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In Reference to Thermal Stability and Reactivity of Heavy Oil Asphaltenes

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Abstract

The thermal stability and reactivity of heavy oil asphaltenes at temperatures below 300 °C were evaluated. In this work, we used an original method of sequential stepwise thermolysis of asphaltenes at temperatures of 120, 230, and 290 °C in the inert gas flow with the removal of the resulting products from the reaction zone at each stage of the process. This approach allows us to minimise the occurrence of secondary reactions to assess the true reactivity of asphaltenes, and also to take into account the differences in the binding energies in their molecules to determine the real thermal stability of asphaltenes within different temperature ranges. It was established that when asphaltenes are heated to 300 °C, they undergo intense thermal degradation with the formation of gas, oils, resins and insoluble coke-like substances. In the process of sequential stepwise thermolysis up to 290 °C, the conversion of heavy oil asphaltenes exceeds 90 %. At a temperature of 120 °C, the conversion of asphaltenes can reach 13 % with the formation of mainly resinous substances (more than 10 mass %). An increase in thermolysis temperature to 230 °C leads to an increase in the conversion of asphaltenes to 40 % due to their ability to generate significant amounts of gas and oils (14–18 mass %), as well as coke-like products (2–10 mass %) under these conditions. In the process of subsequent thermolysis of asphaltenes at a temperature of 290 °C, the maximum amount of coke-like substances (29–37 mass %) is formed. The yield of low molecular weight products is also significant and amounts to about 20 mass %. Thus, at temperatures below 300 °C, asphaltenes of heavy oils are characterised by low thermal stability and extremely high reactivity in thermal processes. The results obtained must be taken into account when developing new and modernising existing oil refining technologies.

Keywords: heavy crude oil, asphaltenes, composition, structure, thermolysis, decomposition, transformations, thermal stability, reactivity

INTRODUCTION

One of the major trends in the change of the resource basis of hydrocarbon raw materials is a steady growth of the production of heavy highly viscous oil [1], enriched with asphaltene substances. Asphaltenes are complicated mixtures of high-molecular hetero-organic compounds with the high content of S, N, O, V, Ni, and characterized by a different structure, molecular mass and physicochemical properties [2–7]. Unlike other components of oil, asphaltenes are inclined to intermolecular interactions with the formation of aggregates in oil. These aggregates are supramolecular colloid particles with different sizes [8, 9]. The set of features characterizing the chemical nature of asphaltene molecules gives rise to a number of problems for heavy oil processing. To solve these problems it is necessary to obtain systematized data on thermal stability and reactivity of asphaltenes under different conditions. It is generally accepted that up to 350 °C asphaltene molecules are highly stable against destruction [10, 11], while above this threshold temperature their intense destruction starts [12–14]. It was demonstrated by means of differential scanning calorimetry (DSC) that within temperature range 50–350 °C asphaltenes are prone to vitrification and melting with the formation of intermediate liquid crystal phases [15–18], however, the majority of phase transitions turned out to be irreversible, which gave rise to doubt whether the observed thermal effects were interpreted correctly. At the same time, it was established that the thermal destruction of asphaltene molecules due to the rupture of covalent bonds is possible at a temperature within 100–300 °C, with the formation of a broad range of products [19–23]. So, the question concerning the true thermal stability and reactivity of asphaltenes remains open, as well as the question concerning the dependence of these characteristics on the chemical nature of initial raw material.

The goal of the present work was the evaluation of the thermal stability and reactivity of asphaltenes of heavy oil during thermolysis at temperatures below 300 °C.

EXPERIMENTAL

The investigation was carried out with asphaltenes of natural bitumen from the Mordovo-Karmalskoye deposit (the Republic of Tatarstan), heavy oil of the Zyuzeevskoye deposit (the Republic of Tatarstan) and heavy oil of the Usinskoye deposit (Komi Republic).

Asphaltenes were isolated from oil by adding *n*-hexane to the portion of the sample to provide the mass ratio 40 : 1 and filtering the resulting solution after 24 h. Asphaltene deposit was purified from deasphaltene by *n*-hexane in the Soxhlet's apparatus for 18 h. Purified asphaltenes were extracted from the filter with chloroform and dried to a constant mass. Thus obtained dry substance was additionally dissolved in a minimal amount of chloroform and re-precipitated by *n*-hexane for the purpose of liberating low-molecular complexes co-precipitated during the isolation of asphaltenes. Purification of re-precipitated asphaltenes corresponded to the procedure described above. It was established by means of multiple re-precipitation of asphaltenes that the fraction of compounds captured by them during precipitation does not exceed 3 mass %.

