,5503
17	32,83	C28 438	1,2985
18	34,70	C29 448	1,1698
			100,0000

Группы

№	Группа	Детектор	Концентрация, % об.
1	бензин-200	ПИД	0,000000
2	дизель топ-200-370	ПИД	65,179222
3	мазут-370-500	ПИД	34,820778
4	гудрон выше- 500	ПИД	0,000000

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Fig. 1. "The chromatogram OBR No. 4 (bottom layer)"

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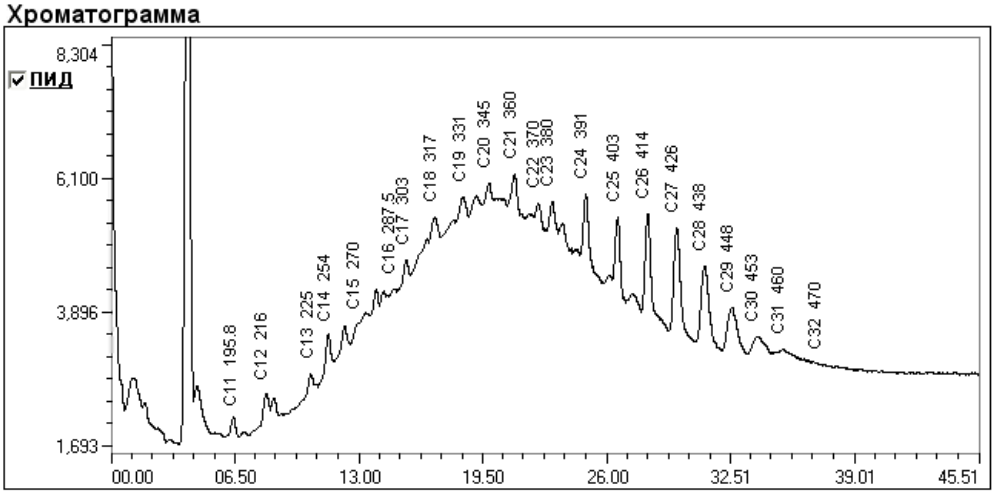

Пики

№	Время, мин	Компонент	Площадь,%
1	6,48	C11 195.8	0,1068
2	8,10	C12 216	0,8014
3	10,47	C13 225	0,9833
4	11,36	C14 254	2,5874
5	12,89	C15 270	2,5538
6	14,77	C16 287.5	3,2289
7	15,47	C17 303	3,4481
8	16,97	C18 317	6,7151
9	18,47	C19 331	6,7127
10	19,78	C20 345	8,1542
11	21,15	C21 360	8,1506
12	22,38	C22 370	8,7435
13	23,11	C23 380	10,5871
14	24,88	C24 391	8,2703
15	26,54	C25 403	7,0532
16	28,11	C26 414	6,7822
17	29,63	C27 426	5,3233
18	31,10	C28 438	3,7812
19	32,53	C29 448	2,6182
20	33,84	C30 453	1,6541
21	35,18	C31 460	1,2163
22	37,09	C32 470	0,5282
			100,0000

Группы

№	Группа	Детектор	Концентрация, % об.
1	бензин-200	ПИД	0,120521
2	дизель топ-200-370	ПИД	41,749981
3	мазут-370-500	ПИД	58,129494
4	гудрон выше- 500	ПИД	0,000000

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Fig. 2. "The chromatogram OBR No. 4 (top layer)"

