Fractionation of Aschalcha extra heavy oil resins and studying their structure

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Abstract. In this paper we isolated resins from a sample of extra heavy oil and from the products of catalytic aquathermolysis in the presence of a cobalt based catalyst and studied their structure. In fact, an oil fraction and 4 resin fractions (R1-R4) have been extracted by liquid adsorption chromatography method in the presence of pure solvents and their binary mixtures in various ratios. Adding the catalyst to the system during heat and steam exposure for 6 hours leads to a significant improvement of the structural-group composition. Thus, the aliphaticity index of R3 decreased as a result of the detachment of alkyl substituents in aromatic fragments under the influence of catalyst and passes into lighter fractions of resins, as well as towards saturated and aromatic hydrocarbons. From another hand, the oxidation coefficient also manifests itself in fractions R1 and R2 as a result of oxidative catalytic cracking processes, which also indicates a redistribution of the group composition. MALDI data have showed that the average molecular weight of resins for each of the fractions has decreased whereas IR spectroscopy has highlighted a change in their structural group composition.

1. Introduction

Nowadays, there is a clear trend towards a decrease in proven reserves and light and medium oils production, however at the same time, the global demand for oil is growing. The problem of oil shortages can be solved by involving unconventional hydrocarbons resources (heavy oils, natural bitumen, etc.) in processing and improving oil refining [1,2].

Improving heavy oils processing and refining as a raw material will lead to an increase in the yield of heavy oil residues containing significant amounts of non-hydrocarbon high molecular weight heteroatomic compounds (HMHC) - resins and asphaltenes containing condensed aromatic structures [3-5]. These compounds complicate the oil processing, as they promote the formation of coke and deactivate the catalysts. In addition, heavy hydrocarbon feedstocks (heavy oils, natural bitumen) contain more than 45 % resins and asphaltenes which are composed mainly of heteroatoms in their feedstock [6].

It is common knowledge that the method of macromolecular compounds complex mixtures fractionation has been widely used for a long time [7-9]. Moreover, the fractionation of resins has been...
always performed by means of the method of liquid adsorption column chromatography [10-12]. In addition to the LAC method, reverse phase chromatography and high-performance liquid chromatography are also considered as widely used methods [12].

Altogether, using fractionation of oil HMHC complex mixtures allows studying the composition and structure of asphaltenes and resins “native” molecules in various oils with different nature in more detail. In addition, separating a set of molecules containing homogeneous, structurally similar molecular properties is obtained by using the fractionation of resins and asphaltenes [13].

2. Methodology

Laboratory modeling of the aquathermolysis process was carried out using a high-pressure reactor with stirring (300 ml volume) manufactured by Parr Instruments, USA. The model system was a mixture of oil and water with a mass ratio of 70:30. The oil-water emulsion was subjected to a temperature of 250°C under the conditions of a catalytic process. A cobalt-based catalyst precursor and a hydrogen donor were introduced at a rate of 0.2 wt % for metal and 1.0 wt % for oil, respectively. Working pressure was fixed at 4 MPa. The duration of the experiment was 6 and 12 hours. At the end of the process, the oil was first separated from water by settling for 16 hours, then centrifuged in an Eppendorf 5804R laboratory centrifuge at 3000 rpm for 1 hour. Fractionation of resins was performed according to [14, 15].

To determine the molecular weights of the resins we have opted the matrix-activated laser desorption/ionization (MALDI) method. MALDI mass spectra were obtained on a Bruker ULTRAFLEX III mass spectrometer where the conditions for recording mass spectra were as follows: Nd laser; YAG, wavelength - 355 nm. The studies were conducted in vacuum: 10⁻⁶-10⁻⁸ mbar (in the source - 6.7×10⁻⁷ mbar, in the analyzer - 9.7×10⁻⁸ mbar), temperature: in standby mode - room temperature (20 °C), during shooting - 500°C, the linear mode, without the accumulation of mass spectra, a metal target was used, 2,5-dihydroxybenzoic acid (DHB) was used as a matrix. During the framework of the presented study, we obtained spectra in a form of Gaussian distribution of the molecular masses of studied samples compounds. The molecular weight of the sample was determined at the maximum region of the spectra.

The method of infrared Fourier spectroscopy was used to study the structural group composition of resin samples. The IR spectra of the resin fractions were recorded on a PERKIN ELMER Spectrum two spectrometer with a UATR (Single Reflection Diamond) attachment in the range from 2000 to 450 cm⁻¹ with a resolution of 4 cm⁻¹. For comparative data correlation, we used spectral coefficients which characterize the structural-group composition of the products: $C_1 = D_{1600} / D_{1720}$ (aromaticity); $C_2 = D_{1710} / D_{1465}$ (oxidation); $C_3 = D_{1380} / D_{1465}$ (branching); $C_4 = (D_{720} + D_{1380}) / D_{1600}$ (aliphatic). The correlation of the bands with the presence of certain structural fragments in the studied objects was based on literature data presented in [9].

3. Results and Discussion

SARA analysis and fractional composition of resins are presented in [14, 15]. The molecular weight increases significantly with the separation of fractions - from R1 to R4. Fig. 1 a-d show the results of MALDI spectroscopy of oil resin fractions after hydrothermal-catalytic exposure for 12 hours.
The picture of adsorption-chromatographic separation of resins components can significantly complement the results of IR spectral analysis.

Table. 1 and Fig. 2 show the results of infrared spectral analysis of oil resins fractions of the control experiment after heat and steam exposure for 6 hours.

| Spectral Coefficients | R1   | R2   | R3   | R4   |
|-----------------------|------|------|------|------|
| C1                    | 0.37 | 0.44 | 0.03 | 0.52 |
| C2                    | -    | 0.04 | -    | -    |
| C3                    | 0.59 | 0.63 | 0.61 | 0.65 |
| C4                    | 7.90 | 6.37 | 34.93| 4.26 |

According to IR spectroscopy results, all indicators are ambiguous due to the different nature of resin fractions constituent components. Literally, during heat and steam exposure for 6 hours, the aromaticity index possessed maximums and minimums and the oxidation coefficient was negligible in fraction R2. However, the heavier fraction R4 was characterized by a minimum aliphatic value (4.26 units) and a maximum aromaticity value (0.52 units), which characterizes the proximity to asphaltenes nature.
Adding the catalyst to the system during heat and steam exposure for 6 hours leads to a significant improvement of the structural-group composition. Thus, the aliphaticity index of R3 decreased as a result of the detachment of alkyl substituents in aromatic fragments under the influence of catalyst and passes into lighter fractions of resins, as well as towards saturated and aromatic hydrocarbons. From another hand, the oxidation coefficient also manifests itself in fractions R1 and R2 as a result of oxidative catalytic cracking processes, which also indicates a redistribution of the group composition.
4. Conclusion

In sum, MALDI spectroscopy results have highlighted a significant decrease in the average molecular weight as each fraction of resins was distinguished from R1 to R4. According to the results of resins fraction IR spectroscopy during catalytic aquathermolysis, the aliphatic index in the R2 fraction decreases by 1.5 times compared to the control experiment while the aromaticity coefficient in the R3 fraction decreased by 2.5 times comparing to the latter experiment. Indeed that the presence of catalyst in oil in addition to heat and steam make the oxidation coefficient also significant in fractions R1 and R2 as a result of oxidative catalytic cracking.

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