

Study of composition and structure of resinous-asphaltenic products of various petroleum oils thermolysis

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Received January 16, 2021; Accepted April 16, 2021

Abstract

An increase in the share of heavy petroleum reserves relative to light petroleum reserves leads to the need to develop new effective technologies or optimize the existing ones, since the current technological schemes are not suitable for processing heavy hydrocarbon raw materials. During the thermal processing of heavy petroleum, resinous-asphaltenic substances are formed; they negatively affect the entire technological process. At this stage, the information on the conversion of oil components is very limited and does not allow assessing the influence of the oils composition on the structure of RAS generated by them; it is the most important fundamental task for optimizing heavy petroleum processing technologies.

Keywords: *Oils; Resins; Asphaltenes; Heavy petroleum; Hydrocarbons; Thermolysis.*

1. Introduction

The decline in light petroleum reserves makes it necessary to develop processes for deep processing of heavy hydrocarbons (HC). One of the problems in the processing of heavy petroleum raw materials is the emergence of new resins and asphaltenes, as well as the formation of heavier products during thermal transformation. To solve such problems, various approaches are used; they range from the use of catalysts to surfactants [1-3]. Despite the active study of the composition and structure, as well as the transformations of native resins and asphaltenes present in the raw materials, the nature and mechanisms of secondary surfactant formation under various conditions remain poorly understood.

In the works [4-7], it was found out that thermolysis of oils and asphaltenes separately as well as their mixtures produces coke-like solid products. It was concluded that the thermal transformations of HC include not only destruction reactions that lead to the formation of gas, but also condensation reactions of HC radicals resulting in the formation of resins, asphaltenes, which are able to expand and form a coke-like residue. In the works [8-10], it was suggested that during the thermolysis of petroleum, the reactions of resinous substance destruction dominate; they are followed by the reactions of polycondensation of resinous substance fragments, which lead to the formation of secondary asphaltenes.

Since most processes involve thermal effects, the study of thermal transformation of oils is a necessary step to gain knowledge about the formation mechanism of resins and asphaltenes, which have a negative impact on the entire technological process: poison the catalyst, reduce the yield of a light product, cause corrosion of equipment and, as a result, its shorter operating time.

2 Experimental part

2.1. Materials

The characteristics of the initial petroleum oils of the Russkii (IM 1), Ziuzeevskii (IM 2) and Usinskii (IM 3) petroleum fields are presented in Table 1.

Table 1. Characteristics of initial petroleum oils

Parameter	IPO ₁	IPO ₂	IPO ₃
Ultimate composition, wt. %:			
C	86.99	83.73	86.0
H	11.86	12.23	11.9
N	0.64	0.38	0.6
S	0.51	4.29	1.6
H/C	1.64	1.75	1.66
Group composition, %			
saturated	44.2	35.3	36.6
mono-, bi - and triaromatic	31.8	53.6	39.4
polyaromatic	24.0	11.1	24.0

Table 1 shows that the low H/C ratio in IPO₁ and IPO₃ (1.64 and 1.66) indicates a small number of aliphatic structures. The proportion of nitrogen is higher in IPO₁ - 0.64 %, the minimum nitrogen content is in IPO₂ - 0.38 %. The highest total content of heteroelements is in IPO₂ (4.67 %), and the lowest one is in IPO₁ (1.15 %). Group composition data show that IPO₂ and IPO₃ are dominated by aromatic compounds (64.7 and 63.4 %), the main share of which is mono-, bi - and triaromatic (53.6 and 39.4 %). The content of saturated HC in IPO₂ is the smallest amount, in comparison with the other oils - 35.29 %. IPO₁ has the highest content of saturated HC (44.2%) in relation to their content in IPO₂ and IPO₃, but polyaromatic compounds in IPO₁ and IPO₃ are observed in equal amounts (24.0 %).

2.2. Equipment and methods

2.2.1. Method of obtaining oil samples

Before obtaining the oils, the petroleum was deasphalted by diluting the petroleum sample with n-hexane in a volume ratio of 1: 40 and a day later, maltenes were filtered out from the precipitate. The resulting precipitate in a paper cartridge was washed with hexane in a Soxhlet apparatus. Then the excess hexane was removed from the mixtures of hexane and deasphaltized petroleum, the remaining part of maltenes was applied on the activated silica gel layer (ratio 1:15). The resulting mixture of silica gel with the adsorbed material was up-loaded in a Soxhlet extractor and oils were successively washed with n-hexane, resins with a mixture of ethanol and benzene (1:1) at the boiling points of the solvents. The oils were obtained after the solvent had been driven off at a rotary evaporator.

