

UDC 665.642:547.9

DOI: 10.15372/CSD2020226

Composition of the Products of Low-Temperature Destruction of Asphaltenes of Heavy Oil and Oil Residues

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Abstract

The ability of heavy oil asphaltenes and oil residues to generate low and high molecular weight components during thermolysis at 290 °C is assessed. It was established that the conversion of asphaltenes exceeds 99 mass %, regardless of the degree of their transformation during the rectification of heavy oil. Oil asphaltenes generate the maximal amount of resins (21.4 mass %), while fuel oil and tar asphaltenes generate 9.4 and 7.3 mass %, respectively. It was shown that thermal transformations of asphaltenes during the rectification of heavy oil lead to the removal of large structural fragments from their molecules, thereby reducing the ability of asphaltenes to generate resinous substances at 290 °C. At the same time, the molecular structure of asphaltenes is compacted, which leads to an increase in their tendency to form coke-like products. The yield of coke-like products of the low-temperature thermolysis of asphaltenes from oil, fuel oil and tar is 42.1, 54.4 and 58.1 mass %, respectively. It is established that the thermal transformations of asphaltenes in the process of heavy oil rectification do not have any significant effect on their ability to generate gas and liquid hydrocarbons during thermal degradation. The results of the study should be taken into account when developing new technologies for the primary processing of heavy crude oils and upgrading the existing ones.

Keywords: heavy crude oil, fuel oil, tar, oil residues, asphaltenes, composition, structure, decomposition, transformations, thermal stability, low-temperature thermolysis

INTRODUCTION

The current trend to a decrease in the resources of light oil and an increase in the world amount of the production of heavy and bituminous oil [1, 2] causes a number of problems in oil processing due to the high content of resinous and asphaltene substances in the raw material [3]. The major reasons of problems in heavy oil processing are connected with the disposition of asphaltene molecules to self-association, the formation of supramolecular structures and particles of different dispersed states [4, 5]. The features of the chemical nature of asphaltenes determine their properties, as well as the regularities of be-

haviour in thermal and thermocatalytic processes which are under extensive investigation at present [6–9]. As a rule, asphaltene transformations are studied at a temperature above 400 °C [10–12]. This is due to the high reactivity of asphaltenes under these conditions due to lability of the majority of covalent bonds in their molecules, while at temperatures lower than 350–400 °C asphaltenes are characterized by thermal stability with the conservation of their molecular structure [13, 14]. However, it is indicated in a number of studies that the thermal destruction of asphaltenes starts at a temperature about 100 °C with the intensification of their decomposition

during subsequent heating to 350 °C with the formation of gaseous substances, liquid hydrocarbons, resins and insoluble carbon residue [15–19]. The disposition of asphaltenes to thermal transformations at low temperatures leads to the formation of additional amounts of resinous and asphaltene substances even at the stage of rectification of heavy oil at atmospheric and residual pressure, which is inadmissible from the viewpoint of reasonable use of heavy hydrocarbon raw material [20, 21]. In this connection, it is necessary to expand the notions on the transformations of asphaltenes in heavy oil and oil residues in low-temperature processes for the development of efficient technologies for processing heavy and bituminous oil.

The goal of the present work was to evaluate the capacity of asphaltenes of heavy oil and oil residues to generate low- and high-molecular components during low-temperature destruction.

EXPERIMENTAL

The studies were carried out with asphaltenes extracted from oil of the Usinskoe deposit, from the residue of atmospheric-vacuum distillation of oil from the Usinskoe deposit (fuel oil), residue of the vacuum distillation of fuel oil (tar). Oil residues were obtained by rectification of initial oil according to GOST 11011–85 using an ARN-2 apparatus (Russia). The maximal temperature of stillage bottoms during oil fractionation did not exceed 290 °C.

