Thermal Conversion of Heavy Oil Systems and Analysis of Structural Changes of their High Components with PMR Method

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Abstract

Heavy oil systems are thermolyzed with different ratios of amount of resins and asphaltenes: 3.4, 3.8, 5.3, and 12.4. The change in yield and composition of gaseous, liquid and solid products of thermolysis is shown depending on the ratio of the resin: asphaltenes. In the liquid products of thermolysis, resins content decreases and s the amount of asphaltenes and oils increases. According to PMR spectroscopy, the distribution of protons is compared in the secondary resin and asphaltene molecules of the initial samples and the thermolysis products. It is shown that the relative content of hydrogen aromatic rings in the molecules of asphaltenes is higher, and for β- and γ- positions relative to the aromatic rings and heterofunction, it is lower than in the resin molecules.

1. Introduction

In the total world production, the share of heavy hydrocarbon raw materials such as heavy oils and natural bitumen increases. This raw material contains significant amount of high-molecular resin-asphaltene components, small amount of light fractions. High content of heteroatoms and metals (V, Ni, Fe, etc.) in the resins and asphaltenes which are catalyst poisons makes it difficult to recycle the heavy oil feedstock with conventional

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methods[1-3]. To increase the depth of processing of such materials, various approaches are used with catalytic and thermal processes to obtain lighter "synthetic" oil with reduced content of resins and asphaltenes[4-7].

The amount of resins and asphaltenes in heavy oil determines properties of dispersion medium and dispersed phase, as well as the stability of raw materials under thermolysis conditions[8-9]. As shown in[10-15], resins and asphaltenes are the components source of light fractions and gaseous products in the thermolysis of heavy oils, they lead to formation of coke. Creation of effective ways of heavy hydrocarbon feedstock processing is impossible without studying the composition and structure of resins and alphaltenes, as well as the direction of their transformation in thermodestructive processes according to their quantitative ratio[12, 14, 16-19].

Proton magnetic resonance (PMR) is of particular importance in the study of the composition and structure of high-molecular compounds of oil. This method allows determining the content of hydrogen atoms of the molecules of the resins and asphaltenes in aromatic rings and the alkyl groups in the α-, β-, γ-positions relative to aromatic, naphthenic rings and heterofunctional groups. Results of PMR spectroscopy in conjunction with the elemental composition and molecular weight form the basis of SGA (structural group analysis) developed by the Institute of Petroleum Chemistry, Siberian Branch of Russian Academy of Sciences[20]. Structural group analysis allows calculating the average distribution of atoms between the structural elements of molecules of oil high molecular weight compounds, which provides information on the size and structure of the molecules, the composition and quantity of various structural groups.

The aim of this work is to study the influence of the ratio of resin and asphaltene from heavy oil feedstock on the composition of the thermolysis products and structure of their components.

2. Experimental part

All experiments were carried out on model mixtures prepared with two heavy oils which differ substantially in content of resins and asphaltenes. Varying the quantitative ratio of resins and asphaltenes in the model system, the qualitative composition of the resin and asphaltene raw material is considered to remain unchanged. Undoubtedly, when preparing model mixtures, change in the dispersion medium leads to changes in the structural organization of the resins and asphaltenes molecules. Nevertheless, this approach is believed to assess the impact of the ratio of resins and asphaltenes in petroleum systems on the transformation direction of these components in thermal processes and changes in their structural characteristics.

Model samples of mixtures in which the ratio of resins and asphaltenes can vary from 3.1 to 12.6 prepared by mixing heavy (ρ = 886 kg/m^3), middle-resinous (7.1%) oil with low content of asphaltenes (0.4%) of Barsukovskoye oilfield and heavy (ρ = 978 kg/m^3) highly-resinous (26.2%) Ashalchinsky bitumen with high asphaltene content (6.2%) (Table 1).