2.2.2. Methods of petroleum oil thermolysis and separation of thermolysis products

Thermolysis of oils was performed in the autoclaves with a volume of 12 cm³. The mass of petroleum oils loaded into the reactor was 4±0.03 g. The experiments were carried out in air; it does not lead to significant changes in the composition of the resulting products due to its small volume, at a temperature of 450°C and a duration of 120 minutes. The choice of thermolysis conditions is determined by the preliminary tests, which showed that at a temperature of 450°C, a sufficient amount of resins and asphaltenes is formed for further investigation of their composition and structure.

After thermolysis, the reactor was cooled with running water, gaseous products were selected, the reactor head was removed and weighed, thereby determining the gas output.

After oil thermolysis, the products were separated according to the state of aggregation (gas, liquid, solid), whereas liquid and solid substances according to the principle of solubility and sorption ability (oils, resins, asphaltenes, coke). Liquid thermolysis products were divided into oils and resins. Solid products in the paper cartridge were placed in the Soxhlet apparatus and washed with n-hexane until the solution is discolored, thereby washing away residual maltenes from the cartridge.

Solid thermolysis products were separated in the Soxhlet apparatus by separating asphaltenes with chloroform, while the coke remained in the paper cartridge since it is not soluble in chloroform. Oils, resins and asphaltenes were separated from the solvent with a rotary

evaporator and brought to a constant mass in a vacuum drying box. Coke was mechanically removed from the paper cartridge.

Due to the oil volatility after thermolysis, their mass was determined indirectly by the formula:

$$m_o = m_s - (m_r + m_{asph} + m_c),$$

where m_s , m_r , m_{asph} , m_c – the masses of the sample, resins, asphaltenes and coke.

Differences in the composition as well as physical and chemical properties of petroleum should cause different features of the composition and structure of the oils isolated from them.

3. Results and discussion

The products of asphaltene thermolysis were oils, gases, resins, asphaltenes and coke. Resins and asphaltenes are so called in accordance with the method of their preparation from a mixture of the products of thermal transformation. Oils, resins and asphaltenes were analyzed by elemental analysis and IR spectrometry. Table 2 shows the "material" composition and yields of oil thermolysis products.

Table 2. Composition of different oil thermolysis products

Oil thermolysis products	Content, wt. %:				
	oils	resins	asphaltenes	coke	gas
IO ₁ thermolysis	94.0	2.2	1.0	0.8	2.0
IO ₂ thermolysis	91.5	4.5	0.3	1.1	2.6
IO ₃ thermolysis	93.5	3.2	0.4	0.7	2.2

The difference in the composition of the resulting products may be explained by the initial oil compositions. It was found that thermolysis of IO₂ containing a large number of heteroatoms and aromatic compounds contributes to a higher yield of resins and a lower yield of asphaltenes than those of thermolysis of IO₁, IO₃. This is due to this fact that the formation of resins is based on a high content of heteroatomic compounds. As already known, resins are the precursors of asphaltenes, but, as can be seen from the material composition of IO₂ thermolysis, resins did not lead to the formation of a large amount of asphaltenes, because we can see a higher content of asphaltenes in the thermolysis products in other material compositions than in this case. In addition to the high content of heteroatoms, the initial oils had a high H/C ratio, a high content of mono-, bi-, and tri-aromatic structures, but at the same time a lower content of polycyclic aromatic structures than other initial oils. It is probable that the formation of asphaltenes in thermal transformations is due to the high content of polycyclic aromatic structures, which were not sufficient for the formation of asphaltenes in thermolysis of IO₂. Thus, the formation of resins and asphaltenes is more affected by the content of heteroatomic compounds in the initial oils as well as the compounds with a polycyclic aromatic structure. What is more, a large amount of gas was formed probably due to the destruction of the aliphatic chains in the composition of the oils.