The asphaltenes of oil and oil residues were obtained using a traditional method, which involved the precipitation of asphaltene residue as a result of the addition of *n*-hexane to the sample portion at the mass ratio of 40 : 1. The resulting solution was filtered, then the asphaltene precipitate was purified from asphalt-free oil by *n*-hexane in the Soxhlet's apparatus for 18 h. Purified asphaltenes were extracted from the filter by chloroform and dried to a constant mass. The resulting dry substance was additionally dissolved in a minimal amount of chloroform and re-precipitated by *n*-hexane for the purpose of liberating the low-molecular components that were co-precipitated during the isolation of asphaltenes. The procedure of purification of re-precipitated asphaltenes corresponded to the procedure described above. It was established through multiple re-precipitation of asphaltenes that the fraction of compounds captured by them during precipitation does not exceed 3 mass %.

Thermolysis of asphaltenes was carried out at a temperature of 290 °C in the flow of inter gas (N_2) with the transportation of the formed products from the reaction zone. The mass of sample portion was 7 g. The choice of thermolysis temperature was due to the results of previous investigation [21] which provided evidence of the active thermal transformations of asphaltenes during the rectification of heavy oil; its stillage bottoms were heated to a temperature not higher than 290 °C. So, it is interesting to evaluate the capacity of the asphaltenes of residues to generate low- and high-molecular compounds exactly under these conditions.

Thermolysis of asphaltenes in the flow of inert gas with the removal of the formed products from the reaction zone allow us to minimize secondary reactions and to evaluate the true potential of the objects of investigation as a source of low-molecular hydrocarbons.

The separation of the products of stepwise thermolysis of asphaltenes was carried out on the basis of their aggregate state, as well as on the basis of solubility and sorption capacity. Maltenes isolated from the products of asphaltene destruction were separated into oily and resinous products by means of column liquid-adsorption chromatography using silica gel of ASK grade as the immobile phase. Elution of oils was carried out with a mixture of *n*-hexane and benzene at a volume ratio of 4 : 1. Resinous substances were isolated with a mixture of ethanol and benzene at a volume ratio of 1 : 1. The solid products of thermolysis were separated into asphaltenes soluble in chloroform, and insoluble coke-like residue. The obtained oils, resins, residual asphaltenes and coke-like substances were brought to the constant mass in a vacuum drying box, and then their mass fraction in the products of asphaltene thermolysis was determined. The yield of gas was determined from the difference taking into account the content of all the formed products.

For asphaltenes, the structural parameters of their averaged macromolecules were calculated by means of structural group analysis (SGA) [22] developed by V. F. Kamyanov at the Institute of Petroleum Chemistry, Siberian Branch of the Russian Academy of Sciences (IPC SB RAS). Structural group analysis is based on the combined use of the data on the elemental composition and average molecular mass of the substances under investigation, and the results of their analyses by means of NMR 1H . Among the parameters calculated by means of SGA for asphal-

tene molecules, here we present f_a , f_n , f_p – relative content of carbon atoms in aromatic, naphthene and paraffin structural fragments, respectively.

Determination of the elemental composition of initial asphaltenes and those isolated from thermolysis products was carried out using a Vario EL Cube CHNSO-analyzer (Germany) by means of sample combustion at 1200 °C and chromatographic analysis of the formed gases.

The average molecular masses of initial and thermally transformed asphaltenes were measured using the cryoscopic method in naphthalene with the help of Krion instrument developed at the IPC SB RAS. The concentration of asphaltene substances in naphthalene was 0.5 mass %.

NMR ^1H spectra of asphaltenes were recorded with the help of an AVANCE-AV-400 Fourier spectrometer (USA), the solvent was CDCl_3 , and internal standard was hexamethyldisiloxane. Asphaltene concentration in CDCl_3 was 1 mass %.