Thermolysis was carried out in reactors of 12 cm^3, at temperature of 450 °C for 2 hours in air. As shown in[10], these conditions ensure maximum yield of liquid products along with acceptable outlet of gas and solid phases. Weight of the sample was 7 g. In the experiments, the reactors with and without the sample prepared for thermolysis the were weighed. After heat treatment of samples, the output of gaseous products was determined by weight loss of the reactor after removal of the gas products from the reactor. Selected gaseous products were analyzed with a gas chromatograph. Liquid products are recovered by washing the reactor with chloroform. After selection of the liquid product, reactor was washed with chloroform and weighed. The resulting difference between the mass of the reactor prior to the experiment and after removal of gaseous and liquid products was defined as the amount of coke formed during the thermolysis.

The content of resins and asphaltenes in the thermolysis products was determined by the method[20]. Asphaltenes were isolated by diluting the sample with n-hexane in ratio 1:40 keeping the solution during the day, filtering the precipitate. The resulting precipitate was placed in a paper cartridge and washed in a Soxhlet apparatus with hexane from oils and resins, asphaltenes are then eluted from the cartridge with chloroform, then the solvent was distilled off, and asphaltenes were dried to constant weight.

Received after reaction maltens were loaded on to silicagel ASK, the resultant mixture was charged in the Soxhlet apparatus. n- hexane extracted oils first (hydrocarbons concentrate) and then resins with a mixture of benzene and ethanol (1:1). From the resulting eluate of oils and resins, solvents were distilled, anddried to constant weight.

Resins and asphaltenes separated from the oil raw material and the thermolysis products were analyzed with NMR-spectroscopy by Fourier spectrometer AVANCE-AV-300 (solvent is deuterochloroform, internal standard is hexamethyldisiloxane) at 1% concentration of substances.

3   Results and Discussion

According to the material balance of the oil system thermolysis with the minimum ratio resin: asphaltenes equal to 3.4 (initial asphaltenes the greatest amount of gaseous (3.9%) and solid (2.3%) products is produced while the thermolysis of oil system with the maximum value of the resin: asphaltenes equal to 12.4 (initial oil), leads to formation of much smaller quantities of gases (1.2%) and solid (0.1 wt. %). products (Table 1).

Table 1 - Composition of initial mixtures and the material balance of thermolysis

Sample	Ratio of resin: asphaltenes	Content,% wt.		Yield of thermolysis products wt%.			
		Asphaltenes	Resins	Oils	Gas	Solids	Liquids
Oil	12.4	0.9	11.1	88.0	1.2	0.1	98.7
Mixture 1	5.3	1.9	10.1	88.0	1.0	0.2	98.8
Mixture 2	3.8	4.2	16.0	79.8	1.5	1.1	97.4
Bitumen	3.4	7.7	25.9	66.3	3.9	2.3	93.8

Methane and ethane are the main hydrocarbonaceous components of the gaseous products of all mixtures thermolysis, besides they contain butanes and pentanes (Table 2). The greatest amount of hydrogen, ethane, and propane was formed by bitumen thermolysis wherein the ratio of resin: asphaltenes is the lowest.

Patterns in the composition of the gaseous products of thermolysis in general depending on the ratio of resin: asphaltenes are not revealed.

Table 2 Composition of gaseous products of thermolysis

Components	Content in the products of thermolysis,% wt.			
	Oil	Mixture 1	Mixture 2	Bitumen
H_2	0.001	0.003	0.001	5.4
CH_4	74.9	42.5	92.6	26.5
CO_2	16.9	17.8	0.6	8.2
C_2H_6	6.5	12.9	3.8	26.4
C_3H_8	1. 6	5.2	1.9	22.4
C_3H_6	0.0	1.1	0.2	0.0
iC_4H_{10}	0.0	8.4	0.3	5.2
nC_4H_{10}	0.0	3.4	0.4	0.3
C_4H_8	0.0	0.8	0.1	0.0
iC_5H_{12}	0.0	5.9	0.03	2.9
nC_5H_{12}	0.0	1.9	0.1	2.7

The most significant changes are observed in the material composition of the liquid products of oil thermolysis : the amount of asphaltenes increased 1.5 times, and resins content decreases 1.7 times compared with the initial oil, and the amount of light fractions increased by 6.0%. The ratio resin: asphaltenes decreases from 12.4 to 4.7 (Table 3).

