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## Composition of Pre-ozonated High-Sulfur Natural Bitumen Cracking Products

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### Abstract

The results analysis of fractional and material composition of the cracking products of Ashalchinskoye and Karmalskoye bitumen deposits was presented in this work. The effect of bitumen ozone-oxygen mixture pretreatment followed by cracking on thermolysis processes was investigated. It was shown that molecules of resins and asphaltene containing large amounts of aliphatic fragments in its structure readily undergo thermal decomposition to form additional distillate fractions. Low content of aliphatic fragments leads to aromatization of the naphthenic cycles in the molecule of resins and asphaltene, the thermal degradation reactions proceed in high yields of gas and coke.

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### 1. Introduction

Because of the depletion of light and medium crudes heavy oil and natural bitumen become an important source of raw materials to meet the growing demand for fuel. World stocks of heavy oils and natural bitumen far exceed the light oils, and it is estimated to be more than 810 billion tons. The largest deposits are located in Canada and Venezuela, there are also significant reserves in Mexico, the US, Russia, China and Kuwait. According to various

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estimates, from 30 to 75 billion tons of heavy oil and natural bitumen<sup>1</sup> are concentrated at the territory of the Russian Federation.

Involvement of crude heavy oils in refining requires modernization of the existing schemes and development of new more effective technologies for their processing to produce the maximum possible amount of light fractions and improve their quality<sup>2</sup>.

At this point, despite the variety of technologies and options for the conversion of heavy oils and natural bitumen, their extraction, transportation, processing and bringing to merchantability are not cost-effective due to the high capital costs, cost of hydrogen and speed poisoning (resinification and carbonization) of the active surface of the catalyst. Heavy oils and natural bitumen are characterized by a high content of aromatic hydrocarbons, resins, asphaltenes, high concentrations of metals and sulfur compounds, high coking. High value of density and viscosity increase significantly the cost of their extraction and make transportation virtually impossible via the existing pipelines. Processing of hydrocarbon feedstock by the classical schemes is uneconomic<sup>2-4</sup>. Extraction and processing of heavier oils and natural bitumen is only economically justified due to the new efficient technologies<sup>5-9</sup>. Therefore, understanding the structures of resins and asphaltenes and their behavior in thermal processes is an important task.

## 2. Experimental

### 2.1. Samples

The objects of the study are natural bitumen deposits of Mordovo-Karmalskoye (№1) and Ashalchinskoye (№2) oil fields in Tatarstan.

Table 1 Characteristics of bitumens

Sample	Content wt%										
	C	H	N	S	O difference	Oils	Resins	Asphaltenes	ibp–200	200–360	>360
# 1	81.2	11.6	1.1	3.7	2.4	70.3	24.5	5.2	6.7	34.6	58.7
# 2	82.1	10.4	1.0	4.7	1.8	67.6	26.2	6.2	4.6	27.9	67.5

### 2.2. Elemental analyses

Elemental analysis of the natural bitumens was performed by the microanalytical method using CHNS Vario EL Cube analyzer, O was defined by differences (Table 1).

### 2.3. Fractionation methods

*Material composition.* The amount of resins and asphaltenes in natural bitumens and their liquid cracking products was determined according to the standard procedure. To isolate asphaltenes, a weighed sample was diluted with a 40-fold hexane and left for a day. The precipitate was filtered off, placed in a paper cartridge, and washed with hexane in the Soxhlet extractor to remove hydrocarbons and resins; then, asphaltenes were washed out of the cartridge with chloroform. The deasphalted samples were applied to ASK silica gel and then successively extracted in the Soxhlet apparatus to isolate the hydrocarbon components and resins with hexane and a 1 : 1 benzene-ethanol blend respectively.

### 2.4. Structural-group analysis

<sup>1</sup>H NMR. Spectra were obtained with the AVANCE-AV-300 Fourier-transform spectrometer (solvent, deuterated chloroform; internal standard, hexamethylsiloxane) taking samples with a 1 % concentration of the substances.

