
YOUNG SCIENTIST'S PAGES

UDC 665.642:547.9

DOI: 10.15372/CSD20180214

Composition and Structure Changes of Asphaltenes of Oil from the Usinsk Field during Sequential Stepwise Thermal Decomposition

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(Received November 7, 2017)

Abstract

Composition and structure changes of the macromolecules of asphaltenes from the Usinsk deposit were studied during sequential stepwise thermal decomposition at 120, 230, and 370 °C. Component composition data of thermolysis products were acquired and changes in structural-group characteristics of asphaltene molecules during thermal treatment were described. It was found that below 230 °C, asphaltene decomposition reactions prevailed over condensation ones, while above this temperature, compaction reactions were prevalent. It was demonstrated that the trend of heteroatoms towards accumulation in compaction products during stepwise thermolysis of oil asphaltenes from the Usinsk field increased in the series S → N → O.

Keywords: heavy oil, stepwise thermolysis, asphaltenes, composition, structural-group analysis

INTRODUCTION

Oil raw materials are traditionally one of the most important branches of the world and Russian fuel and energy complex [1]. At the present stage of development of the oil industry, there is a tendency of the transition from light hydrocarbon raw materials to heavy oil and natural bitumen [2–4]. The main problems in the extraction and processing of heavy hydrocarbon raw materials are associated with a high content of high molecular mass heteroorganic substances, *i.e.* asphaltenes, therein [2].

It is obvious that without understanding the chemical nature of asphaltenes, it is extremely difficult to predict their behaviour in industrial processes and develop efficient approaches to heavy and bituminous oils mining and processing.

Currently, the composition, properties, and structure of asphaltene molecules and aggregates are being extensively studied [5]. One of the most important trends in the study of the structural organization of asphaltene compounds is their separation into fractions due to different solubility and sorption capacity of as-

TABLE 1

Physicochemical properties of oil from the Usinsk deposit

ρ_{20} , kg/m ³	ν_{20} , m ² /s	Elemental composition, mass %					Material composition, mass %		
		C	H	N	S	O	Oils	Resins	Asphaltenes
966.7	3.9	84.9	12.0	0.6	2.0	0.5	73.9	18.0	8.1

phaltene components followed by the analysis of the obtained fractions using physicochemical methods [6–10]. In addition, considerable attention is being paid to the study of the composition and structure of asphaltene molecules and aggregates using thermal and thermocatalytic destruction [11–14], and also the trend of their transformation in cracking processes of heavy oil systems [15, 16]. Despite the active research of asphaltene molecules and aggregates, the nature of their existence and behavior have not been studied deeply enough, and therefore it is relevant to continue theoretical and experimental work to acquire new data and systematize the available ones on the composition, structural organization, and thermal stability of asphaltenes.

The goal of the present work was to study the composition and structure changes of molecules of asphaltenes from the Usinsk deposit during stepwise thermolysis.

EXPERIMENTAL

To carry out experiments, asphaltenes of high-viscosity oil from the Usinsk deposit with high asphaltene content were isolated (Table 1). These compounds were separated according to the standard technique by the addition of 40 % excess of *n*-hexane to the sample

and oil sample ageing in the dark place for 1 day. Being insoluble in low alkanes [2], asphaltenes were precipitated and filtered off to separate them from the solution. The asphaltenes extracted from oil were purified with *n*-hexane from sorbed oils and resins in the Soxhlet apparatus. The maximum possible degree of treatment of asphaltenes proved to be achieved when the solvent, repeatedly passing through the layer of asphaltenes, became colourless, which was defined as the absence of maltenes (oil + resin) in their composition. Purified asphaltenes were released from the solvent and dried to constant mass.

Characteristics of asphaltenes from the Usinsk deposit were determined using structural-group analysis (SGA) [17]. The latter was developed in the ICS SB RAS and enabled quantifying average structural-group parameters of substances and describing their averaged hypothetical molecule on the ground of the data obtained (Table 2).

The SGA is based on elemental composition data, molecular mass (MM) of the sample and ¹H ЯMP spectroscopy. The elemental composition of asphaltenes was determined using a CHNS Vario EL Cube analyser. The MM was measured by the cryoscopic method in naphthalene and ¹H NMR spectra were recorded using the Avance-AV-300 Fourier spectrometer (CDCl₃ solvent, hexamethyldisiloxane as internal standard) at a concentration of 1 %.

