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Fractionation of asphaltenes for determination of their composition and structure in case of heavy oil from Ashal'cha field

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Abstract. The asphaltene fractions from initial crude oil of Ashal'cha field were extracted for the further investigation. Moreover, the non-catalytic and catalytic products of aquathermolysis in the presence of cobalt-containing catalyst precursor and hydrogen donor dependent on treatment time were studied. Five fractions of asphaltenes and carben-carboids were obtained by batch extraction method. The catalytic hydrothermal treatment revealed a redistribution of group composition and the reduction of resins and asphaltenes because of destructive hydrogenation processes mainly on carbon – heteroatom bonds. In this paper, we have obtained comprehensive results regarding the redistribution between the asphaltene fractions (extracted by solvents with various compositions) due to catalytic aquathermolysis.

1. Introduction

In the modern oil refining industry, the tendency of crudes is toward the heavy hydrocarbons. In its term, it requires development and introduction of additional oil processing units that are based on structural destruction of heavy molecules of oil and thus, increasing the content of light fractions of crude oil. The most well-known methods of increasing the yield of light fractions such as thermal, radio-thermal and etc. is based on the destruction of heavy oil components. Therefore, it is important to know the structure of resins and asphaltenes, as well as content and the nature of molecule fragments that contain heteroatoms. The role of last is crucial in destruction of high-molecular compounds. However, the problem of heavy components of crude oil can be solved in reservoir formations by introduction of water- and oil-soluble catalyst precursors prior to steam injection techniques. The catalyst precursor activates only in reservoir conditions and leads to conversion of oil without significant constructive changes in downstream installations [1-5]. Injection of catalytically active metals into the productive formations intensifies the ability of mineral matrices to convert the crude oil in-situ. It is not only increasing the sweep of reservoir due to decreasing molecular masses of resins and asphaltenes, but also irreversibly reducing the viscosity of produced oil and the content of hard-to-refinery components. Using the catalysts at oil recovery stage increases the energy efficiency of thermal recovery methods and significantly decreases the environmental



risks during the development of heavy oil fields. Currently, most studies on the structure of asphaltenes are carried out with the whole mass of asphaltenes and resins. However, fractionation of asphaltenes provides to determine the structure of molecules more accurately [6–11].

The fractionation method of complex mixtures of high-molecular compounds were well known and widely used. The main goal of which was separation of mixtures that compose of many various components (in case of carbene-carboids – several thousands) to the narrower fractions, each of which has a close composition to homogeneous one (set of molecules with similar properties). Consequently, the separate fraction may differ enough sharply by physical and chemical characteristics [12].

2. Materials and Methods

The model system was consisted of oil and water with a mass ratio of 70:30. This water-in-oil emulsion was exposed to the catalytic and non-catalytic thermal treatment processes (250 °C). The oil-soluble Co carboxylates obtained by means of exchange reaction between sodium salt of tall oil and non-organic salts of cobalt were used as the catalyst precursor. Then the catalyst precursor (1.5 wt % by oil) was injected to the oil sample.

The initial pressure was fixed at 0.3 MPa. The duration of the experiment was 6, 12, 24 hours. At the end of thermal process, the oil was separated from water by precipitation for 16 hours. After that, it was centrifuged on a laboratory centrifuge Eppendorf 5804r at 3000 rpm for 1 hour. Then, the content of the water in all samples were determined by the Dean and Stark method. The asphaltenes were precipitated from the oil samples (5-10 gr) by warm isooctane (200 ml) through filter paper. Then they were placed in Soxhlet apparatus with further stepwise solvent treatment by the mixture of isopropyl alcohol and benzene (the share of latter was 20, 40, 60, 80 %), as well as pure benzene. The given solvents are characterized by almost similar boiling temperature (isopropyl alcohol -82°C and benzene – 80°C) and gradually increasing dissolving abilities [13]. In each separation, maltene fraction (M), five fractions of asphaltenes and residue on filter were obtained. Maltene fractions were separated into 3 compositional groups by SARA-method (saturates, aromatics and resins) according to ASTM D4124-09. The glass chromatography column was used to gradually elute the aliphatic and aromatic hydrocarbons from adsorbent – initially dehydrated neutral aluminum oxide. The elemental analysis (CHNS) was carried out in CHNS-analyzer 2400 Series II (USA, Perkin Elmer) at temperature of 1000 °C.