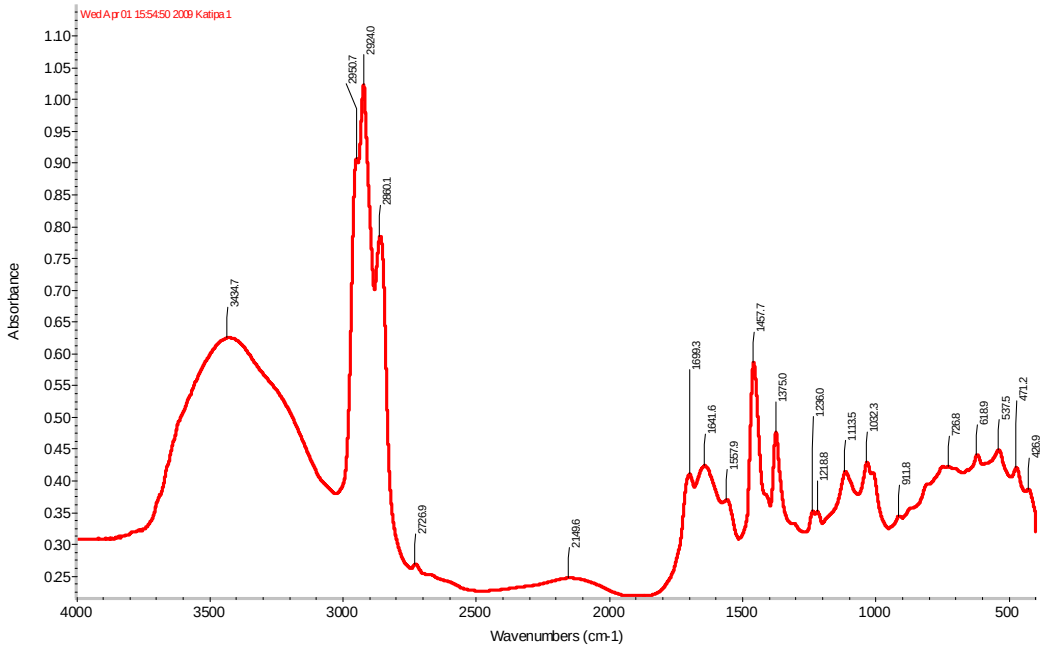

Fig. 3. - IR spectra of bitumen extracted from the OBR

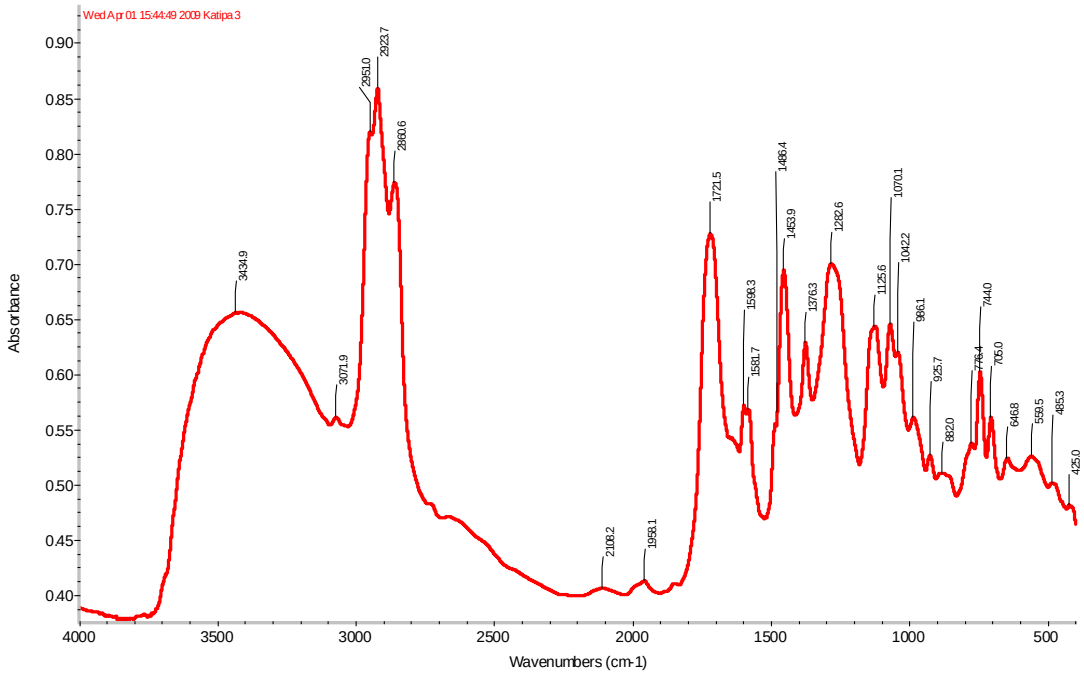

Fig. 4. - IR spectra of the reaction product of bitumen with polyester