Flash pyrolysis of insoluble coke-like products of asphaltene thermolysis was carried out at 750 °C (1.5 min) with the help of a Pyroprobe 5000 Series pyrolytic attachment (USA). Volatile products were analyzed with the help of an HP 6890 gas chromatograph (USA) with the mass selective detector. The products of flash pyrolysis were separated using an HP-5MS chromatographic column 30 m long, with the inner diameter 0.25 mm and 0.25 μm thickness of supported phase. The temperature programme of the gas chromatograph was: 40 °C (4 min) \rightarrow 5 °C/min to 290 °C \rightarrow 290 °C (10 min). The mass spectrometer is characterized by the following working parameters: ionizing voltage, 70 eV, emission current, 200 mA, temperature of the ion source, 230 °C, of the quadrupole, 150 °C, of the interface, 300 °C. Identification of the compounds was carried out over the characteristic ions in the mass fragmentogram, m/z : 55 (alkenes), 57 (alkanes), 69 (cyclopentanes), 83 (cyclohexanes), 123, 149, 163, 177,

191, 205 (terpanes), 217, 218 (regular steranes), 91, 105, 119, 133 (alkylbenzenes), 128, 142, 156, 170 (naphthalenes), 178, 192, 206, 220, 234 (phenanthrenes), 134, 147, 161, 175, 189 (benzothiophenes), 184, 198, 212, 226, 240 (dibenzothiophenes), 202 (pyrene, fluoranthene), 228 (chrysene, triphenylene, benz[a]anthracene).

RESULTS AND DISCUSSION

We demonstrated in our previous work [21] that asphaltenes (1.2 mass %) and resinous substances (4.3 mass %) are additionally formed during rectification of heavy oil at atmospheric pressure before fuel oil is obtained. Further accumulation of low-boiling fractions at residual pressure leads to the new formation of asphaltenes (2.9 mass %) and resins (18.9 mass %) (Table 1). Results of the analysis of elemental composition of initial oil and oil residues provide evidence of hydrogen redistribution between light and heavy fractions, as well as of disproportionate changes of the content of heteroelements in the bottoms during the primary treatment of heavy oil. For instance, sulphur content in oil, fuel oil and tar is almost the same, varying within the range of 1.95–1.98 mass %, unlike for oxygen: its content in fuel oil is higher than in oil and in tar by 0.15 and 0.09 mass %, respectively (see Table 1). On the basis of the obtained data, it was concluded that intense chemical reactions proceed between oil components during the atmospheric-vacuum rectification of oil. These reactions may be initiated by the most reactive resinous-asphaltenous substances. This is additionally confirmed by the changes in the structural group composition of asphaltenes. Thus, the content of hydrogen atoms in aromatic fragments of the asphaltene molecules of fuel oil (AF) is higher by 7.2 rel. % than in the molecules of the asphaltenes of oil (AO).

TABLE 1

Composition of oil, fuel oil and tar

Object	Content, mass. %							H/C _{at}
	Resins		Asphaltenes		Heteroelements			
	Exp	Calc.	Exp.	Calc.	N	S	O	
Oil	18.0	—	8.1	—	0.63	1.98	0.47	1.68
Fuel oil	29.1	24.8	12.4	11.2	0.78	1.95	0.62	1.34
Tar	53.5	34.6	18.5	15.6	0.93	1.96	0.53	1.34

Note. Exp. – resin and asphaltene content determined experimentally according to a standardized procedure; Calc. – resin and asphaltene content calculated according to equation [21].

TABLE 2

Structural group analysis of asphaltenes of oil (AO), fuel oil (AF) and tar (AT)

Parameter	AO	AF	AT
AMM, a.m.u.	1600	1790	1365
Content of heteroelements, mass %:			
N	1.16	1.58	1.80
S	3.00	2.49	2.23
O	4.41	4.40	3.84
Distribution of carbon atoms over structural fragments, rel. %:			
f_a	34.0	41.2	42.2
f_n	59.3	53.8	53.6
f_p	6.7	5.0	4.2

