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High temperature transformation of tar-asphaltene components of oil sand bitumen

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Abstract: Transformations of high-molecular-weight compounds of oil sand natural bitumen under the heat treatment were studied in this work. For that purpose the natural bitumen isolated from oil sand taken from the Beke field (Kazakhstan) was used as a substrate. Thermal processing of natural bitumen leads to a general change in the chemical composition of components and to an increase in the output of certain fractions. The contents of oil, tar and asphaltenes were determined and the elemental composition of tar-asphaltene compounds was evaluated. Molecular structures of the tar and asphaltene components of natural bitumen before and after cracking have been defined from the data of elemental analysis, NMR spectroscopy and molecular weight. The high molecular compounds were presented as giant molecules containing small aromatic islands some of which were linked by aliphatic chains, that was proved by infrared spectroscopy.

Keywords: natural bitumen; cracking process; asphaltene; tar; molecular structure; infrared spectroscopy.

INTRODUCTION

One of the areas of increasing the resource base of hydrocarbon feedstock is the development of unconventional sources of hydrocarbons, which includes natural bitumen and heavy oil, which are close to bitumen, according to the physical–chemical properties. Over the next few decades, their role in the energy balance will increase significantly as a result of reduction in the reserves of conventional petroleum and necessity for their reproduction.[1] According to the Geological Survey of USA and Canada in North America hydrocarbon feedstock reserves of the untraditional sources – are larger than traditional reserves of oil and gas in all of the Middle East, accounting more than 1 trillion barrels in

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Canada and in the United States as well. The development of cost-effective technologies for the utilization of these vast reserves represents a great challenge.[2] The composition and physicochemical properties of oil sand natural bitumen differ significantly from conventional oils. Natural bitumen has higher content of tar-asphaltene compounds, petroleum acids, sulfur compounds and metals, as well as higher density and viscosity than conventional oil.[3] Production methods of natural bitumen are mainly related to two issues:

1) Unfavourable properties – low thermal conductivity, low permeability, lack of reservoir energy;
2) The bitumen layers of oil sand is an inactive state.

The main strain for the effective solution of this problem is the study of the chemical composition of heavy or high-molecular-weight of petroleum components, which in the current refining technology represent 25–30% of the incoming crude oil processing and has been called "heavy oil residues". If we consider that more than a half of these "residues" are so-called non-carbon components of oil or tar-asphaltene substances, it is understandable that analyzing the composition, structure, properties, chemical reactions and the main areas of chemical processing and technical use of petroleum tars and asphaltenes is of great importance.[3,4] Currently, a considerable amount of empirical data on the molecular structure of asphaltenes was accumulated, obtained using chemical and physical methods. Physical methods give the most reliable information on the structure of asphaltenes as a whole, which allows the development of the idea of their average structure. This is of great practical value. However, without the involvement of chemical methods in the case where it is necessary, the instrumental methods cannot give a full picture of the object being studied. The research of asphaltenes chemical transformations has shown that the asphaltene components may serve as a perspective cheap natural source for practically important products. They include: radiation-ion exchange materials having high dynamic and kinetic characteristics, agents for non-sulfur vulcanization of unsaturated rubbers, fillers, curatives and others. Asphaltene components are in the colloidal state in high-viscosity petroleum, heavy oil residues and natural bitumen. In the presence of an excess of low-molecular-weight alkanes asphaltenes coagulated.[5]

The aim of this investigation was to establish the changes of tar-asphaltene molecules during the thermal cracking of the natural bitumen.

EXPERIMENTAL

Materials

The sample of oil sand used in this study was collected from the Beke field (Kazakhstan). A distinctive feature of this field is the output of bituminous rocks to the ground surface. In such reopen reservoirs and areas of active water exchange a light fractions were lost and residual oil components were affected by various secondary processes, which led to the increase of the content of high-molecular weight components and the formation of inactive extra heavy oil and solid bitumen.[6,7] Bitumen deposits occur in them in small sized lens and interlayers. Natural bitumen was extracted from oil sand by Soxhlet's method using a chloroform as the solvent. The amount of the extracted natural bitumen from the oil sand of Beke field is 12 wt. %. The sulfur content in the bitumen is 1.5 wt. %. Natural bitumen is characterized by the low content of the fraction having boiling point in range 200–350 °C. Tars and asphaltenes in natural bitumen and its thermal transformation products were studied in detail.