In thermolysis of IO₁, the highest stability is observed due to the low conversion rate (6 %). This behavior may be attributed to the high content of saturated structures, some of which could lead to the formation of gas during destruction, while the initial oils had a lower content of heteroatomic components in comparison with the other oils. Having a high content of polycyclic compounds, a high H/C ratio and a low content of heteroatoms, such properties of the initial oils could contribute to a high yield of asphaltenes, compared to the yield of asphaltenes by thermolysis of the other oils.

The composition of gaseous products of different oil thermolysis was quite similar. Therefore, Figure 1 shows the composition of the gaseous products of IO₂ thermolysis as an example. Alkane HC: methane (39.23 %), ethane (26.39%) and pentane (24.57%) are predominant in the gaseous products. Moreover, gaseous products are characterized by a low content

of alkane HC: i-butane and i-pentane (5.09 % and 1.11 %, respectively), which indicates the C-C bond breaking reactions.

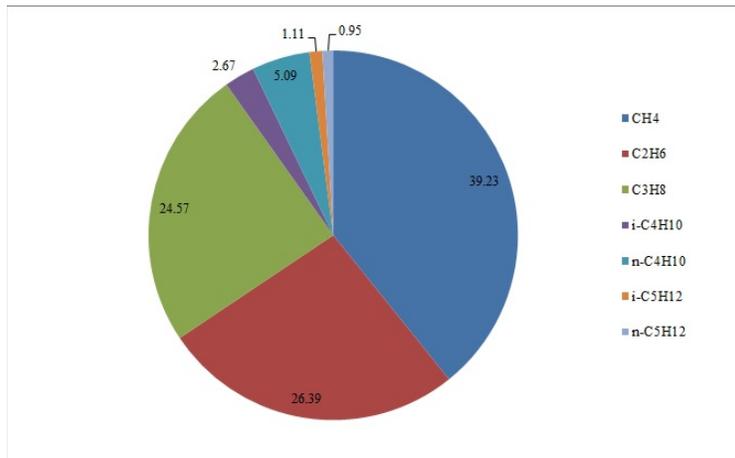


Figure 1. Composition of gaseous products of IO₂ thermolysis

Differences in the composition of oils should cause different features of the composition and structure of the oils obtained from them. The results of the study of the initial oils, oils after thermolysis and resins are shown in Table 4. The oils obtained after thermolysis have a low H/C ratio compared to IO₁, the ratio decreased from 1.64 to 1.55. A decrease in the H/C ratio of the oils after thermolysis indicates a high content of aromatic cycles in the structure, the proportion of which increased due to the destruction of the aromatic cycles with the alkyl substituents. Sulfur was not found in O₁, possibly due to the recombination of polyaromatic components and formation of resinous substances, which included sulfur. The content of sulfur in R₁ (1.03 %) increased compared to the content of sulfur in the initial oils (0.5%), which indicates the enrichment with the sulfur-containing compounds during thermolysis of oils. The nitrogen content increases in the series IO₁→O₁→R₁, which can also be caused by the enrichment during heat treatment of the initial oils.

In the oils (O₂) obtained after thermolysis of IO₂, the value of the H/C ratio decreased by 1.3, compared to the initial oils. It may be explained by the fact that as a result of thermal transformation, the alkyl fragments in the aromatic structures were split off, therefore, the saturation of the oil structure with hydrogen decreased. R₂ is significantly enriched with sulfur- and nitrogen-containing structural fragments compared to the initial IO₂ (2.8 and 0.48%, respectively).

All resins obtained from the products of oil thermolysis are enriched with heteroelements (S and N), and their content in the products of thermolysis exceeds the content in the initial oils. As a result of such an increase in the content of sulfur and nitrogen in the thermolysis products, it can be supposed that during thermolysis of the initial oils, the resin molecules are capable of being enriched with sulfur- and nitrogen-containing structural fragments. The most heteroatomic IO₂ was significantly enriched with sulfur- and nitrogen-containing structural fragments (7.10 and 0.44%, respectively). The sulfur content in R₃ decreased compared to the initial oils possibly due to the formation of hydrogen sulfide.