Preliminary thermal analysis of asphaltenes was carried out by means of DSC using a synchronous thermal analyzer Netzsch STA 449F3 (Germany) at a temperature within the range of 25–750 °C in the flow of inert gas (N_2) with the flow rate of 20 mL/min. The rate of sample heating was 25 °C/min.

Asphaltene thermolysis was carried out sequentially at a temperature of 120 (30 min), 230 (15 min), 290 °C (5 min) in the flow of inert gas (N_2) with sampling, separation and analysis of the formed products after each temperature step of the process. The mass of the portion of the initial sample was 7 g. Residual asphaltenes isolated from the products of thermolysis at the first step at 120 °C were placed into the reactor once more and subjected to thermolysis at the second step etc. until the temperature of 290 °C was achieved. The choice of temperature points for thermolysis was due to the results of DSC of asphaltenes, which provided evidence of their possible thermal destruction under these conditions. The above-mentioned duration of thermolysis at each step provides the completeness of thermal transformations because the composition of destruction products does not change after an increase in process duration above the time indicated above.

Asphaltene thermolysis in the flow of inert gas with the removal of products from the reaction zone allows the minimization of secondary reactions, which is important in the evaluation of the true reactivity of asphaltenes at low temperatures. The stepwise process allows us to take into account the differences in the energies of bonds in asphaltene molecules. This provides the possibility to determine their thermal stability reliably under different temperature conditions.

Thermolysis products that were present in the gas phase were removed from the reaction zone, and then the components that are liquid under normal conditions were condensed in a water-cooled condenser. Thermolysis products that remained in the reactor were quantitatively transferred into a paper cartridge, which was then placed in the Soxhlet's apparatus and treated sequentially with *n*-hexane and chloroform to isolate maltenes (resins – oils) and residual asphaltenes, respectively. Coke-like substances that are insoluble in chloroform were mechanically removed from the paper cartridge. The resulting maltenes and liquid products of thermolysis were condensed in the water-cooled condenser, brought together and separated into oils and resins by means of column liquid adsorption chromatography. Oils were eluted with a mixture of *n*-hexane and benzene with the volume ratio of 4 : 1. Resinous substances were extracted with a mixture of ethanol and benzene at the volume ratio of 1 : 1. The yield of gaseous products of thermolysis was determined from the difference taking into account the content of all the formed components.

To characterize initial asphaltenes, we calculated averaged structural parameters of their macromolecules by means of structural group analysis (SGA) [24, 25] developed at the Institute of Petroleum Chemistry, Siberian Branch of the Russian Academy of Sciences (IPC SB RAS). Carbon content in aromatic, naphthene and paraffin fragments of asphaltene molecules was determined by means of SGA. Then the relative content of carbon atoms (%) in aromatic (f_a), naphthene (f_n) and paraffin (f_p) structural fragments was calculated.

The determination of the elemental composition of asphaltenes was performed with a CHNS-analyzer Vario el Cube (Germany) by burning the samples at 1200 °C.

The average molecular masses (AMM) of 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 Fourier spectrometer AVANCE-AV-400 (USA), the solvent was $CDCl_3$, the internal standard was hexamethyldisiloxane. The concentration of asphaltenes in $CDCl_3$ was 1 mass %.

RESULTS AND DISCUSSION

To reveal temperatures at which asphaltenes are inclined to thermal transformations, we used DSC allowing detection of thermal effects during sample heating. These effects were evidence of phase transitions and/or destructive processes.

During heating asphaltenes to 300 °C, several endothermic thermal effects are observed on DSC curves. For the asphaltenes of Karmal bitumen (AKB) and asphaltenes of oil from the Usinskoye deposit (AUO), the occurrence of three temperature intervals in which heat absorption was recorded is characteristic (Fig. 1). The maxima of endothermic effects fall on temperature points, °C: 106 and 105 (the first effect), 226 and 230 (the second effect), 273 and 280 (the third effect), respectively. The DSC curve of asphaltenes of oil from the Zyuzeevskoye deposit (AZO) was quite different: only one broad endothermic effect with the temperature peak at 127 °C is observed. It is possible that AZO samples have low thermal stability within a temperature range up to 300 °C, which leads to the formation of only one broadened region due to the superposition of several strong thermal effects. The results of DSC provide evidence that asphaltenes of heavy oil may exhibit a similar set of thermal effects observed during heating. The presence of these common properties points to the presence of similar structural fragments in asphaltene molecules, which determined their stability and reactivity in thermal processes.