3. Results and Discussion

3.1. SARA-analysis and fractionation of asphaltenes

According to the Figure 1, the content of saturate hydrocarbons increased, while resins and asphaltenes decreased after adding catalyst and hydrogen donor. In order to obtain the detail and reliable information about the composition and the structure of high-molecular oil components, we have to separate a set of thousand different molecules - resins and asphaltenes to the possible narrower fractions that contains molecules with similar properties. The batch extraction of each fraction was continued until the solution in Soxhlet extractor became bleach. After that, the obtained fractions were distilled off from the solvent and evaporated in rotational evaporator until the constant mass was achieved.

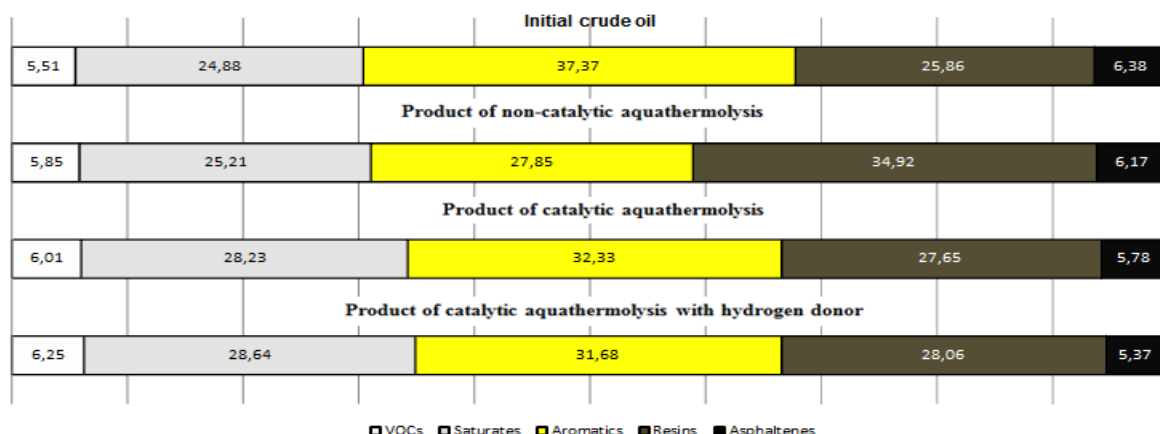


Figure 1. The SARA-analysis of initial crude oil and the products of non-catalytic and catalytic aquathermolysis with hydrogen donor (treatment time -6 hours).

According to the Figure 2, the main mass of asphaltene is concentrated in A2 fraction (60% isopropyl alcohol + 40 % benzene) that probably justifies the polar characteristics of asphaltene components of oil. The stimulation of catalytic hydrothermal treatment in the presence of hydrogen donor leads to transition of the most high molecular compounds from solvation layer – A1 toward the most heaviest fraction – A5 and carben-carboid (residue in filter paper). Moreover, the least heavy fractions of asphaltenes (A1-A2) shift into aromatic and saturate hydrocarbons. The conversion can be presented by the following scheme:

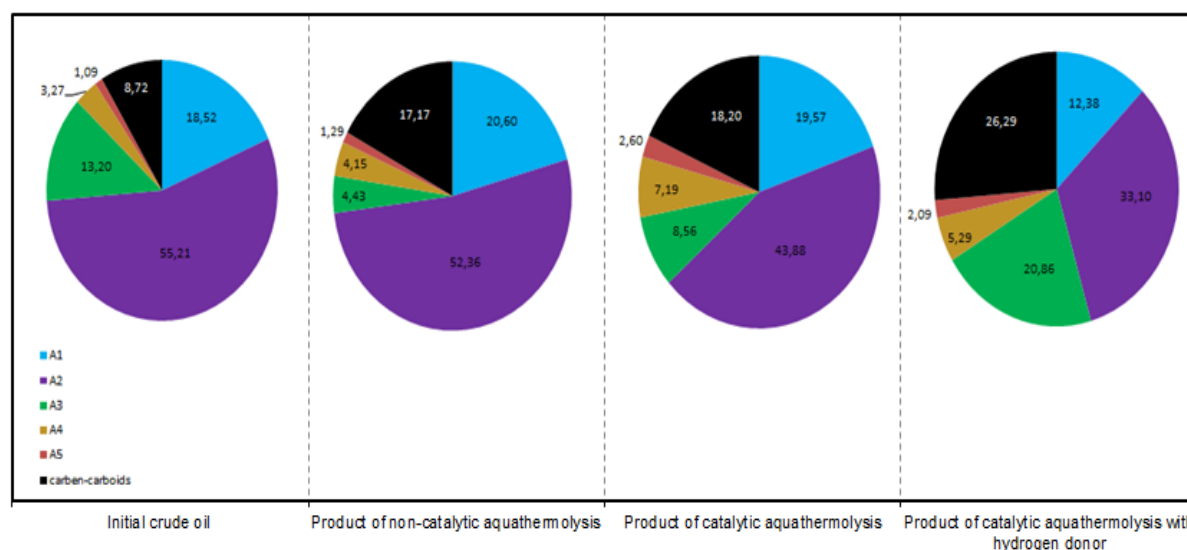
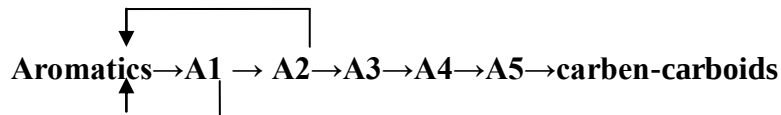