Experimental procedure

The experimental scheme of cracking process and analysis of the obtained products is given in Fig. 1.

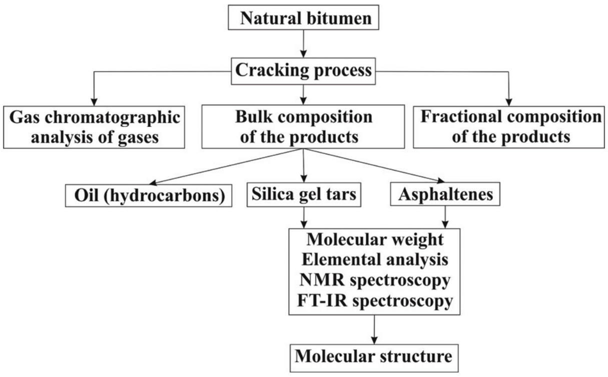


Fig. 1. Experimental scheme of cracking process and analysis of the obtained products.

The cracking of bitumen and study of the cracking products were described in detail elsewhere.[6]

The molecular weights of tars and asphaltenes of natural bitumen and their cracking products were measured in naphthalene by cryoscopic method developed in the Institute of Petroleum Chemistry using the "Krion" instrument.

Infrared spectra of the tar-asphaltene components were obtained from Spectrum-65 Fourier transform IR spectrometer. Samples were prepared as KBr tablets and measurements were performed in the range from 4000 to 400 cm^{-1}.

Elemental compositions of samples were determined by the elemental analyzer Vario Micro cube (Germany). Samples are fed automatically into a combustion zone. Combustion gases are passing a catalytic post combustion zone and then a reduction zone. Operating temperature was 1200 °C. The formed analyte gases N_2, H_2O, CO_2 and SO_2 carried by helium gas were sequentially separated by a temperature programmed desorption column (TPD) and quantitatively determined using a thermo-conductivity detector (TCD). The attached software calculates the element concentrations from the detector signals and the sample weights.

RESULTS AND DISCUSSION

Bulk composition of initial bitumen and cracking products

The cracking process of natural bitumen leads to the formation of gas, liquid oil products and the solid residue as coke (Table I). The thermal upgrading of natural bitumen reduces the oil viscosity. Viscosity was measured by a capillary viscosimeter (Cannon–Fenske opaque). Viscosity of bitumen decreased from

26×10^{-5} to 4.3×10^{-5} m^2 s^{-1} by cracking process. Heat treatment resulted in the increase of oil proportion, whereas the amount of the bitumen high-molecular-weight components decreased. The thermal treatment leads to the formation of coke and gas as well as to the destruction of tar-asphaltene components, resulting in the formation of light petroleum products. The content of the tars in oil decreased by cracking from 44.89 to 28.27 %. The contents of gas and coke formed by thermal process were 1.40 and 30.90 %, respectively (Table I).

TABLE I. Composition of initial bitumen and cracking product

Process	Yield, wt. %			Composition of liquid products, wt. %		
	Gas	Liquid	Coke	Oil	Tar	Asphaltenes
Initial bitumen	0.00	100.00	0.00	49.17	44.89	5.94
Cracking product	1.40	67.70	30.90	61.29	28.27	10.44

Elemental composition of asphaltenes and tars

Asphaltenes play an important role in the extraction and processing of heavy oil and natural bitumen. The asphaltenes are highly complex structures, containing naphthenic, aromatic and aliphatic carbocyclic and heterocyclic rings. Large fragments of molecules are linked by bridges containing methylene groups and heteroatoms, sometimes by metals (V, Ni and Fe). The most common substituents attached to the rings have short alkyl chain and functional groups, such as: carbonyl, carboxyl, hydroxyl, ether and sulfoxide.