*Structural-group analysis.* The resins and asphaltenes isolated from the samples of the original bitumen and their cracking products were subjected to structural-group analysis according to the procedure designed at the Institute of Petroleum Chemistry, Siberian Branch, Russian Academy of Sciences<sup>10</sup>. On the basis of elemental analysis, molecular mass and <sup>1</sup>H NMR data, the structural-group analysis makes it possible to calculate the mean distribution

of atoms between the structural elements of the high-molecular-mass molecules. This distribution gives information on the size and structure of the molecules, composition, and amount of different structural groups.

## 2.5. Method of experiment

The experiments were carried out in the autoclave of 12 cm<sup>3</sup> volume. The bitumen weight in the experimentation was 7 g. The experiments were conducted at temperature of 450 °C for 60 – 120 min in the air environment. The mass of the reactor was registered without the sample and with the sample prepared for thermolysis. After conducting natural bitumen heat treatment, the gaseous products yield was determined by weight loss of the reactor with the sample after removing the gas products from the reactor.

After draw off of the liquid products, the reactor was washed with chloroform and weighed. The resulting difference between the mass of the reactor before and after the experiment was referred as coke.

Pre-ozonation was conducted in the bubble reactor, the ozone-oxygen mixture and consumption of ozone was 6 g per 1 kg of bitumen.

## 3. Results and discussion

### 3.1. Composition of bitumen cracking products

Bitumen cracking (#1) for 60 minutes reduces the yield of oil and asphaltenes by 4.0 % and 0.4 % respectively, the total yield of coke and gas was 1.6 %, and the increase in content of resins was 2.8 % wt. (Table 2). After 100 minutes of cracking destruction of resinous components begins to form additional oil components, increased content of oils components was 3.4 %, and the total yield of coke and gas was 4 %, while the destruction of high-molecular components was 6.6 % wt. Increasing the process time up to 120 minutes leads to profound destruction of resins and asphaltenes to form significant amounts of gas and coke.

At the cracking of bitumen (#2) an increase in the yield of gas and coke, destruction of resin and a small rise in oil components are observed. Initial boiling point is not significantly improved as well as fractional composition of cracking products. The maximum yield of i.b.p.-360 fraction was 6.2 % wt. after 60 minutes of the process. Also, the amount of asphaltenes is increasing in all experiments, and the maximum destruction of resins was observed during 120 minutes of cracking, it was 8.2 % wt.

Table 2 Composition of bitumen cracking products #1 and #2

Conditions	ibp, °C	Fractional composition, % wt.			Component composition, % wt.				
		ibp-200	200-360	>360	Oil	Resins	Asphaltenes	Gas	Coke
# 1	111	6.7	34.6	58.7	70.3	24.5	5.2	0	0
60 minutes	128	6.5	36.9	55.0	66.2	27.4	4.8	0.6	1.0
100 minutes	74	12.7	39.4	44.1	72.9	17.9	5.4	1.8	2.0
120 minutes	72	16.7	32.7	30.2	65.4	11.6	2.8	14.2	6.2
# 2	109	4.6	27.9	67.5	67.6	26.2	6.2	0	0
60 minutes	113	7.7	31.0	59.8	70.4	20.7	7.4	0.4	1.1
100 minutes	106	7.7	30.1	59.4	70.2	19.7	7.3	1.0	1.8
120 minutes	103	8.3	29.6	56.1	68.9	18.0	7.1	2.6	3.4

### 3.2. Composition of pre-ozonated bitumen cracking products

Pre-ozonated bitumens are characterized by a high resin content - 26 and 24 % wt., they contain a significant amount of heteroatoms and aromatic compounds in its composition. It is well known that ozone actively reacts with sulfur-containing aromatic compounds and form ozonides<sup>11</sup>. Ozonides as well as other organic peroxides are easily destroyed at temperatures above 120 °C. Ozonides can play the role of the initiator in radical chain reactions

including the cracking processes of high boiling bitumen components. Therefore, we carried out cracking of the bitumen pretreated with ozone.