The content of naphthene and paraffin carbon in AF is lower than in AO by 5.5 and 1.7 rel. %, respectively. The average molecule mass (AMM) of asphaltenes during the process of obtaining fuel oil increased by 190 a.m.u. (Table 2). Then, during the process of obtaining tar, asphaltenes undergo less substantial changes in the distribution of carbon atoms over structural fragments. The values of f_a , f_n and f_p for the asphaltenes of fuel oil and the asphaltenes of tar (AT) differ by not more than 1 rel. %. However, AMM of AT is lower than AF by 425 a.m.u., which points to a substantial destruction of the carbon framework of their molecules. One can see in the changes of the elemental composition of asphaltenes that the fraction of nitrogen in them increases from 1.16 (AO) to 1.80 mass % (AG), while the content of sulphur and oxygen decreases by 0.77 and 0.57 mass %, respectively. Evidently, nitrogen-containing fragments of asphaltene molecules are mainly stable un-

der these conditions, while sulphur- and oxygen-containing structures are prone to intense destruction.

Results obtained in the previous investigation [21] determine great scientific and practical interest to the dynamics of the changes in the products of low-temperature destruction of the asphaltenes of heavy oil and oil residues obtained from it. This approach will allow one to evaluate the potential of asphaltenes in the formation of substances of different chemical nature and to broaden the notions of the directions of thermal transformations of asphaltenes during primary processing of heavy oil.

Asphaltene conversion during thermolysis at a temperature of 290 °C in the inter gas flow is characterized by almost the same values (99.2–99.5 mass %), independently of oil system from which the objects of investigation were isolated. Compounds with lower molecular mass (gas + oils + resins) may be formed in the amount of 40–60 mass % with respect to asphaltenes, and the same amount of high-molecular coke-like substances. However, the composition of the products of destruction of asphaltenes from oil and oil residues exhibits a number of characteristic differences and specific features. For instance, AO generate the maximal amount of resinous substances (21.4 mass %), while AF and AT generate substantially smaller amount – 9.4 and 7.3 %, respectively (Fig. 1). The yield of coke-like products (“coke”) from the thermolysis of AO is 42.1 mass %, which is smaller by 12.3 and 16.0 than in the products of destruction of AO and AT, respectively. The observed pattern of a decrease in the ability of asphaltenes to generate resins in the row AO → AF → AT is due to the destruction of their molecules

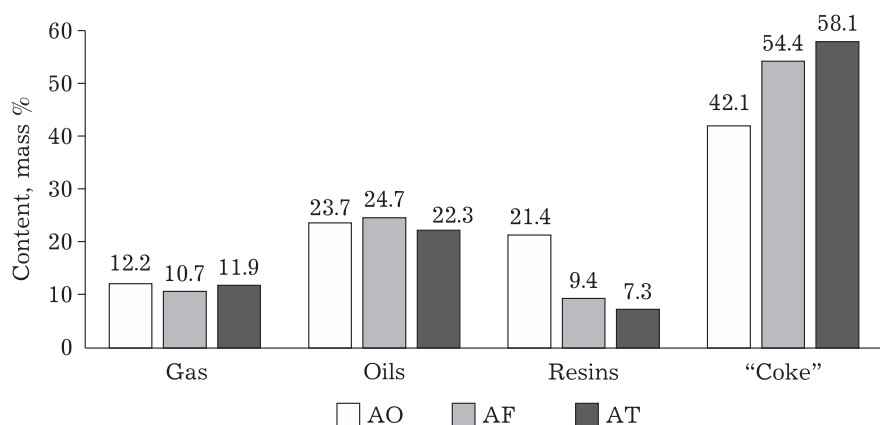


Fig. 1. Composition of asphaltene thermolysis products. AO, AF, and AT are asphaltenes of oil, fuel oil, and tar, respectively.