The heat treatment of natural bitumen from the Beke field oil sand reduces the molecular weights of high macromolecular components by 30 % compared to the initial data (Table II). It means that the thermal processing under similar experimental conditions can affect pure asphaltenes at the same way. Significant changes in the structure and properties of asphaltenes were observed. The asphaltenes lost the main feature – solubility in aromatic solvents and then changed into an insoluble substance, such as coke. According to the elemental analysis (Table II) in asphaltene structure, the oxygen and the sulphur content decreased, while the content of carbon increased. At high temperature the molecular cyclization, recombination with benzyl and heterocyclic radicals, dehydrogenation and con-

TABLE II. Elemental composition of asphaltenes and tars before and after cracking

Element	Initial asphaltenes	Cracking asphaltenes	Initial tars	Cracking tars
C	77.30	81.91	79.70	81.01
H	7.59	7.00	9.77	10.52
S	1.00	0.64	0.56	0.26
N	1.07	1.45	0.72	0.10
O	13.04	9.00	9.26	8.11
C/H	10.18	11.69	8.16	7.69
Molecular weight, amu	2044	1304	751	499

densation occurred. All these processes led to an increase of the degree of condensation and of the aromaticity of the system. Chain transfer processes and recombination can occur between two or more asphaltene plates, which results in the formation of a cross-linked insoluble product – coke. Consequently, C/H ratio increased from 10.18 to 11.69 (Table II).

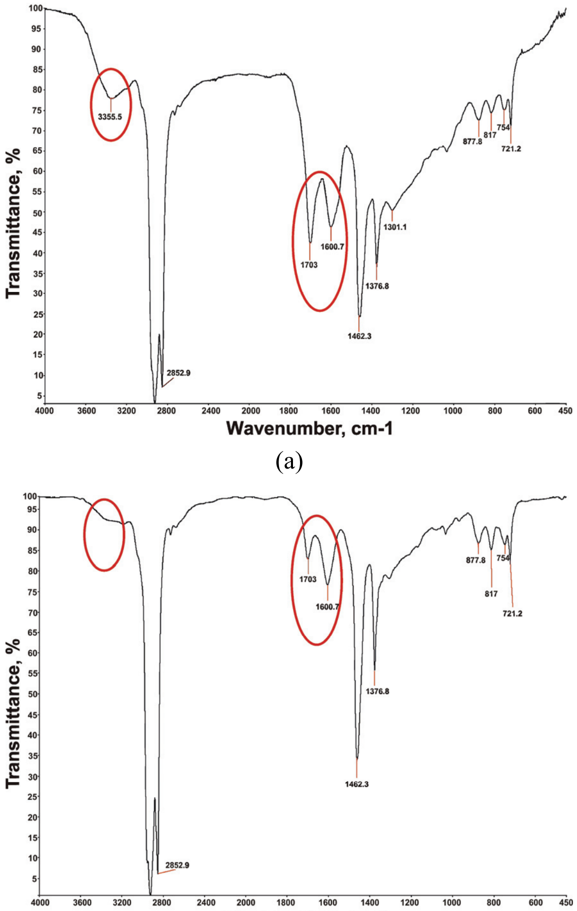
The elemental composition of tars in cracking products is characterized by lower amounts of heteroatoms (O, S and N) in comparison to the initial tars. On the other hand contents of C and H increased. The atomic C/H ratio of tars slightly decreases by cracking. Among these changes, the removal of heteroatoms is related to the cleavage of C–R (R = S, O, N) bonds. It can be explained by the lower energy of C–S, C–N and C–O bonds in comparison to C–H and C–C bonds.

