Influence of asphaltene esterification conditions on product composition

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Abstract. The article is devoted to the study of reactivity and composition of oil asphaltene esterification products formed in reactions of various duration with and without solvent. As a result of the study, high reactivity of asphaltenes in reaction of esterification with isopropyl alcohol for 40 hours was first shown. Products contain 40 % wt. of fractions soluble in n-heptane and isopropyl alcohol. The increase in the duration of the reaction from 40 to 120 hours leads to counter reaction with the decrease in forming less polar substances by 5-6 % wt. Adding solvent (benzene) into the reaction mixture also negatively influences the effectiveness of asphaltene esterification for 40 hours. The results obtained show that the suggested approach is promising for chemical processing of asphaltene concentrates into less polar low-molecular products.

1. Introduction
At present, heavy oil extraction, transport and processing are impeded due to its high asphaltene content [1]. Asphaltene molecules are high in S, N, O and metal content, contain condensed naphtheno-aromatic rings with lateral aliphatic substituents and various functional groups [2-4]. The variety and structural peculiarities of asphaltene molecules cause their aggregating in oil disperse systems with nanoparticle formation; changing external conditions leads to growing supramolecular structures with further sedimentation [5-7]. As a rule, asphaltene colloid particles are formed due to π-π-interactions between aromatic systems of their molecules, acid-base interactions, hydrogen bonding, metal-coordination complex formation, etc. [8-10]. To inhibit asphaltene molecule aggregating in real oil systems, it is common to use various amphiphilic chemical agents [11-13], whose mechanism of action is that of surfactants [14]. Along with classical methods of inhibiting asphaltene containing sediment, there is an alternative approach based on chemical modification of asphaltene molecules. The essence of this approach is changing asphaltene molecular structure, which allows, on the one hand, to reduce their tendency to aggregating and, on the other hand, to improve their solubility in lower alkanes. For example, to inhibit sedimentation, asphaltenes were phosphorylated and phosphopropoxylated [15, 16]. It is found that adding modified asphaltenes into oil disperse system improves its aggregative stability and contributes to increasing the conversion of raw material by 9-10 % in the process of catalytic hydrocracking. Asphaltene alkylation reactions are under study, both reductive alkylation and alkylation with Lewis acid catalyst [17-19]. The main idea of alkylation is transformation of asphaltenes into malthenes (soluble in n-alkanes) as a result of introducing long alkyl substituents and partial destruction
of aromatic and heterofunctional fragments. The results obtained show that, due to complex chemical nature of asphaltenes, alkylation may involve practically all the components of the reaction mixture (catalysts, solvents, etc.), which often causes chaotic and undesirable transformations of asphaltenes. Thus, chemical transformation of oil asphaltenes is a promising and under-researched area. Finding new methods to selectively functionalize asphaltenes is a highly relevant task.

The aim of this research is to study the composition of oil asphaltene esterification products with varying conditions of reaction.

2. Material and methods
The focus of the research is asphaltenes extracted from heavy oil deposits of the Republic of Tatarstan. Asphaltenes were isolated from oil by adding n-hexane to the sample to provide the mass ratio 40:1 and filtering the resulting solution after 24 hours. Asphaltene sediment was purified by n-hexane and dried to constant weight.

Asphaltene esterification was carried out with isopropyl alcohol excess for 40, 80 and 120 hours at a temperature of 80 ± 5 °C and atmospheric pressure. Asphaltene sample weight was 0.1 g. Asphaltene esterification products were separated by paper filtration of the reaction mixture, after that the resulting sediment was purified by isopropanol. The concentrate of components soluble in isopropyl alcohol was isolated from the solvent and dried to constant weight. Components insoluble in alcohol were extracted from filter by minimal amount of CHCl3 and, as with asphaltene extraction from crude oil, were precipitated by adding n-hexane to the sample to provide the mass ratio 40:1 and filtering the resulting solution after 24 hours. Asphaltene sediment was purified by n-hexane, after that hexane-soluble concentrates were mixed and dried to constant weight.

The impact of solvent on asphaltene esterification for 40 hours was also assessed. To do it, benzene was added as an asphaltene solvent to the initial mixture in a benzene:isopropanol volume ratio of 1:4. It was expected that in the presence of solvent, big supramolecular particles of asphaltenes would be destructed and their reactivity would increase. After the experiment the reaction mixture was boiled out of benzene and isopropanol and the resulting product was solved in minimal amount of chloroform, then n-hexane was added to the mixture in a mass ratio of 1:40. The resulting sediment was filtered, purified by n-hexane and dried to constant weight.

Elemental composition of initial asphaltenes was determined using CHNS-analyser Vario EL Cube by direct combustion at a temperature of 1200°C.

The initial asphaltene NMR 1H spectra were obtained using Fourier-transform spectrometer Bruker AVANCE-AV-400 at an operating frequency of 400 MHz. Sample preparation involved sample solving in CDCl3; asphaltene concentration was 1 % wt. (CH3)3–Si–O–Si–(CH3)3 was used as the internal standard.

The initial asphaltene IR-spectrum was recorded with the help of FTIR-spectrometer «NICOLET 5700» within the range of 2000-400 cm⁻¹. Asphaltene samples for analysis were prepared by compressing the mixture of their powder and optically pure KBr.