Cracking of pre-ozonated bitumen (#1) is characterized by low yield of coke and gas, the maximum total yield does not exceed 3 % wt. An increase in oil content was 11.4 % at the bitumen cracking for 120 minutes at the expense of deep destruction of resins (15 % wt.). An increase in the content of the fractions boiling up to 360 °C was 11.5 % wt.

As follows from the data presented in Table 3, pre-treatment of ozone followed by bitumen cracking (#2) leads to a decrease in boiler point temperature by 44 °C after 120 minutes. Increase in ibp-200 fractions was 14.2 % wt. The total yield of coke and gas in this experiment was 14.2 %, whereas the destruction of resins was 16.6 % wt. After 100 minutes of cracking, boiler point temperature decreased by 29 °C, and the content of ibp-200 and 200-360 fractions increased by 9.1 and 5.2 % wt respectively. The yield of gas and coke was 10.5 %, and destruction of resins was 14.7 % wt. With a minimum duration of some minimal destruction of resin (4 %), the total yield of gas and coke was 1.2 % and the fraction of ibp-360 increased by only 3.2 % wt.

Table 3 Composition of pre-ozonated bitumen cracking products №1 and №2

Conditions	ibp, °C	Fractional composition, % wt.			Component composition, % wt.				
		ibp-200	200-360	>360	Oil	Resins	Asphaltenes	Gas	Coke
# 1	111	6.7	34.6	58.7	70.3	24.5	5.2	0	0
60 minutes	85	7.5	36.1	54.3	79.0	13.5	5.4	0.5	1.6
100 minutes	76	12.7	39.1	45.5	81.9	10.0	5.4	0.8	1.9
120 minutes	70	15.3	37.5	44.2	81.7	9.5	5.8	1.1	1.9
# 2	109	4.6	27.9	67.5	67.6	26.2	6.2	0	0
60 minutes	91	5.7	30.0	63.1	69.1	22.2	7.5	0.6	0.6
100 minutes	80	13.7	33.1	42.9	70.7	11.5	7.5	6.4	3.9
120 minutes	65	18.4	28.3	39.1	68.7	9.6	7.5	9.6	4.6

### 3.3. Structural-group analysis

To determine the main directions of the destruction of high-molecular components we carried out structural-group analysis of the asphaltenes and resins extracted from the original bitumen, cracking products and pre-ozonated bitumen cracking products (temperature is 450 °C, duration is 100 min.). In Tables 4-5, the parameters are presented: the number of carbon atoms  $C_a$  - in aromatic and  $C_n$  - in naphthenic rings,  $C_p$  - in the aliphatic moiety,  $C_\alpha$  - in  $\alpha$ -position to the aromatic ring,  $C_\gamma$  -  $\beta$  at the positions further from the aromatic ring, the number of rings:  $K_{all}$  - total,  $K_a$  - aromatic,  $K_{nas}$  - saturated, the ratio  $f_a$  of carbon atoms in the aromatic moiety.

The average asphaltenes molecule of original bitumen (№1) has a molecular weight of 1921 a.m.u., it consists of 24 rings including 15 aromatic and 9 naphthenic rings in the four structural units. The H/C atom ratio is only 1.23. A significant amount of heteroatoms should be noted in the average molecule: 6 oxygen, two sulfur, and four nitrogen atoms. The average molecule of original bitumen resins has a molecular weight of 743 a.m.u., and it consists essentially of aliphatic fragments and naphthenic rings. The content of aromatic carbon atoms  $C_a$  amounts only 1/3 of the total number of carbon atoms, the aromaticity factor is low. The molecules of resins are mainly composed of two blocks, the structural block contains on average 13 rings including 4 aromatic and 9 naphthenic. The low H/C ratio (1.28) is due to the high content of rings and high degree of substitution ( $\sigma_a$ ) of resins molecular structure. In the molecule the resin contains a significant amount of heteroatom: 2 oxygen atoms, and one atom of sulfur and nitrogen.