Infrared spectroscopy (IR) analysis of macromolecular components

The structural changes of bitumen before and after reaction were characterized by the Fourier transform infrared spectroscopy. Peaks absorbance bands in IR spectrum of tars (Fig. 2) at 754, 817 and 877.8 cm^{-1} represent condensed aromatic hydrocarbons. Absorption bands at 721.2 cm^{-1} characterizes the alkyl groups (CH_3 and CH_2) within long-chain branched structures. The high intensity band at 1377 cm^{-1}, belongs to the compounds with methylbenzene pattern (Fig. 2a). Absorption band at 3355.5 cm^{-1} shows the acidic hydroxyl group. Absorption bands at 1600.7 and 1703 cm^{-1} represent stretching vibrations C–O–C and C–OH in carboxyl groups. After the heating, the intensity of peaks of the oxygen groups in tar components declined (Fig. 2). The reduction of these pearks resulted from the transformation reactions, which are followed by removal of water, carbon dioxide and molecular oxygen. Absorption band at 1462.3 cm^{-1} belongs to the stretching vibrations of methylene groups, which characterize the degree of branching of aliphatic paraffinic chains.

Broad absorption bands in asphaltenes at 3694 and 3619 cm^{-1} (Fig. 3) are characteristic for polycyclic aromatic hydrocarbons, such as compounds with phenanthrene skeleton. After the cracking, Fig. 3b, these peaks have dissappeared, which indicates the destruction of polycyclic aromatic hydrocarbons by transferring them to aliphatic components. Absorption bands with maxima at 2850 and 3055.9 cm^{-1} are typical for alkyl substituents ($–CH_3$, $=CH_2$). The presence of intensity band at 1032 cm^{-1} belongs to the carbonyl groups associated with aromatic ring.

These functional groups disappeared after the heat treatment (Fig. 3b), consistent with results of elemental analysis (Table II). The peak position of 1696 cm^{-1} provides information about the >C=O with the two aliphatic chains or saturated rings. The absorption band in the spectrums about 1110–1160 cm^{-1} represents the sulfonyl group from RSO_3H and RSO_3^-. Low intensity peaks (912 cm^{-1})



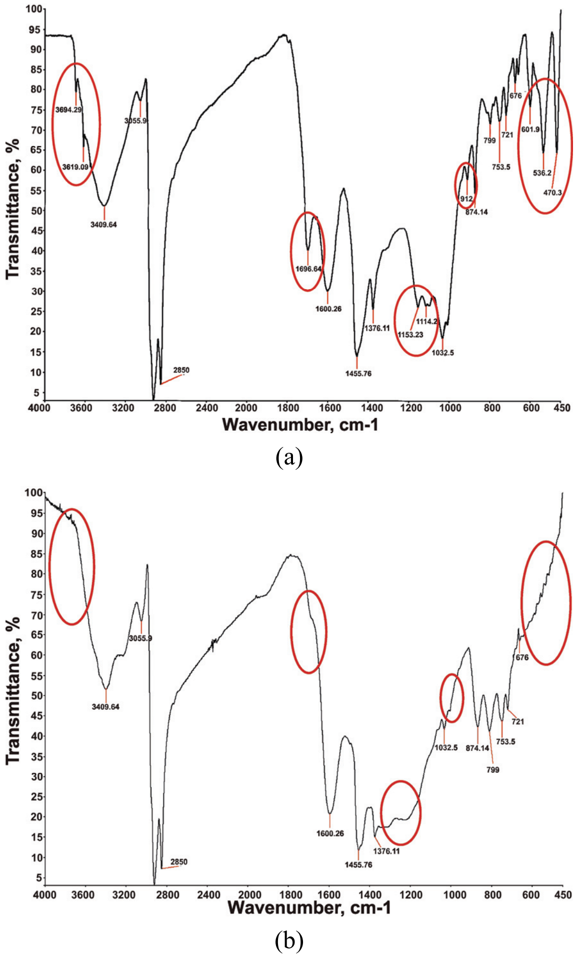
(a)

(b)

Fig. 2. IR spectra of tars: a) from initial bitumen and b) after cracking of bitumen.

which represent oxygenates, are not clearly allocated at the initial asphalttene spectrum. The aromatic structures (754, 799 and 874 cm^{-1}) are captured clearly in the asphaltene spectrum. The result suggests that after aromatic components reach a critical concentration, the phase separation occurs giving a denser and more aromatic liquid phase. Aromaticity is the dominant factor that controls this phase separation. This observation implies that the increase of the molecular weight is a significant factor in the formation of coke from bitumen. Fig. 3 shows that the absorption peaks from 600 to 470 cm^{-1} became weaker, indicating that some of aliphatic chains were removed, due to the occurrence of polycondensation reactions.