TABLE 2

Average parameters of initial asphaltene molecules of oil from the Usinsk deposit

MM, amu	Elemental composition, mass %					Carbon atom distribution, %			m_a	Number of different carbon atoms, u.					Ring composition, u.		
	C	H	N	S	O	f_a	f_n	f_{al}		C_a	C_n	C_{al}	C_α	C_γ	K_o	K_a	K_{sat}
1600	83.6	7.8	1.2	3.0	4.4	42.1	52.7	5.2	3.3	47.0	58.7	5.8	16.5	5.8	26.0	11.5	14.5

Note. MM is molecular mass; f_a , f_n , and f_{al} are carbon atom fractions in aromatic, naphthenic and aliphatic fragments, respectively; C_a , C_n , and C_{al} are of carbon atom numbers therein; C_α and C_γ are carbon atom numbers in the α -position to aromatic rigs and heterofunctions (C_α), and also in terminal methyl groups (C_γ); m_a is number of structural units in molecules; K_o , K_a , and K_{sat} are total number of rings in a molecule, number of aromatic and saturated rings, respectively.

The average MM of oil asphaltenes from the Usinsk deposit is 1600 amu. According to SGA data, the molecule of the initial asphaltenes is three structural blocks consisting of 11–12 aromatic and 14–15 naphthenic rings that have up to six aliphatic carbon atoms in their surroundings (see Table. 2). Heteroatoms (*e.g.* O, N, S) with a total content of 8.6 mass % are present in the composition of asphaltene molecules in significant quantities.

To select the temperature mode of stepwise thermolysis of asphaltenes, differential scanning calorimetry (DSC) data were used. Endothermic effect peaks are recorded at 120, 230, 370 °C (Fig. 1). This may attest to stepwise thermal decomposition driven by the presence of chemical bonds differed by the energy in asphaltene molecules. Above 400 °C, there is an area of intense exothermic effects that overlap on each other, which is obviously due to the predominance of condensation reactions over cracking. Thus, structural changes in asphaltene molecules during thermolysis to 370 °C may be mainly due to thermal decomposition processes, and above 400 °C – condensation reactions with generating significant amounts of compaction products.

Proceeding from DSC data, thermolysis temperatures of 120, 230, 370, 450, 550, and 650 °C, at which thermolysis of asphaltenes accompanied by products carrying off in each step was consistently carried out, were selected as thermolysis stages.

The DSK study was performed using the Netzsch STA 449 F3 A0010M instrument in the 30–750 °C temperature range with a heating rate of 20 °C/min. The sample was 8 mg. Data processing was carried out using the Netzsch Proteus software.

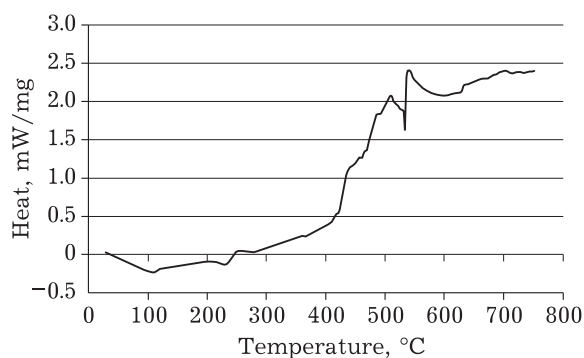


Fig. 1. DSC of asphaltenes from the Usinsk deposit.

Thermal decomposition of asphaltenes was carried out in a 25 cm³ quartz tube with a heating rate of 20 °C/min. The sample of asphaltenes (3 g) was loaded in a quartz crucible which was placed in a quartz crucible. Thermolysis took place in an inert atmosphere in the nitrogen current at a volumetric feed rate of 25–30 cm³/min until the reaction products were completely removed from the thermolysis zone. Thus, the flow regime of the process allowed withdrawing the substances formed from the reaction zone and minimizing the progression of secondary reactions. The volatile thermolysis products are received in the condenser-fridge, which was allocated the liquid phase, while gaseous products were located at the outlet of the refrigerator. After thermolysis, the asphaltenes were loaded into the paper cartridge and purified from maltenes by *n*-hexane in a Soxhlet apparatus, as described above. Further, they were extracted with chloroform, dried to constant mass and loaded into a quartz crucible for thermolysis at the next stage. Water-soluble compaction products, *i.e.* carbeno-carboides (“coke”), left in the paper cartridge were dried to constant mass. Maltenes collected during thermolysis and dried in the process of asphaltene treatment were combined and also dried out to the constant mass.