On the basis of DSC data for asphaltenes, temperature points of 120, 230, 290 °C were chosen to carry out sequential thermolysis with the analysis of the formed products.

Analysis of the composition and structure of initial asphaltenes showed that they differ from each other substantially in the average molecular mass (AMM), which decreases in the sequence AZO → AKB → AUO from 2565 to 1600 a.m.u. According to the data of the elemental composition of asphaltenes, their ratios H/C_{at} are very close to each other and are within the range 1.11–1.13 (Table 1). The content of N atoms decreases in the sequence AZO → AKB → AUO from 1.76 to

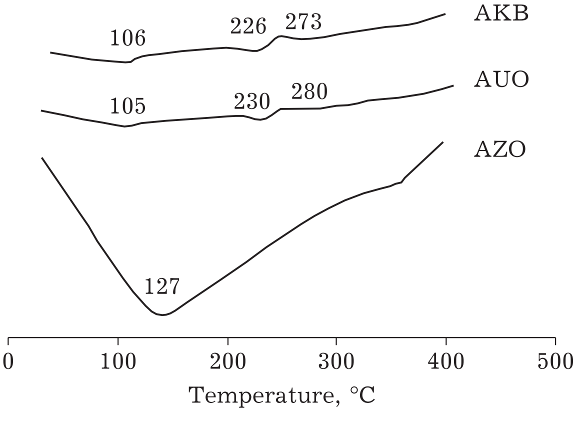

Fig. 1. DSC curves of asphaltenes: natural bitumen from the Mordovo-Karmalskoye deposit (AKB), heavy oil from the Usinskoye deposit (AUO), and heavy oil from the Zyuzeevskoye deposit (AZO).

1.16 mass %. The highest S content (>5 mass %) is characteristic of AZO and AKB, while it is only 3 mass % for AUO. The content of O atoms in AZO and AKB is high, too (6–7 mass %), unlike for AUO, in which the fraction of O does not exceed 4.5 mass %. Attention should be paid to the distribution of C atoms in the structural fragments of asphaltenes. The values of fn in all objects under investigation are within a narrow range 57.5–59.3 %, that is, the content of naphthene structures in them is practically equal. However, differences are observed in the relative content of carbon incorporated into aromatic and paraffin fragments. For example, fa is minimal for AKB and equals 26.3 rel. %, while AUO exhibit increased aromaticity factor: f_a = 34.0 rel. %. The fraction of carbon in paraffin fragments, quite contrary, is maximal in AKB and minimal in AUO: 16.2 and 6.7 rel. %, respectively. It should be stressed that AZO and AUO are similar in the distribution of carbon atoms in different fragments, the difference in the values for each structural fragment does not exceed 2 rel. %. So, it was established that asphaltenes exhibit substantial differences in structural group parameters, which may affect their reactivity and the directions of transformations in thermal processes.

It was demonstrated previously in [21] that the formation of gas, oils and resins is observed at the first stage of asphaltene thermolysis at 120 °C (Table 2). The presence of gaseous products in thermolysis products is an unambiguous indication of destructive processes with the rupture of covalent bonds in asphaltene molecules at this temperature. The highest transformation degree exceeding 13 % is characteristic of AKB and AUO with the formation of mainly resinous substances (10.1–11.2 mass %). The conversion of AZO does

TABLE 1

Structural group composition of asphaltenes

Parameter	Object of investigation		
	AZO	AKB	AUO
AMM, a.m.u.	2565	2040	1600
Elemental composition, mass %:			
H/C_{at}	1.11	1.13	1.12
N	1.76	1.39	1.16
S	5.05	5.35	3.00
O	6.87	6.02	4.41
Distribution of carbon atoms over structural fragments, rel. %:			
f_a	32.8	26.3	34.0
f_n	58.7	57.5	59.3
f_p	8.5	16.2	6.7

Note. f_a, f_n, f_p – relative content of carbon atoms n aromatic, naphthene and paraffin structural fragments, respectively.

