CHANGE OF COMPOSITION AND STRUCTURAL CHARACTERISTICS OF RESINS AND ASPHALTENES AT THE "RECREATION" OF OIL DISPERSION SYSTEM

G. Pevneva, N. Voronetskaya, D. Korneev, A. Golovko

Institute of Petroleum Chemistry, SB of the Russian Academy of Sciences, Tomsk, Russia

Introduction

The study of intermolecular interactions in petroleum systems is of great theoretical and practical interest. The influence of various external factors, among which the changes in the composition of the dispersion medium and temperature are the most common, promote dimensional changes of molecules in resins and asphaltenes aggregates, as well as their structural transformations. The increase in volume and depth of information about the composition of high-molecular petroleum compounds and formation of nano-aggregates depending on the composition of dispersed petroleum systems are required to solve fundamental and applied problems associated with the formation of asphalt-resin-paraffin deposits and the development of rational technologies to control their formation.
The following experiment was carried out to identify the structural organization of resin-asphaltene components: resins, asphaltenes and oils (hydrocarbons HCs) have been isolated from heavy petroleum in Usinsk oilfield, and then the same amount of these components were mixed without any solvent. The initial petroleum contains 18.0 % of resins and 8.1% of asphaltenes.

Results

It has been shown that despite the saving of quantitative proportions and the use of “source” resins, asphaltenes and oils (HCs) we failed to obtain the petroleum system fully identical to the initial petroleum. Both quantitative and qualitative changes are observed in the characteristics of petroleum components. The content of resins increased by 2.9 % in the "recreated" petroleum, while the amount of oils (HCs) and asphaltenes decreased by 2.7 % and 0.2 %, respectively, as compared with the initial oil. Probably the increase of resins amount in the "recreated" petroleum at simultaneous decrease of oils amount is associated with the involvement of hydrocarbons and heteroorganic compounds in resins formation.

According to the group structure analysis [1] the average asphaltene molecule of the initial Usinsk petroleum consists of ~ 3 structural blocks containing 27 rings, including 11 aromatic and 16 naphthenic ones, which create a naphthene-aromatic system framed with 6 aliphatic substituents. On the average resin molecules are bi-block, on the average their polycyclic nucleus contains 4 aromatic, 5 naphthenic rings and 5 aliphatic chains with 18 carbon atoms. Sulfur, nitrogen and oxygen atoms are included in the polycyclic nuclei and aliphatic chains.

The recreation of petroleum has resulted in integration of average asphaltene molecules. Their molecular weight (MW) has increased from 1410 to 1570 amu, although the average molecule remained tri-block. The MW of the resins has decreased from 810 to 570 amu and the number of blocks has decreased to one. The MW of the average oil molecule remained practically unchanged. Apparently these structural changes are associated with the formation of other intermolecular interactions in the newly formed oil dispersion system.

The carbon atoms are distributed in the fragments of average molecules of the initial resins almost evenly: the relative content of carbon atoms in aromatic rings (f_{arom}) is 31.8%, in naphthenic (f_{naph}) - 34.8% and the portion of the aliphatic carbon (f_{paraf}) accounts for 33.4% (Fig. 1). In initial asphaltenes the main portion of carbon atoms is concentrated in aromatic cycles (45.6%) and in oils - in naphthenic ones (44.1 %).

It has been found that all the components of the "recreated" petroleum have changes in the structural characteristics as compared with the initial petroleum: portion of aliphatic (f_{paraf}) and aromatic (f_{arom}) carbon atoms is decreased and portion of carbon atoms in naphthenic structures (f_{naph}) is increased. This fact is confirmed by the data of IR spectroscopy of the resins and asphaltenes in the "recreated" petroleum, where the conventional content of paraffin structures (D725 / D1465) is lower as compared with the initial petroleum.

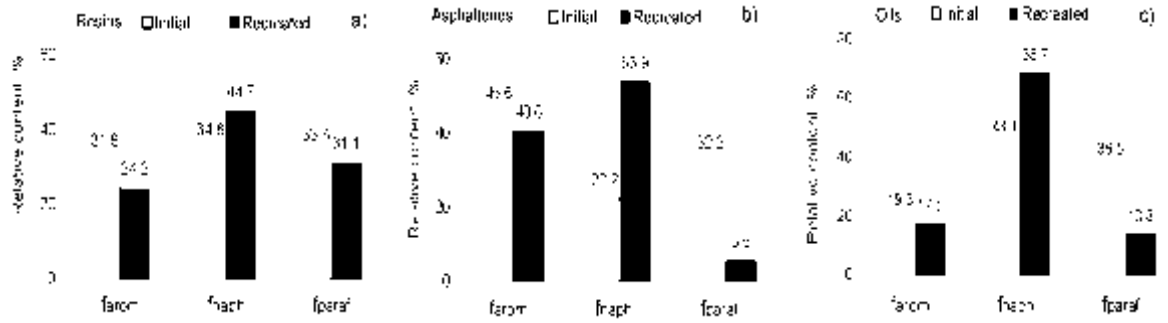

Figure 1 *Distribution of carbon atoms in a) resins, b) asphaltenes, c) oils in the initial and "recreated" petroleum*

Due to the creation of the petroleum the composition of the dispersion medium has changed. If in the initial petroleum the content of saturated hydrocarbons is 3.25 % and that of monoaromatic hydrocarbons is 11.2%, then their contents have increased ~ 1.1 times in the "recreated" petroleum. The amount of bi-, tri- and polyarenes is decreased 1.2 ÷ 1.3 times. The decrease of the amount of aromatic hydrocarbons containing more than 2 aromatic rings in the molecule is probably due to their involvement in the formation of the resins, the content of which in the "recreated" petroleum is higher than in the initial one.

Conclusion

Thus, despite the fact that during the isolation and separation of the petroleum system into components - oils, resins and asphaltenes, the intermolecular interactions are disturbed. The occurrence of heteroatomic sulfoxide (a.b. 1030 cm^{-1}), carbonyl (a.b. 700 cm^{-1}) and hydroxyl (a.b. 3257-3428 cm^{-1}) groups in the resins and asphaltenes promotes the formation of other associative interactions at mixing of isolated petroleum components. At the same time the changes in both quantitative and qualitative characteristics of “recreated” petroleum components are observed.

References

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