TABLE 3

Composition of the products of flash pyrolysis of low-temperature "coke"

Component	Content, rel. %
Alkenes	10.1
Alkanes	37.0
Cycloalkanes	3.4
Alkylbenzenes	33.0
Naphthalenes	5.4
Phenanthrenes	2.1
Benzothiophenes	6.3
Dibenzothiophenes	2.2
Tetracyclic arenes	0.5

during oil rectification through the rupture of the weakest bonds with the detachment of mainly high-molecular fragments because the structure of the main carbon framework of asphaltene molecules is stable under these conditions. At the same time, a series of thermal transformations of asphaltenes proceed to the densification of their molecular structure, which is evidenced by an increase in the disposition of asphaltenes to the formation of "coke" from AO to AG. It should be stressed that the most noticeable transformations of asphaltenes affecting their ability to generate various groups of substances occur during the process of obtaining fuel oil, which is additionally confirmed by the change in the structural group composition of asphaltenes (see Table 2). The content of both gaseous and oily components in the products of thermolysis of oil asphaltenes and the asphaltenes of oil residues is at a comparable level and equals 10.7–12.2 and 22.3–24.7 mass %, respectively (see Fig. 1). So, thermal transformations of asphaltenes during rectification of heavy oil do not have a substantial effect on their ability to generate low-molecular compounds through thermal destruction.

Taking into account the high yield of "coke" from asphaltene thermolysis under soft conditions (290 °C), it appears interesting to study further decomposition of insoluble coke-like substances for the purpose of evaluating their thermal stability and reactivity at higher temperatures. For low-temperature "coke" obtained in AO thermolysis as example, destruction of coke-like substances was carried out by means of flash pyrolysis at a temperature of 750 °C. Analysis of the composition of the formed products showed that the major volatile products of "coke" flash pyrolysis are alkanes and alkylbenzenes; their con-

tent is 37.0 and 33.0 rel. %, respectively (Table 3). A substantial amount of alkenes is also formed – 10.1 rel. %, while the fraction of cycloalkanes, bi-, tri- and tetracyclic aromatic compounds including thiophene derivatives is insignificant. The results of investigation showed that the fraction of aliphatic fragments and aromatic structural units composed of 1–3 condensed rings is substantial in the structure of low-temperature "coke", which provides intense destruction of "coke" at 750 °C with the formation of a broad range of low-molecular saturated and aromatic hydrocarbons, as well as sulphur-containing compounds.

CONCLUSION

In the course of the present investigation, thermolysis of asphaltenes of oil and oil residues (fuel oil and tar) was carried out at a temperature of 290 °C in the flow of inert gas with the removal of destruction products from the reaction zone. It was established that the conversion of asphaltenes exceeds 99 mass % independently of the degree of thermal transformation of oil system from which they have been isolated. Asphaltenes of oil generate the maximal amount of resinous substances (21.4 mass %), while asphaltenes of fuel oil and tar generate 9.4 and 7.3 mass %, respectively. It was established on the basis of the data obtained that thermal transformations of oil components accompanying rectification of heavy oil at atmospheric and residual pressure lead to the detachment of large structural fragments from asphaltene molecules, thus decreasing the ability of asphaltenes to generate resinous substances at 290 °C. At the same time, some processes take place that lead to the densification of the molecular structure of asphaltenes and an increase in their inclination to form coke-like products in low-temperature thermolysis; the yield of these products is 42.1, 54.4 and 58.1 mass % for the asphaltenes of oil, fuel oil and tar, respectively. It is demonstrated that the most important transformations of asphaltenes determining their thermal stability and reactivity occur during the process of obtaining fuel oil. It is established that the thermal transformations of asphaltenes during rectification of heavy oil do not have any significant effect on their ability to generate gas and oils during thermal destruction. It is necessary to take into account the results of the investigation when developing new technologies

of primary processing of oil raw material and upgrading the existing ones.

The work was carried out within the State Assignment for the IPC SB RAS (Project V.46.2.2), financed by the Ministry of Science and Education of the Russian Federation.

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