TABLE 2

Composition of the products of stepwise thermolysis of asphaltenes, mass %

Component	Object of investigation								
	AZO			AKB			AUO		
	Thermolysis temperature, °C								
	120	230	290	120	230	290	120	230	290
Gas	1.2	2.6	5.2	0.7	3.9	5.1	0.6	3.9	7.7
Oils	2.0	13.6	15.8	2.4	14.7	14.8	1.6	11.2	10.9
Resins	2.8	4.9	1.4	10.1	8.7	1.5	11.2	8.7	1.5
Asphaltenes	94.0	62.3	2.8	86.8	57.4	7.0	86.6	56.3	0.6
“Coke”	0.0	10.6	37.1	0.0	2.1	29.0	0.0	6.5	35.6

Note. Total content of thermolysis products at each step corresponds to asphaltene content at the previous step.

not exceed 6 %, and the fraction of resins in thermolysis products is 3–4 times lower than in the products of AKB and AUO thermolysis. The amounts of gas and resins formed during the destruction of asphaltenes at 120 °C are within the ranges of 0.6–1.2 and 1.6–2.4 mass %, respectively.

Subsequent thermolysis of residual asphaltenes at 230 °C is characterized by the intense destruction of their molecules, which is evidenced by the formation of substantial amounts of gaseous and liquid products, as well as high-molecular coke-like substances (“coke”). The degree of asphaltene transformation may exceed 40 mass % with respect to initial samples. The yield of gaseous products of thermolysis is 2.6–3.9 mass %, while the content of oils is substantially higher – 11.2–14.7 mass % (see Table 2). The products of thermal destruction of asphaltenes at 230 °C contain 4.9–8.7 mass % of resinous substances, while “coke” content varies within a broader range (2.1–10.6 mass %).

Further thermal transformations of asphaltenes at a temperature of 290 °C lead to practically complete conversion, and the major products are coke-like substances that are insoluble in $CHCl_3$. The content of residual AZO and AKB after the third step of thermolysis is 2.8 and 7.0 mass %, respectively, while for AUO it does not exceed 1 mass % (see Table 2). It should be noted that the thermolysis of asphaltenes at 290 °C results in the formation of a small amount of resins: 1.4–1.5 mass %. It may be assumed that the thermal destruction of asphaltenes at the third step is so intense that the fragments of their molecular structure related to resins according to isolation method and possessing low thermal stability comparable with that of asphaltenes undergo instantaneous transformations into low-molecular (gas and oils) and coke-like products. In this connection, thermolysis of asphaltenes at 290 °C is accompanied mainly by the formation of gas, oils and “coke”, while the content of resinous-asphaltene thermolysis products is minimal. Gas content in the products from the third step of thermolysis of AZO and AKB is 5.2 and 5.1 mass %, and the fraction of oils is 15.8 and 14.8 mass %, respectively. The content of gas and oils in the products of thermal destruction of AUO is 7.7 and 10.9 mass %, respectively.

CONCLUSION

It was established in the investigation that heating of asphaltenes to 300 °C involves not only phase transitions but also intense thermal destruction with the formation of a broad range of products. It was demonstrated that independently of the composition of asphaltenes and their structures, the destruction of their molecules starts at a temperature slightly higher than 100 °C. It was established that the conversion of asphaltenes from heavy oil reaches more than 90 % in sequential stepwise thermolysis at a temperature of 120, 230 and 290 °C in the flow of inert gas with the removal of the formed products. At 120 °C, the degree of asphaltene transformation may exceed 13 % mainly with the formation of resinous substances (more than 10 mass %). An increase in thermolysis temperature to 230 °C leads to an increase in asphaltene conversion to 40 % due to their ability to generate substantial amounts of low-molecular components (gas and oils, 14–18 mass %) under these conditions. The thermal transformations of asphaltenes at 230 °C also promote the formation of insoluble coke-like products. Their content may reach 10 mass %. Subsequent thermolysis of asphaltenes at a temperature of 290 °C results in the formation of the maximal amount of coke-like substances (29–37 mass %); the yield of low-molecular products is substantial too: it is about 20 mass %. So, at temperatures below 300 °C asphaltenes of heavy oil are characterized by low thermal stability and extremely high reactivity in thermal processes. It is necessary to take into account the obtained results in the development of new technologies of hydrocarbon raw processing and the improvement of the existing ones.

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