Heat treatment of bitumen №1 leads to significant changes in the molecular structure of asphaltenes. The molecular weight is reduced to 1668 a.m.u., the molecule consists of 7 structural blocks containing three fused rings (aromatic or saturated), the number of carbon atoms in the alkyl moiety ( $C_p$ ) decreases by 12, the length is reduced by an average of 2- 3 carbon atoms. The molecular weight of the resins increases slightly (to 768 a.m.u.), the amount of naphthenic rings is reduced by 2 (one ring is subjected to aromatization, the another one is cracked).

Pre-treatment with ozone followed by cracking leads to profound destruction of asphaltene molecules of bitumen №1, the molecular weight (539 a.m.u.) significantly reduces. The number of structural blocks per molecule decreases by 1, naphthenic rings - by 3. The number of aromatic rings is practically unchanged as a result of naphthenic rings flavoring. The alkyl moieties of the molecules are destroyed (Cp is reduced threefold), the length (C $\gamma$ ) is reduced more than twofold. The structure of the resin molecules varies weakly, the molecular weight is reduced by 41 a.m.u., there is an opening to 5 naphthenic cycles to form a significant amount of alkyl moieties (Cp increases by 10 atoms).

Table 4 – Structural-group analysis of bitumen №1

Parameters		Asphaltenes			Resins		
		Original	Cracking	Pre-ozonated	Original	Cracking	Pre-ozonated
Molecular weight, a.m.u.		1921	1668	1382	743	768	702
The number of atoms in the average molecule:	C	130.1	111.7	94.3	49.7	51.7	46.0
	H	157.4	143.6	93.1	59.4	60.8	57.3
	N	3.1	2.5	1.4	0.6	0.9	0.7
	S	3.9	2.5	2.7	1.2	1.1	1.1
	O	2.2	4.2	3.1	2.5	2.4	3.0
Ring composition:	Kall	24.3	21.2	20.7	12.7	11.6	8.1
	Ka	14.7	10.8	13.6	3.8	5.0	4.3
	Kn	9.6	10.4	7.1	8.9	6.6	3.5
The number of blocks in the molecule, ma		4.0	6.6	3.4	1.7	1.9	1.9
$\sigma a$		0.54	0.36	0.40	0.6	0.57	0.57
$f a$		43.1	54.0	54.5	30.6	39.3	41.0
The number of carbon atoms of different types in the average molecule:	Ca	56.1	60.3	54.7	15.2	20.3	18.8
	Cn	39.0	28.4	28.2	30.9	26.8	14.0
	Cp	35.0	23.0	11.4	3.6	4.6	13.2
	C $\alpha$	19.4	16.8	14.0	7.3	8.3	7.7
	C $\gamma$	7.8	5.3	3.1	3.6	3.3	2.9

The molecules of the original resins of bitumen (№2) have the molecular weight of 640 a.m.u., they are mainly composed of naphthenic rings and aliphatic fragments - the number of aromatic carbon atoms (Ca) amounts only a third of the total quantity, aromaticity factor is respectively low. The molecules consist of two units, the structural block contains 8 rings including 3 aromatic and 5 naphthenic.

According to the data of the structural-group analysis (Table 5), the average molecule of original asphaltenes of bitumen №2 has a molecular weight of 1285 a.m.u. and it consists of three units. The carbon skeleton consists of 44% of the aromatic structures ( $f a = 44.3$ ) and has a high degree of substitution ( $\sigma a = 0.54$ ). The average structural block is composed of 20 rings including 10 aromatic and 10 naphthenic.