Figure 2. The fractional composition of asphaltenes from initial crude oil, products of non-catalytic and catalytic aquathermolysis, and in the presence of hydrogen donor.

The next step was investigation of elemental composition of asphaltenes. The elemental composition of oil is necessary, particularly for choosing the refinery method and compiling

material balance of some refining processes. The data of elemental composition and structural group composition of narrow fractions of saturates, aromatics and heavy residues, from which extraction of individual substances is not possible, provides significantly enlarge the understanding of structures and build their “average” molecule model [14]. Table 1 presents the elemental composition of asphaltene fractions.

Table 1. Elemental composition of asphaltene fractions

Asphaltene fractions	Content, wt %				
	C	H	N	S	O
Initial crude oil					
Oil	83.88	11.35	0.37	1.76	2.64
A1	80.76	8.24	1.63	3.75	5.62
A2	81.43	8.1	1.54	3.66	5.27
A3	79.78	7.33	1.61	4.51	6.77
A4	79.32	7.44	1.66	4.98	6.6
A5	78.89	6.36	1.58	5.79	7.38
carben-carboids	78.69	6.5	1.76	5.87	7.18
Product of non-catalytic aquathermolysis (6 hours, 250 °C, 30 bar)					
A1	75.93	7.64	1.62	6.22	8.59
A2	80.07	7.87	1.48	4.34	6.25
A3	80.26	7.97	1.55	4.29	5.93
A4	75.08	5.8	0.6	7.96	10.56
A5	76.47	6.28	0.59	7.33	9.33
carben-carboids	77.54	7.42	0.56	6.52	7.96
Product of catalytic aquathermolysis with hydrogen donor (6 hours, 250 °C, 30 bar)					
A1	79.02	7.88	1.64	4.58	6,88
A2	80.43	7.94	1.54	4.04	6,05
A3	80.21	7.87	1.67	4.10	6,15
A4	80.03	7.63	1.70	4.26	6,38
A5	79.72	7.84	1.68	4.3	6,46
carben-carboids	75.04	7.71	1.67	7.01	8.57

From the results above, the “average” molecule of Ashal’cha oil is characterized by small content of heteroatoms, particularly sulfur and oxygen. According to the results of elemental analysis, H/C ratio significantly increased. In initial crude oil sample, the content of sulfur is higher in heavier fractions. The non-catalytic thermal treatment significantly increased the content of heteroatoms (S, O). However, the catalytic thermal treatment decreased the content of sulfur and oxygen to the initial crude oil values. The decrease in sulfur content under catalyst influence was observed mostly in high-molecular A5 fraction [15].

4. Conclusion

Upgrading of heavy oil from Ashal'cha field by introduction of oil-soluble catalyst precursor within hydrogen donor during hydrothermal treatment gave promising results. The content of high-molecular heteroatom substances in resins and asphaltenes was decreased in contrast with non-catalytic thermal treatment. Significant redistribution of group composition took place due to cracking and hydrogenolysis reactions, primary in C-S, C-O bonds of asphaltenes, that was justified by the data obtained from elemental composition of A1-A5 fractions.

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