3. Results and discussion
Table 1 data show that the initial asphaltenes have a high heteroelement content, with the predominance of S and O, whose content is 3.88 and 4.10 % wt. respectively. Hydrogen content in aromatic fragments of asphaltene molecules exceeds 10 %, while the bulk of H-atoms are normally in aliphatic structures.

Table 1. Composition and structure of initial asphaltenes.

| Element content (% wt.) | Hydrogen distribution in structural fragments (% rel.) |
|-------------------------|------------------------------------------------------|
| C 83.97                 | Saturated 10.85                                      |
| H 7.52                  | Unsaturated 89.15                                    |
| N 1.75                  |                                                      |
| S 3.88                  |                                                      |
| O 4.10                  |                                                      |
2921 and 2851 cm\(^{-1}\) (Figure 1). Moreover, asphaltene structure has hydroxyl, carbonyl, S=O functional groups. IR spectrum also has characteristic absorption bands at 1310, 1261, 1097 cm\(^{-1}\), indicative of C-O bond stretch which can be part of ester groups.

The initial asphaltene IR spectrum analysis points at possible presence of carboxyl groups in their structure, which are able to take part in esterification. Classical reaction of forming ester from carbon acid and alcohol proceeds under the conditions of acid catalysis with strong mineral acid. However, high reactivity of asphaltenes to mineral acids makes it impossible to use them as catalysts. On the basis of scientific data on high polarity of asphaltene molecules, presence of many various functional groups in their structure, autocatalysis was suggested as a possible reaction in asphaltene esterification. Figure 2 shows the hypothetical mechanism of asphaltene esterification with isopropyl alcohol, proceeding in four stages. The presented mechanism is based on the classical reaction of forming ester, which has the mechanism of nucleophilic substitution. Stage I is the protonation of the oxygen atom of the carbonyl group; stage II is a nucleophilic attack of a stabilized carbocation by an alcohol molecule; stages III and IV are the sequential elimination of the intermediate product (H\(_2\)O) and a proton with the formation of an ester. The idea of asphaltene esterification with the transformation of carboxyl groups into ester groups pursues several interconnected goals: 1) lessening asphaltene molecule polarity, decreasing their tendency to hydrogen bonding and other intermolecular interactions; 2) introducing additional alkyl fragments into asphaltene structure to increase steric barriers to their molecule aggregating; 3) improving their solubility in n-alkanes due to the chemical reactions mentioned above.

The 40-hour composition analysis of oil asphaltene esterification products shows forming considerate amount of n-hexane and isopropanol soluble fractions, whose total content is 38 % wt, while the content of the most polar and high-molecular fraction soluble in CHCl\(_3\) is 62 % wt. (Table 2). This indicates high reactivity of asphaltenes in esterification and points at prospects of using this approach in asphaltene concentrate processing into low-molecular products of less polarity. The increase in duration from 40 to 120 hours decreases the content of n-hexane and isopropanol soluble fractions by 4.6 and 1.8 % wt. respectively. The content of the most polar fraction, soluble in CHCl\(_3\), naturally rises by 6.4 % wt. It is evident that maximum conversion of asphaltenes is achieved at a duration of less than 40 hours, while exceeding this period leads to changing chemical balance and, as a result, to counter reaction.
Studying the impact of benzene as asphaltene solvent on esterification product composition for 40 hours shows that adding benzene to reaction mixture leads to a higher content of the most polar fraction, soluble in CHCl₃, by almost 22 % wt., while n-hexane soluble fraction content decreases by 12.3 % wt.

Benzene molecules are likely to prevent esterification by blocking reactive centers of asphaltenes and stabilizing supramolecular particles. As a result, asphaltene esterification becomes less effective. It should be noted that along with chemical transformations of asphaltenes, isopropanol and/or benzene destroy the solvation sheath of asphaltene aggregates. Due to this, some resultants are polycyclic naphteno-aromatic substances, which stabilized asphaltene colloid particles when extracted from oil. The impact of solvation on the esterification product composition will be evaluated in further research.

**Table 2. Impact of asphaltene esterification duration on product composition.**

| Reaction duration (hrs) | Esterification product composition (% wt.) |
|------------------------|--------------------------------------------|
|                        | CHCl₃-soluble | n-C₆H₁₄-soluble | C₃H₇OH-soluble |
| 40                     | 62.0          | 28.0            | 10.0           |
| 80                     | 64.4          | 26.5            | 9.1            |
| 120                    | 68.4          | 23.4            | 8.2            |

**Table 3. Impact of solvent on asphaltene esterification product composition (40 hrs).**

| Composition of reaction mixture | Esterification product composition (% wt.) |
|--------------------------------|--------------------------------------------|
|                               | CHCl₃-soluble | n-C₆H₁₄-soluble | C₃H₇OH-soluble |
| Asphaltenes:isopropanol       | 62.0          | 28.0            | 10.0           |
| Asphaltenes:benzene:isopropanol | 83.7          | 16.3            | -              |
4. Conclusions
This research is the first to analyze asphaltene esterification. It is found that asphaltenes have high reactivity in esterification with isopropyl alcohol for 40 hours, which results in forming about 40 % wt of fractions soluble in n-hexane and isopropanol. The increase in duration from 40 to 120 hours leads to counter reaction resulting in lower content of less polar fractions. Adding solvent (benzene) into the reaction mixture negatively affects asphaltene esterification for 40 hours.

Acknowledgments
The research was carried out with the support of the Science Foundation of FSBEI HE «Yugra State University» within the project No. 17-02-07/74.

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