Cracking of bitumen (the duration is 100 min) increases the molecular weight of asphaltenes to 1390 amu, and thus the substitution degree is reduced by 7%. The number of carbon atoms in aromatic and aliphatic fragments increases by 7 and 8 atoms, respectively. The molecular weight of the resins increases to 678 a.m.u. due to the increase in naphthenic rings from 2.5 to 4.1 in the composition of the average molecule. The amount of carbon in the aliphatic fragments reduces by 2 carbon atoms but the length of the substituent increases from 2,2 to 4 carbon atoms.

Pre-treatment with ozone followed by cracking results in an insignificant increase in molecular weight of asphaltenes to 1292 a.m.u. The number of naphthenic rings reduces by 1 due to molecule aromatization processes: the number of aromatic rings increases by 2, the aromaticity factor rises from 44.3 to 53.1%. The resins under these conditions change more strongly, molecular weight reduces up to 525 a.m.u., the number of aromatic rings

decreases from 4.2 to 3.1, and Cp falls from 15.3 to 5.2 at the same time increasing the amount of naphthenic rings from 2,5 to 4 rings.

Table 5 – Structural-group analysis of bitumen №2

Parameters		Asphaltenes			Resins		
		Original	Cracking	Pre-ozonated	Original	Cracking	Pre-ozonated
Molecular weight, a.m.u.		1285	1390	1292	640	678	525
The number of atoms in the average molecule:	C	83.6	91.0	87.0	42.1	45.3	35.0
	H	91.7	96.4	87.0	54.6	60.0	43.5
	N	1.5	1.6	1.4	0.7	0.7	0.5
	S	3.9	3.0	6.5	1.1	1.2	0.7
	O	2.8	5.2	4.5	2.2	1.6	1.9
Ring composition:	Kall	19.7	19.7	20.5	6.7	8.0	7.2
	Ka	9.7	11.7	11.6	4.2	4.0	3.1
	Kn	9.9	8.0	8.9	2.5	4.1	4.1
The number of blocks in the molecule, ma		2.9	3.2	3.1	1.7	1.7	1.5
$\sigma_a$		0.54	0.47	0.44	0.53	0.56	0.58
$f_a$		44.3	49.9	53.1	40.4	35.2	37.5
The number of carbon atoms of different types in the average molecule:	Ca	37.0	45.4	46.2	17.0	16.0	13.1
	Cn	40.0	32.1	35.9	10.0	16.6	16.7
	Cp	6.5	13.4	4.8	15.3	12.8	5.2
	C $\alpha$	12.8	13.8	13.2	6.6	6.6	5.9
	C $\gamma$	4.2	3.7	3.7	2.3	4.0	2.4

#### 4. Summary and conclusions

It is found that the structure of high-molecular components of natural bitumen influences the direction of thermal processes and composition of the obtained products. High aromaticity of resins and asphaltenes structures of bitumen (№2), as well as the low content of aliphatic fragments leads to a small additional yield of the gasoline and diesel fractions with small total output of gas and coke in the process of thermal cracking. The high content of aliphatic fragments, smaller aromaticity factor of resin and asphaltene of bitumen from Karmalskoye field allow achieving deep destruction of high molecular weight components (to 50% rel.) with a high total yield of coke and gas – 20 wt % in the process of thermal cracking. Probably, coming off from the asphaltenes aliphatic moieties form the components of distillate fractions and gaseous products, and aromatic nuclei condense to form coke.

It was found that treatment with ozone-oxygen mixture followed by cracking leads to significant changes in the direction of the destruction reaction of high-molecular components of natural bitumen. Preliminary ozonation of bitumen (№2) can significantly increase the depth of the thermal destruction of resin and asphaltene molecules containing highly flavored condensed structural fragments. In the cracking products, the high content of motor fuels and oil distillates is found, the total yield of gas and coke does not exceed 15 wt %. Pretreatment of bitumen (№1) with ozone-oxygen mixture increases the depth of destruction of high-molecular components greatly lowering yields of gas and coke (the amount does not exceed 3 %) to give additional quantities of oil (11 %) and distillate fractions.

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