Study of Asphaltene Structure Precipitated from Oil Sands

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Abstract

In the paper microscopic structure and physicochemical characteristics of asphaltenes were investigated. Asphaltene was precipitated from natural bitumen of oil sand of Munaily-Mola deposit using organic solvent of petroleum ether. According to results of our work, we found that the largest yield of asphaltens was reached by using the petroleum ether in 40-fold amount in relation to the initial hitch of bitumen. Chemical composition of precipitated asphaltenes aggregates were studied on FT-Infra red spectrometer Spectrum-65 at 450-4000 cm^{-1}. At the Infrared spectrum, that the broad absorption band of asphaltenes at 3000-3600 cm^{-1} are characterizing the presence of polycyclic aromatic hydrocarbons and aliphatic chains in the samples of asphaltens. Elemental composition of the samples of asphaltenes on the installation of x-ray fluorescent spectrometer "Focus-M2". Also found the presence of two crystalline phases. One - quartz content is less than one percent. Another phase is also present in very small quantities and is represented by a single line of diffraction d = 4.158 Å. The microstructures and microanalysis of asphaltenes were investigated with an scanning electron microscopy (Quanta 3D 200i) at an accelerated voltage of 20 kV and a pressure of 0.003 Pa at National Nanotechnological Laboratory of Open Type of Kazakh National University. Microscopic images showed that the asphaltenes have a medium-ordered structure, the main component of the surface is represented by amorphous carbon.

Introduction

Asphaltenes are a fraction of crude oil defined operationally by their solubility in toluene and solubility in n-heptane. This fraction has been studied extensively because of its role in oil field flow assurance and more recently because of its application as a geochemical marker that can indicate the geologic structure of oil reservoirs. It is the most refractory and often the heaviest component, highly aromatic and polar. Because of these fundamental characteristics, asphaltene is considered an important factor that causes hindrance in many petroleum operations, production, transportation, refining, even wax crystallization, crude oil emulsification, and de-emulsification. Though many of these claims are not fully proved or understood, asphaltene does have a negative effect on many of the above operations. It is natural to attribute these negative impacts to particular molecular and thermodynamic properties associated with asphaltene. Additionally, asphaltenes are known to be a complex mixture containing thousands of distinct molecular formulas 4,5. Despite this scrutiny, some fundamental aspects of asphaltene chemistry are still debated. Most strikingly, the average asphaltene molecular mass is still unknown to within an order of magnitude [1-3].

The asphaltenes are molecules the properties of the petroleum. In recent years the industry that form aggregates of colloidal sizes in the crude with a wide range of molecular weights (Ï1000-50 000 Da) and diameters ranging from Ï30 to 50 A° [4]. G.A. Camacho-Bragado et al. offered the cross-sectional model of the structure of the asphaltene (at Fig. 1).

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In nature, asphaltenes are hypothesized to be formed as a result of oxidation of natural resins. On the contrary, the hydrogenation of asphaltic compound products containing neutral resins and asphaltene produces heavy hydrocarbon oils, i.e., resins and asphaltenes are hydrogenated into polycyclic aromatic or hydroaromatic hydrocarbons. They differ, however, from polycyclic aromatic hydrocarbons by presence of oxygen and sulfur in varied amounts. On heating above 300-400 ºC, asphaltenes are not melted, but decompose, forming carbon and volatile products. They react with sulfuric acid forming sulfonic acids, as might be expected on the basis of the polyaromatic structure of these components. The color of dissolved asphaltenes is deep red at very low concentration in benzene as 0.0003% makes the solution distinctly yellowish. The color of crude oils and residues is due to the combined effect of neutral resins and asphaltenes. The black color of some crude oils and residues is related to the presence of asphaltenes which are not properly peptized [5].

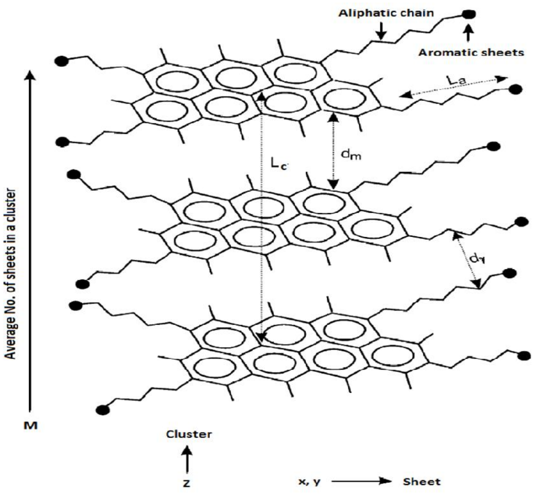

Fig. 1. Cross-sectional model of the structure of the asphaltene [4].