RESULTS AND DISCUSSION

The composition of products of stepwise thermolysis of asphaltenes from Usinsk deposit (Table 3), and also elemental composition, MM, and structural-group parameters of asphaltene molecules (Table 4) were determined. It is worth noting that thermolysis of asphaltenes at 370 °C leads to their complete conversion, therefore experiments were not carried out at temperatures of 450, 550, 650 °C due to the absence of the object of study. Thermolysis of initial asphaltenes at 120 °C is accompanied by generating 6.7 mass % of maltenes and minor amounts of gaseous products, *i.e.* 0.2 mass % (see Table 3), which unambiguously attests to thermal decomposition of asphaltenes. Chloroform-insoluble compaction products (“coke”) are absent in the first step of asphaltene thermolysis. As demonstrated by analysis of the data of changes in the structural-group composition (see Table 4), the MM of

TABLE 3

Product composition of stepwise asphaltene thermolysis

Thermolysis temperature, °C	Composition, mass %				
	Gas	Maltenes	“Coke”	Residual asphaltenes	Total
120	0.2	6.7	0.0	93.1	100
230	8.6	19.6	5.0	59.9	93.1
370	3.9	17.5	38.5	0.0	59.9
Total yield	12.7	43.8	43.5	0.0	100

asphaltene molecules increases by 360 amu firstly due to an increase in naphthenic and aromatic rings by 15 units.

Resulting from this, average parameters of residual asphaltenes (A120) are four structural units, which is by one greater than that for mean characteristics of initial asphaltene molecules (A0). Herewith, there are no significant changes in carbon atom distribution in structural fragments: the values of f_a , f_n , and f_{al} for A0 and A120 are different by almost 1 rel. %. This speaks of the structural similarity of the initial molecules of asphaltenes and the fragments attaching to them. In other words, dur-

ing thermal transformations of asphaltenes at 120 °C, the integrity of structural blocks of the initial macromolecules and the resulting fragments is preserved.

According to the elemental composition of residual asphaltenes after thermolysis at 120 °C, the content of C, H, N, and S is reduced by 7, 12, 4, and 6 mass %, respectively, in relation to their initial mass in A0, and oxygen content remains almost unchanged. Considering that in oil and oil products nitrogen atoms are mainly present in the composition of thermally stable pyrrole and pyridine cyclic systems, it is obvious that thermal decomposition

TABLE 4

Changes in average structural-group parameters of asphaltene molecules during stepwise thermolysis

Indicator	Sample		
	A0	A120	A230
MM	1600	1960	1980
<i>Carbon atom distribution in structural fragments, rel. %</i>			
f_a	42.1	41.4	47.9
f_n	52.7	53.9	49.0
f_{al}	5.2	4.7	3.1
<i>Carbon atom number, u.</i>			
C_a	47.0	57.5	66.8
C_n	58.7	74.8	68.3
C_{al}	5.8	6.6	4.3
C_α	16.5	20.9	22.5
C_γ	5.8	6.6	4.3
<i>Ring composition, u.</i>			
K_o	26.0	41.1	46.0
K_a	11.5	14.3	16.8
K_{sat}	14.5	26.7	29.2
<i>Number of structural units in molecules, u.</i>			
m_a	3.3	4.0	4.4

of the initial asphaltenes at 120 °C occurs due to degradation of unstable sulphur-containing structural fragments. On the basis of the obtained data, it can be concluded that during thermolysis at 120 °C, asphaltene molecules undergo structural and group changes resulting from: 1) thermal decomposition of labile aliphatic sulphur-containing structures to give 6.7 mass % of maltenes and 0.2 mass % of gaseous products; 2) attachment of large naphthenoaromatic units through aliphatic chains with an increase in MM by 360 amu.

The subsequent thermal decomposition of asphaltenes left after thermolysis at 120 °C was carried out at 230 °C and accompanied by almost 40 % transformation of the initial asphaltenes accompanied by the formation of lower amounts of the coke-like residue, *i.e.* 5.0 mass % (see Table 3). This attests to the predominance of asphaltene cracking reactions, while condensation ones contribute less to thermolysis product generating. Herewith, the residual asphaltenes (A230) are characterised by a minor increase of the average molecular mass compared to A120 (by 20 amu). Whereby, they undergo severe structural-group changes, in particular, there are compaction and A230 macromolecules aromatization. Thus, the average number of structural blocks increased by 4–5 units due to an increase in rings by 5 units. Herewith, the contribution of aromatic and naphthenic rings is almost the same. The number of carbon atoms in aliphatic fragments decreased by 2.