Thermal reactions usually conduct the formation of high-molecular-weight aromatic components in solution of liquid phase. Reactions that contribute to this process are the cracking of side chains from aromatic groups, dimerization reactions, dehydrogenation of naphthenes (to form aromatics) and cyclisation reactions. The loss of side chains always accompanies the thermal cracking. The formation of oligomers is enhanced by the presence of olefins.



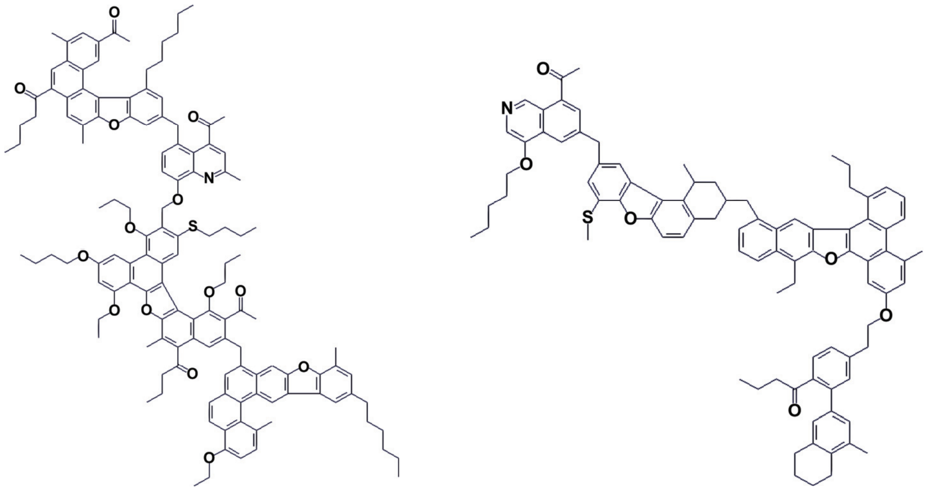
(a)

(b)

Fig. 3. IR spectra of asphaltenes: a) from initial bitumen and b) after cracking of bitumen.

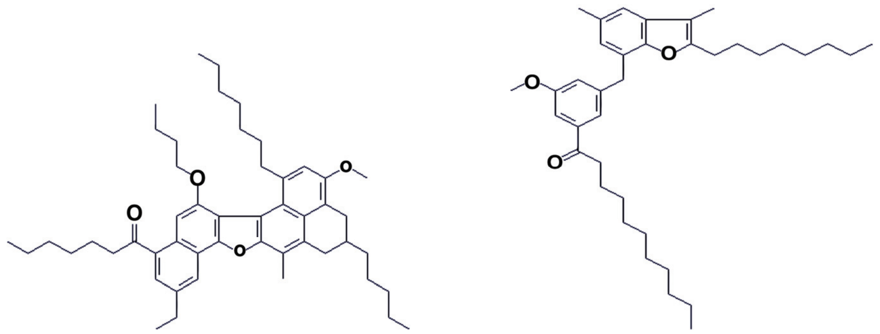
Molecular structure of asphaltenes and tars

The Monte Carlo method was used to construct the molecular structure of macromolecular compounds. This method is used in cases where it is impossible to obtain the accurate information about the structure of the chemical compound, or when there are many possible representations of structures of the classes of compounds, such as in asphaltenes and tars. The program that constructed molecular structures was written in Fortran, version 6.6. This program used the analytical data as input parameters and calculated the average molecular structure of tars and asphaltenes based on the structural-group analysis. The program includes expanded polycyclic structures library, which is used for the construction of high molecular weight components of bitumen by comparison with published data. The input parameters are the analytical data obtained from the elemental analysis, NMR spectroscopy, and molecular weights of tars and asphaltenes (Figs. 4 and 5).