Asphaltenes are present in most petroleum materials, and in all heavy oils and bitumens from oil sands. So, they are widely using in many industries. For analytical purposes, the concentration of asphaltene in a crude oil is defined by precipitation with either n-pentane (C_5) or n-heptane (C_7). A standard method exists to quantify resins by a completely different approach. It involves a time-consuming chromatographic separation of deasphalted oil into saturates, aromatics, and resins, the so-called SARA analysis. It is presenting at Fig. 2.

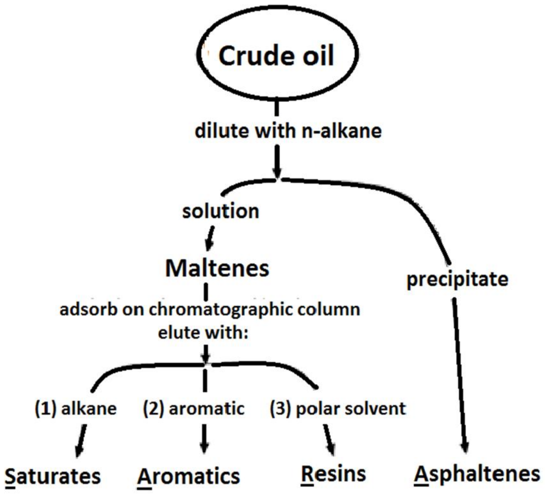

Fig. 2. Schematic illustration of SARA analysis [6].

Experimental

In our work we started with natural bitumen, from oil sands of Munayli-Mola deposit, extracted by Soxhlet Apparatus with benzene as an organic solvent. The extracted natural bitumen was mixed with a small quantity of toluene in order to dissolve it. Then we added a 40-fold amount of petroleum ether in relation to the initial hitch of bitumen and put it to the dark place that it couldn't reached by light to allow the precipitation of insoluble components. The resulting precipitate is dissolved again in toluene and petroleum ether. The procedure is repeated several times, and each step eliminates resins. This changes the external appearance of the precipitate from glassy black solid to brownish carbonaceous material. The separation was continued until no more changes in the residue were observed.

The microstructures and microanalysis of asphaltenes were investigated with an scanning electron microscopy (Quanta 3D 200i) at an accelerated voltage of 20 kV and a pressure of 0.003 Pa at National Nanotechnological Laboratory of Open Type of Kazakh National University. Infra-red spectra of the asphaltene aggregates were taken on FT-IR spectrometer Spectrum-65 at 450-4000 cm^{-1}. Elemental composition of the samples of asphaltenes on the installation of X-ray fluorescent spectrometer «Focus -M2» was studied. And samples were carried out on a installation of DRON-3M digitally.

Results

During the experimental work we carried out the precipitation of asphaltenes from oil sand of Munayli-Mola deposit using organic solvent of petroleum ether. We varied a number of organic solvents from pentane, hexane to petroleum ether. According to results of our work, we found that the largest yield of asphaltens was reached by using the petroleum ether in 40-fold amount in relation to the initial hitch of bitumen.

Visual analysis of the precipitated asphaltenes showed that the samples are like a brownish fine powder with a distinctive black gloss. It is presenting at Fig. 3.

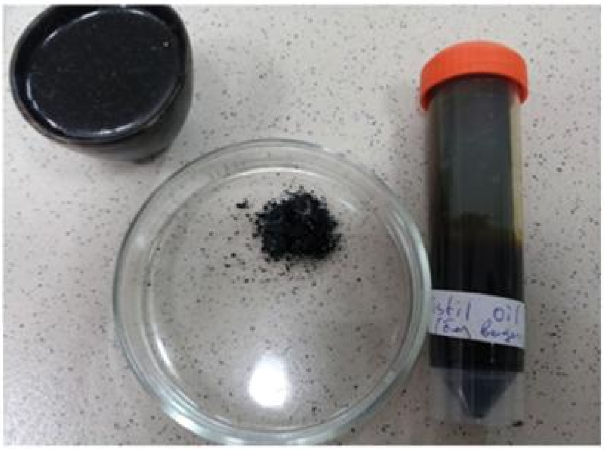

Fig. 3. Image of precipitated asphaltene samples.