The main trends in the structure of asphaltene molecules in the process of step thermolysis can be judged by the relative distribution of carbon atoms in structural fragments: for A230, the value of f_a increased by 6.5 rel. %, and those of f_n and f_{al} decreased by 4.9 and 1.6 rel. %, respectively, compared to A120. It is obvious that a decrease in f_n and f_{al} is due to decomposition of aliphatic chains and naphthenic rings in asphaltene molecules, while aromatic rings seem to be stable at this temperature. The data on the dynamics of changes in the elemental composition of asphaltenes was unexpected: the molecule A230 contains 98.2 rel. % of oxygen atoms from their initial amount in A0. Almost half of the original sulphur remained in the A230 structure, which, considering the decomposition of sulphide

bonds at 120 °C, indicates the aromatic nature of sulphur fragments in A230. About 30 rel. % of nitrogen is also a part of A230 molecules.

Thermolysis of asphaltenes of residual A230 at a temperature of 370 °C leads to their complete transformation and the formation of 3.9 mass % of gas 17.5 mass % of maltenes and 38.5 mass % of “coke”. The high yield of the insoluble coke-like residue is due to the reduced potential for the formation of low molecular mass reaction products compared to high molecular mass ones due to the more compacted and aromatic structure of molecules of residual asphaltenes in A230 exposed to thermolysis at 370 °C. Thus, condensation reactions prevail over decomposition ones at the third stage of thermolysis of asphaltenes.

As demonstrated by dynamics analysis of changes in the elemental composition of asphaltenes, there is a trend in the accumulation of oxygen in high molecular mass thermolysis products: its content in A230 is 98.2 % of the initial amount in A0. Whereas, in K370 “coke”, it is 86.6 rel. % (Table 5). The fraction of sulphur in the series A120 > A230 > K370 decreased by 5.8, 39.3, 16.4 rel. %, respectively, which points out at its intense removal from asphaltenes at thermolysis temperature of 230 °C. Thus, 28.5 rel. % of sulphur atoms remain in “coke”. During thermal cleavage at 230 °C, the maximum amount of nitrogen is also removed from asphaltenes (25.1 rel. %), and in the next stage of thermolysis – only 12.8 rel. %. Proceeding from the findings, it is found that during thermolysis of asphaltenes of oil from the Usinsk deposit, the trend of heteroatoms to accumulation in compaction products increases in the series S → N → O.

CONCLUSION

Resulting from consecutive stepwise thermal decomposition of asphaltenes of oil from the Usinsk deposit, it is demonstrated that decomposition reactions prevail over condensation ones to 230 °C. At the same time, with a further increase in temperature, equilibrium shifts towards generating compaction products and condensation reactions of asphaltene macromolecules prevail. Thermolysis at 120 °C is accompanied by the decomposition of sulphur-containing aliphatic chains with integrity pres-

TABLE 5

Elements removal dynamics from asphaltene composition during stepwise thermolysis, rel. %

Element	Sample			
	A0	A120	A230	K370
C	100	93.1	59.6	39.5
H	100	87.9	48.4	9.9
N	100	96.1	71.0	58.2
S	100	94.2	54.9	28.5
O	100	99.9	98.2	86.6

ervation of naphthenoaromatic structural units. The A120 asphaltenes are interaction products of alkyl radicals of the initial molecules and the resulting fragments that are structural analogues. An increase in the number of naphthenic and aromatic rings by 15 leads to an increase in the molecular mass of A120 by 360 amu. At the next stage of thermolysis (230 °C), decomposition of aliphatic chains and naphthenic rigs proceeds, which is expressed in a decrease in the carbon atoms fraction in naphthenic (f_n) and aliphatic (f_{al}) fragments at 4.9 and 1.6 rel. %, respectively, and an increase in their fraction in aromatic fragments (f_a) by 6.5 rel. %. It is found that during sequential thermolysis of asphaltenes of oil from the Usinsk field, the trend to the ac-

cumulation of heteroatoms in compaction products increases in the series S → N → O.

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