

MUTUAL INFLUENCE OF RESINS AND ASPHALTENES OF THE HEAVY CRUDE OIL AT THERMOCRACKING

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Introduction

Now a day the influence of resins and asphaltenes, their properties and structures on the cracking reactions of heavy hydrocarbon feedstock has not been investigated. During the thermal action petroleum resins and asphaltenes form various radicals, which are involved in the cracking reactions. The resins and asphaltenes are a source of the components of light distillate fractions and gaseous products, according to a free-radical mechanism of the process. The lack of knowledge about the reactivity of the resins and asphaltenes at the thermal action, their role and mutual influence specifies the investigation of these processes on model systems consisting only of resins and asphaltenes, and on the systems representing a mixture of oils and resins (maltenes), a mixture of oils and asphaltenes, and a mixture of oils, resins and asphaltenes (petroleum).

The aim of this work is to study the mutual influence of petroleum resins and asphaltenes in the simulation of thermal transformations. Therefore we carried out experiments on the thermolysis of the model mixture (R + A) comprising 68.6% of resins and 31.4% wt. of asphaltenes, which corresponds to their ratio in the initial petroleum. We also investigated thermolyses of resins and asphaltenes separately to identify the mutual influence of resins and asphaltenes.

Results

Reactions of condensation predominate at thermolysis of both resins and asphaltenes separately and their mixture (R + A), as evidenced by high yield of solid products, insoluble in chloroform. The destruction of resins and asphaltenes leads to the formation of gaseous and liquid products (table 1). The degree of conversion into liquid products reaches 62.0 % for thermolysis of mixture (R + A), where the portion of oils (hydrocarbons) is ~ 58 %. The amount of resins in thermolysis products decreases to 10.3 % as compared with the initial mixture, the amount of asphaltenes decreases to 15.6 %.

Table 1 Composition of thermolysis products in the model mixtures.

| Products | Content, % wt. | | | | | |
|---------------------|--------------------|--------------|--------------------|--------------|--------------------|--------------|
| | Resins (R) | | Asphaltenes (A) | | 68.6 % R+31.4 % A | |
| | <i>Before</i> | <i>After</i> | <i>Before</i> | <i>After</i> | <i>Before</i> | <i>After</i> |
| | <i>thermolysis</i> | | <i>thermolysis</i> | | <i>thermolysis</i> | |
| Solid | - | 38.9 | - | 57.1 | - | 35.2 |
| Gaseous | - | 2.40 | - | 4.60 | - | 2.75 |
| Liquid, including: | - | 58.6 | - | 38.3 | - | 62.0 |
| Resins | <i>100</i> | 7.2 | - | 4.1 | <i>68.6</i> | 10.3 |
| Asphaltenes | - | 17.8 | <i>100</i> | 13.8 | <i>31.4</i> | 15.6 |
| Oils (hydrocarbons) | - | 33.6 | - | 20.3 | - | 36.1 |

The content of residual asphaltenes in thermolysis products of mixture (R + A) 1.5

times exceeds the amount of residual resins, whereas the ratio resins: asphaltenes in initial mixture is 2.2. This fact can evidence about more intensive involvement of resins in destruction processes.

The qualitative composition of oils (hydrocarbons) in all thermolysis products is similar and close to that of the initial petroleum: n-alkanes C₁₂ – C₃₆₋₄₀, isoprenoids – pristane, phytane, homologous series of n-alkylbenzenes and alkyltoluenes C₁₀ – C₃₃, naphthalene and its C₁-C₄ methylsubstituted homologues, phenanthrene and its homologues, anthracene, methylanthracene, benzo- and dibenzothiophenes are identified.

The absence of alkenes, the formation of which is observed during the thermolysis of resins and asphaltenes, is a distinctive feature of hydrocarbon composition in thermolysis products of mixture (R + A).

The resins, formed during thermolysis process of mixture (R + A), have lower molecular weight (MW) as compared with resins in thermolysis products of both resins and asphaltenes, whereas asphaltenes have higher values of the same parameters (fig. 1). It evidences that destruction reactions largely affect resins molecules, while reactions of condensation - molecules of asphaltenes.

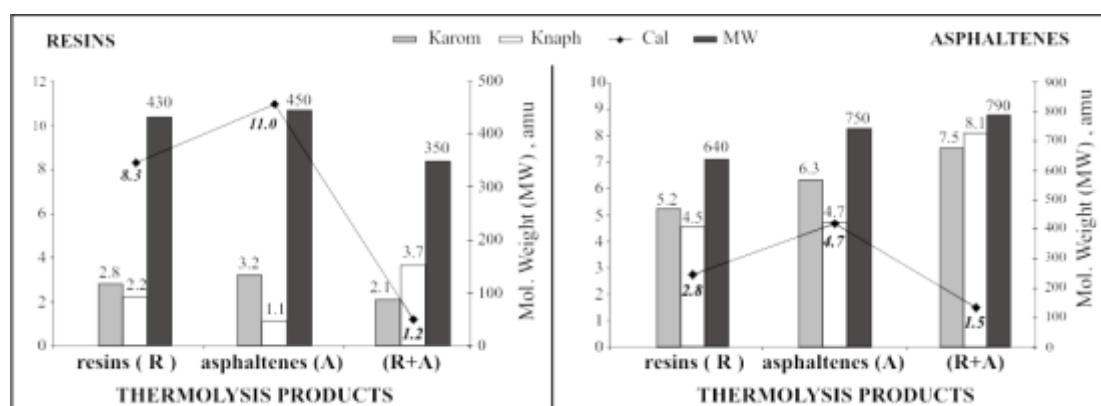


Figure 1 Structural - group characteristics of resins and asphaltenes in thermolysis products of resins, asphaltenes and their mixture (R + A)

The number of aromatic rings in average molecules of resins and asphaltenes in thermolysis products of both resins and asphaltenes predominates over the number naphthenic rings, whereas the excess of number of naphthenic rings over aromatic ones is observed for average molecules of resins and asphaltenes in thermolysis products of mixture (R + A). It is caused by the occurrence of cyclization reactions of aliphatic radicals, which is clearly expressed in sharp number decrease of carbon atoms in the aliphatic chains (C_{al}) (fig. 1).

Conclusion

Thus, the joint presence of the resins and asphaltenes in the thermolysis decreases the yield of solid and increases the yield of liquid products as compared with the thermolyses of both resins and asphaltenes.

It has been shown that reactions of destruction largely affect resins molecule, whereas reactions of condensation - molecules of asphaltenes.

It has been revealed that resins and asphaltenes have a mutual influence at the thermolysis of model mixture (R+A), changing the directivity of their thermal transformations.