The chemical composition of precipitated asphaltenes has been studied by IR spectroscopy. According to the IR-spectrum (Fig. 4), it can be concluded that the broad absorption band of asphaltenes at 3000-3600 cm^{-1} are characterizing the presence of polycyclic aromatic hydrocarbons and aliphatic chains in the samples of asphaltens. These hydrocarbons have free functional groups (carboxyl, carbonyl, hydroxyl) at their ends, which are forming the hydrogen bonds. The peak of the absorption band at 3570 cm^{-1} determines the stretching vibrations of the-OH group, which is actively involved in the formation of intermolecular hydrogen bonds. In IR – spectrum we can also see the presence of specific absorption bans which can characterize the presence of the alkyl substituents (-CH_3, -CH_2) with minima at 2853, 2922 cm^{-1}. Also presented the stretching and bending vibrations and the groups -CH_2-CH_3 at 1451 and 1376 cm^{-1}.

The IR-spectroscopic analyzes helped to approximately determine the chemical, group composition of received asphaltenes.

Also during the research was made the attempt to establish the elemental composition of the samples of asphaltenes on the installation of x-ray fluorescent spectrometer "Focus-M2". The results of elemental analysis are presented in diagram and in the following Table 1.

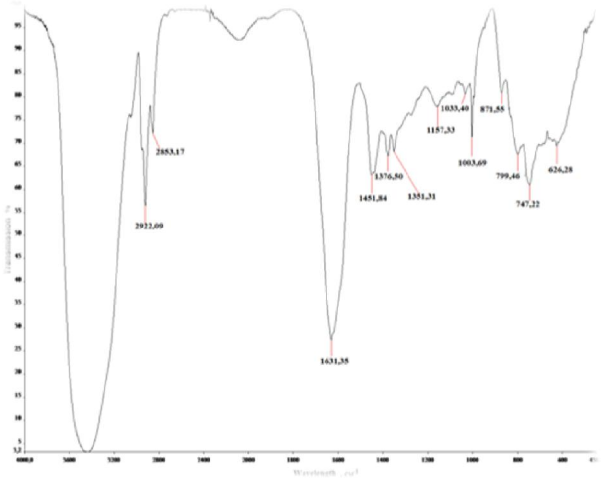

Fig. 4. The IR-spectrum of asphaltenes precipitated from natural bitumen of Munayli-Mola deposit by 40-fold amount of petroleum ether.

Table 1
The results X-ray fluorescent analysis of asphaltenes of Munayli-Mola deposit received from diagram (Fig. 5)

Element	Concentration	Intensity
Fe	42.445	34.81
S	28.05	0.71
Ca	11.672	3.10
Ni	2.640	1.21
Zn	6.332	2.85
Ti	0.644	0.24
As	1.756	0.64
K	3.517	0.37
V	2.994	2.28

Table 1 shows the presence of certain elements in the asphaltenes received from natural bitumen of Munayli-Mola deposit. From the table, it can be concluded that this natural bitumen, exactly its heavy residue after various treatment processes in the future can be used as an alternate resource for such important elements as vanadium, titanium, nickel and zinc, because the amount of these element in bitumen is enough to be mastered.

Figure 5 shows the diagram which was obtained by processing the results of analysis of spectrometer "Focus-M2" by computer.

The following X-ray diffraction analysis of the samples was carried out on a installation of DRON-3M digitally. According to the results of X-ray diffraction analysis (Fig. 6) it was found that the basis of a sample of asphaltenes precipitated from natural bitumen Munaily-Mola, is X-ray amorphous phase. Also found the presence of two crystalline phases. One - quartz content is less than one percent. Another phase is also present in very small quantities and is represented by a single line of diffraction d = 4.158 Å. As known, it cannot be carried out the X-ray diffraction analysis by one phase line, because it may belong to a plurality of phases which are not present in the sample.

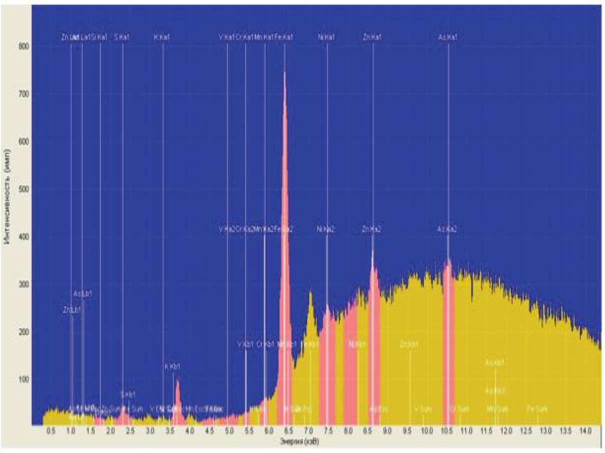

Fig. 5. The diagram of X-ray fluorescent analysis of asphaltenes of Munayli-Mola deposit.