Table 4. Characteristics of initial oils as well as oils and resins after thermolysis

Parameter	IO ₁	O ₁	R ₁	IO ₂	O ₂	R ₂	IO ₃	O ₃	R ₃
Ultimate composition, wt. %:									
C	87.0	87.82	86.93	83.7	84.23	83.46	86.0	89.00	86.24
H	11.7	11.47	11.25	12.2	11.71	8.55	11.9	11.50	11.62
N	0.6	0.71	0.79	0.4	0.50	0.88	0.6	0.60	0.69
S	0.5	-	1.03	4.3	3.56	7.10	1.6	1.66	1.45
H/C	1.64	1.56	1.55	1.75	1.67	1.23	1.66	1.55	1.62

The content of the heteroatoms in the initial oils affected the ultimate composition of the obtained resins; in the series $R_1 \rightarrow R_3 \rightarrow R_2$ the total content of the heteroatoms increases, as well as in the initial oils. The content of sulfur and nitrogen in R_2 increased almost 2 times compared to the initial oils.

The presence of the aromatic structures is confirmed by the absorption bands 755, 809 and 1603 cm^{-1} (Figure 2). The presence of the oxygen-containing groups is indicated by the spectra of the bands 1185, 1708 and 1712 cm^{-1} . Sulfoxide groups are identified by the absorption bands 1020 and 1032 cm^{-1} .