In the products of thermolysis of mixtures 1 and 2, resin and asphaltene content varies less considerably and therefore value of ratio resin: asphaltenes does not decrease so sharply.

In thermolysis of bitumen, content of resins is reduced by 10% compared to the initial sample, whereas the amount of asphaltenes changes slightly.

Table 3 - Material composition of the thermolysis products

Sample	Ratio of resin: asphaltenes	Content,% wt.		
		Asphaltenes	Resins	Oils
Oil	4.7	1.4	6.5	90.8
Mixture 1	4.0	2.2	8.8	87.8
Mixture 2	2.9	4.6	13.5	79.2
Bitumen	2.1	7.0	14.9	71.9

Thermolysis of the mixture 2 and bitumen at 450 °C increases the yield of light fraction X.I.-350 °C to 7 - 8% (according to the fractional composition), whereas content of the fraction X.I.-350 ° C is virtually unchanged in the thermolysis of oil and the mixture 1.

Table 4 shows the results of analysis of the asphaltenes and resins model mixtures before and after thermolysis by PMR spectroscopy. When comparing the distribution of protons in the molecules of the HMC samples, it can be seen that the relative content of the hydrogen atoms of the aromatic ring in the asphaltene molecules is higher, and in β- and γ- positions relative to aromatic ring and heterofunctions, it is lower than in resin molecules. This is probably due to the greater number of cycles and a smaller number of substituents on the aromatic ring of asphaltenes relative to rings of resinous substances.

Table 4 - Characteristics of resins and asphaltenes according to PMR spectroscopy

Sample	The average content in the molecule,%							
	asphaltenes				resins			
	Har	Hα	Hβ	Hγ	Hap	Hα	Hβ	Hγ
Initial								
Oil	13.4	24.3	51.8	10.5	8.9	18.1	56.2	16.9
Mixture 1	10.2	22.0	54.7	13.1	6.2	19.2	57.2	17.4
Mixture 2	9.4	22.6	52.4	15.6	6.2	21.1	53.41	19.2
Bitumen	7.6	25.2	54.2	13.0	6.7	20.0	55.1	18.2
After thermolysis								
Oil	13.8	20.0	50.4	15.8	8.7	17.9	54.7	18.6
Mixture 1	11.0	20.4	52.4	16.2	7.5	17.0	55.7	20.3
Mixture 2	16.6	26.6	52.2	13.6	8.6	20.8	54.2	16.4
Bitumen	16.2	26.7	46.8	10.4	7.7	21.3	54.3	16.6

Har – the number of protons in the aromatic rings, Hα – the number of protons in the groups CH3, CH2 and CH in α-position to the aromatic rings and heterofunctions, Nβ - number of protons in the CH2 and CH groups in β-position to the aromatic rings and heterofunctions, Nγ - the number of protons in the terminal methyl groups

It can be assumed that because of low molecular weight compared with asphaltenes, resins have smaller proportion of aromatic rings in their structure which causes the contents of the resins Har to be about 5.9-8.9%. However, resin structure α-position is less saturated than asphaltenes which may indicate a high degree of branching of the aliphatic chain carbon structure in the α-position relative to the aromatic rings, heterofunctional groups and atoms in molecules nonaromatic links.

It can be seen that as a result of thermal transformations, relative content of hydrogen atoms in the aromatic rings in resin and asphaltene molecules increased confirming the reactions of degradation, and this increase is inversely proportional to ratio resin: asphaltene in the samples. Protons of aliphatic chains are redistributed by α-, β-, γ- position due to destructive processes and reactions of substitution, addition, isomerization, recombination, etc.

It is shown that in the process of thermal cracking reactions, resinous components degrade leading to formation of low molecular weight resins and light hydrocarbons, and polycondensation reaction occur parallelly promoting formation of additional amounts of asphaltenes and solid.

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