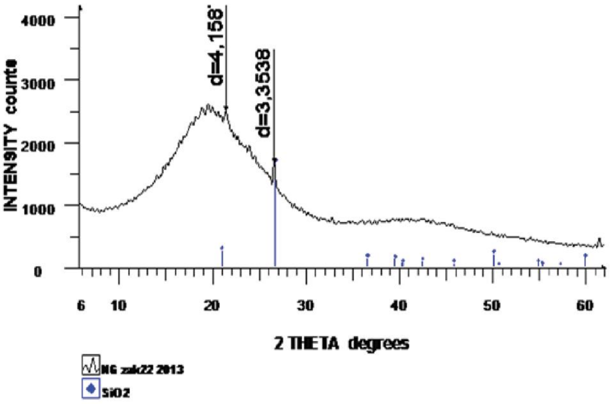

Fig. 6. The detail of diffraction diagram of asphaltenes in the range of angles of diffraction of 6-60 degrees 2θ.

To study the structure and aggregation of asphaltene surface, the produced samples were examined by scanning electron microscopy. The resulting surface images are given some information about the characteristics of asphaltogenic aggregation. Figure 7 shows SEM image of precipitated asphaltene from natural bitumen of oil sands.

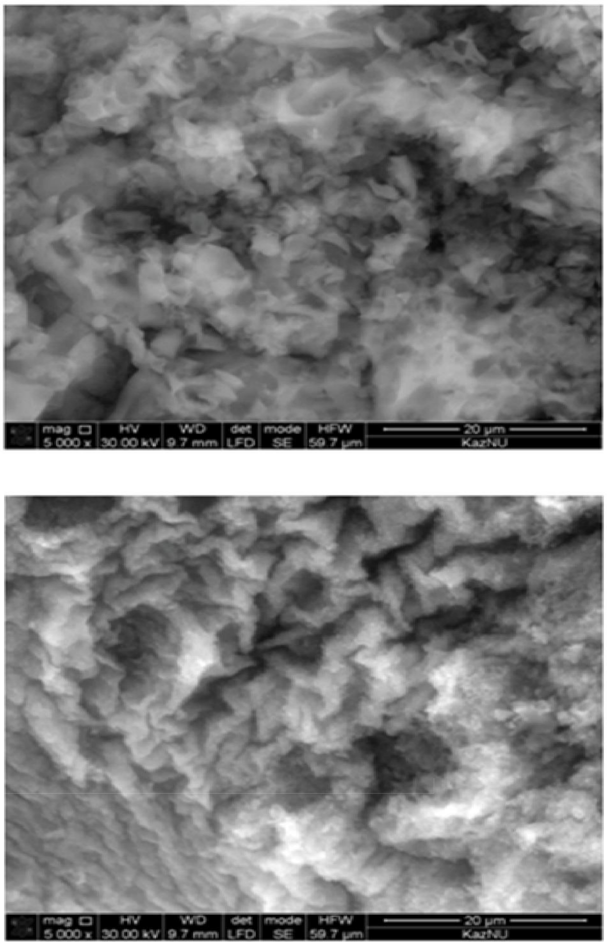

Fig. 7. Electron microscopic images of asphaltene surface.

As seen in Fig. 7, derived asphaltenes have a medium-ordered structure, the main component of the surface is represented by amorphous carbon. There are more subtle areas of carbon layers, about structure and aggregation, which electron microscopy data does not seen.

Conclusion

During the experimental work we carried out the precipitation of asphaltenes from oil sand of Munaily-Mola deposit using organic solvent of petroleum ether. Visual analysis of the precipitated asphaltenes showed that the samples are like a brownish fine powder with a distinctive black gloss. According to the IR-spectrum, that the broad absorption band of asphaltenes at 3000-3600 cm^{-1} are characterizing the presence of polycyclic aromatic hydrocarbons and aliphatic chains in the samples of asphaltens. The peak of the absorption band at 3570 cm^{-1} determines the stretching vibrations of the-OH group, which is actively involved in the formation of intermolecular hydrogen bonds. In IR-spectrum we can also see the presence of specific absorption bans which can characterize the presence of the alkyl substituents (-CH_3, -CH_2) groups -CH_2-CH_3. From the experimental results, it can be concluded that this natural bitumen, exactly its heavy residue after various treatment processes in the future can be used as an alternate resource for such important elements as vanadium, titanium, nickel and zinc, because the amount of these element in bitumen is enough to be mastered. X-ray diffraction analysis was found that the basis of a sample of asphaltenes precipitated from natural bitumen Munaily-Mola, is X-ray amorphous phase. Also found the presence of two crystalline phases. One - quartz content is less than one percent. Another phase is also present in very small quantities and is represented by a single line of diffraction d = 4.158 Å. Microscopic images showed that the asphaltenes have a medium-ordered structure, the main component of the surface is represented by amorphous carbon.

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