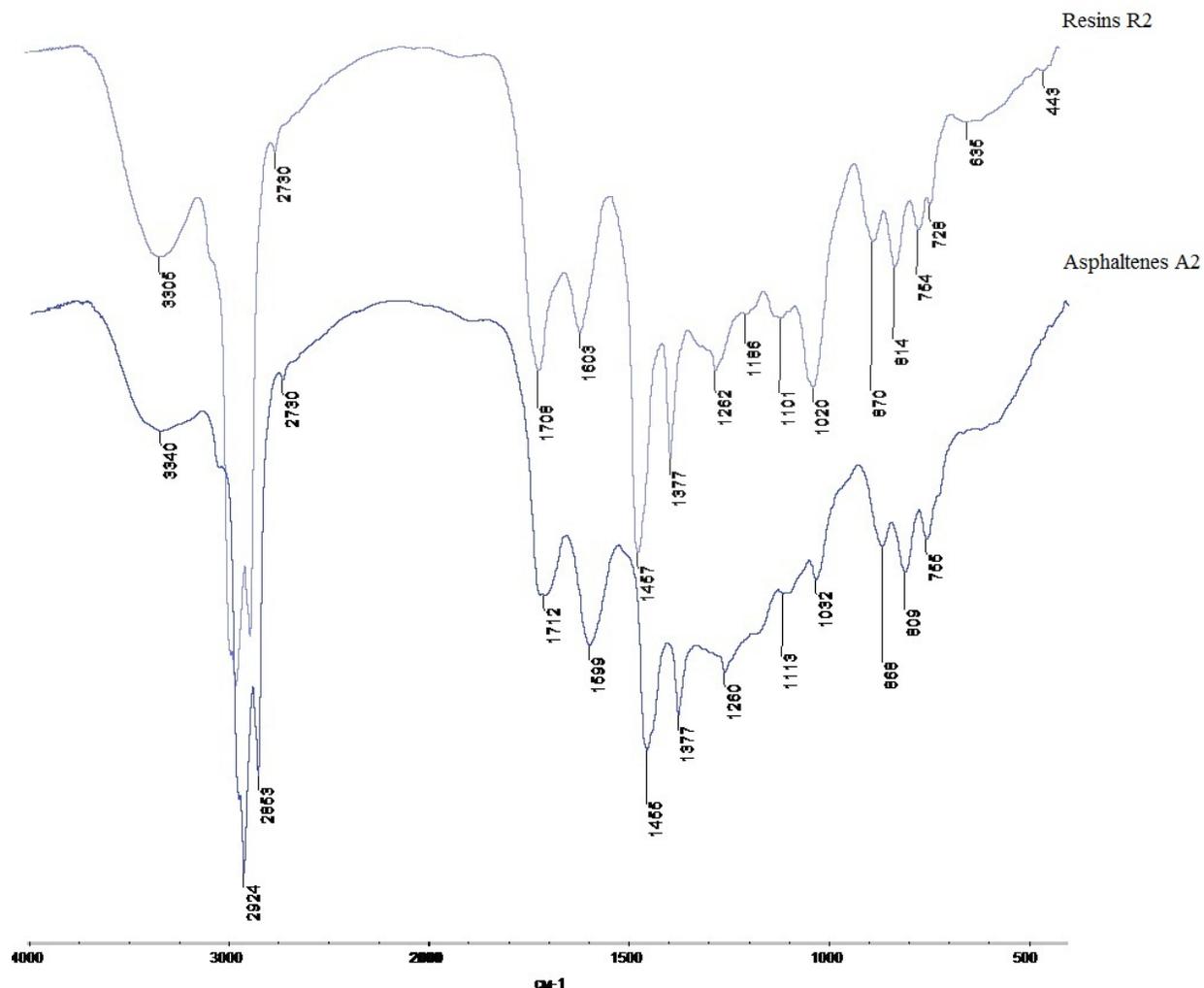


Figure 2. IR-coefficients of the resins and asphaltenes obtained by oil thermolysis of IO_2

Based on the results of IR spectroscopy, the spectral coefficients that characterize the structure of the resins and asphaltenes are calculated. The highest coefficient of aromaticity is specific for resins obtained by thermolysis of the O_2 sample, in which the content of the aromatic compounds prevailed. The content of the aliphatic structures in the thermolysis resins depends on the H/C ratio in the initial oils (Figure 3).

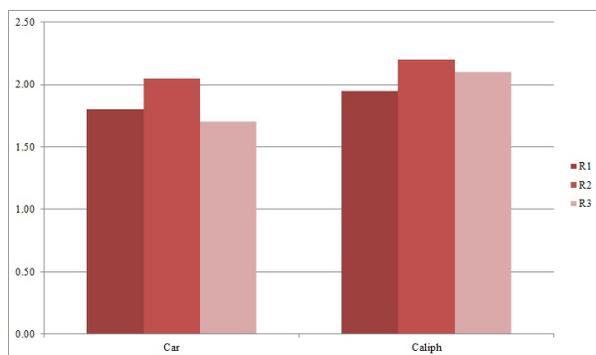


Figure 3 IR coefficients of aromaticity and aliphaticity of resins

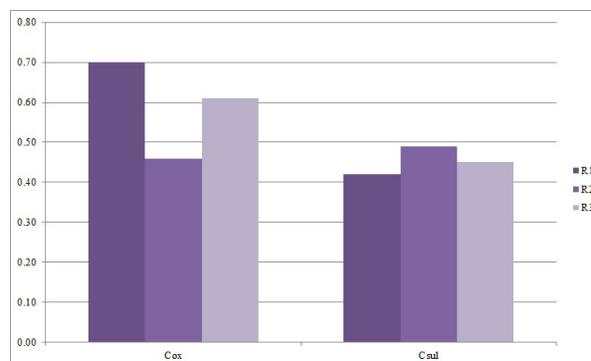


Figure 4. IR coefficients of oxidation and sulfurization of resins

It was found that there were more sulfoxide groups in R₂ in terms of the sulfuration coefficient, due to the fact that the sulfur content was the highest in the initial oils of O₂ (Figure 4).

Since most processes involve thermal effects, the study of the thermal transformation of oils is a necessary step to gain knowledge about the formation mechanism of resins and asphaltenes, which have a negative impact on the entire technological process: they poison the catalyst, reduce the yield of a light product, cause corrosion of equipment and, as a result, its shorter operating time.

4. Conclusions

To account for the influence of various factors in the thermal processes, the following regularities were determined:

1. With the increase in the oil content of heteroatoms and aromatic HC, the formation of tar and coke increases in the oils of heavy petroleums, while asphaltene content reduces during oil thermolysis;
2. Heavy petroleum oils, which are characterized by the lowest nitrogen content during thermolysis, generate resinous substances with the highest nitrogen content, while sulfur passes from oils to resins during thermolysis more naturally. Heavy petroleum oils, which are characterized by a high H/C content, generate resinous substances with the lowest H/C value during thermolysis;
3. Resins obtained during thermolysis of oils with the highest content of aromatic HC are characterized by the highest proportion of aromatic fragments;
4. The H/C ratio in heavy petroleum oils has a decisive influence on the content of aliphatic fragments in the structure of newly obtained resins;
5. With the increase in the sulfur content in the initial oils, the sulfuration degree of the thermolysis products rises.

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