(a) (b)

Fig. 4. Average hypothetical molecular structures of: a) initial and b) cracking asphaltenes.



(a) (b)

Fig. 5. Average hypothetical molecular structures of: a) initial and b) cracking tars.

Proton NMR spectroscopy (Table III) was employed to characterize the aromaticity of hydrocarbons and to measure the inside changing of the molecules. From the results of NMR the aromatic carbon content was the key structural information. The initial asphaltenes and tars contained 14.28 and 4.82 wt. % of aromatic hydrogen, respectively, which is consistent with the high content of coke. The easily reacted side chains attached to aromatics and sulfides would be cracked and evolved as gases which reduced the hydrogen content (Table II). In contrast, the aromatic compounds were intact and preserved in the course of thermal cracking, except for the significant yield of coke. The net concentration of aromatics in liquid product increases with the removal of aliphatics as fragments in the gas fraction. Aromatics in the liquid product can be created either from naphthenes or from the side chains of aromatic compounds in bitumen. For example, the olefins produced by the cracking of side chains can form aromatics *via* addition reactions followed by dehydrogenetion.[12]

TABLE III. NMR results (wt. %) of macromolecular compounds

Sample	H			
	Aromatic	CH_3	CH_2	CH
Initial asphaltenes	14.28	24.97	45.94	14.81
Cracking asphaltenes	14.75	24.63	50.19	10.43
Initial tars	4.82	14.41	67.21	13.56
Cracking tars	7.45	14.88	63.29	14.38

Based on the calculation data the most stable conformations of tar and asphaltenes molecules was determined. It was found that the stability of the molecules depended on the structural characteristics such as the number of structural blocks, their size and spatial arrangement of atoms with respect to each other. The molecules consisting of more structural blocks of smaller size are more thermodynamically stable than monoblock structure. The molecules which form the burst structure are the thermodynamically more stable than non-layered structures.

It should be noted that the asphaltenes of natural bitumen have high aromaticity, which also affects the formation of coke. These polydisperse compounds are not stable and the amount of coke produced from heat treatment of bitumen depends on the concentration and structural characteristics of asphaltenes.

The thermal processing of bitumen at temperature 450 °C formed intermediates of the lower molecular weight asphaltene and tar components compared with initial, highly aromatized thermally-resistant molecule, which has been in part transformed into coke. The high temperature of this process leads to the shortening of side-chain substituents and reduces the aromaticity of the high molecular weight compounds.

CONCLUSIONS

Based on the results of the analysis of the high molecular weight components in bitumen and its cracking products, it can be concluded that *via* the thermal cracking process the hydrocarbons generated the free radicals which led to the formation of light gases and coke products. Thermal processing is the most widely used method for the upgrading of heavy oil and bitumen. Several observations from the thermal processing have led to the conclusion that coke formation is triggered by the phase separation of asphaltenes. In these experiments, the asphaltene content increased to 1.5 %. This phenomenon indicates that the hetero intermediate bridges form strong bonds. The proton NMR and IR analyses provided aliphatic and aromatic carbon distributions of the initial and cracking tars and asphaltenes. The amount of substituted and unsubstituted peripheral aromatic carbons and the mean size of aromatic clusters were the important parameters estimated by Monte Carlo method. Challenges in the modeling of asphaltene composition include the matching of elemental composition and the balance between aromatic and aliphatic carbon and hydrogen atoms. There are multiple polycyclic aromatic hydrocarbons units containing 2–5 or more rings inside asphaltene molecules.

ИЗВОД

ТРАНСФОРМАЦИЈА КОМПОНЕНАТА КАТРАНСКО-АСФАЛТЕНСКИХ КОМПОНЕНТИ НАФТНОГ ПЕСКА НА ВИСОКОЈ ТЕМПЕРАТУРИ

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Проучаване су трансформације једињења високих релативних моларних маса природног битумена из нафтног песка под утицајем термичке обраде. За ту намену је као супстрат коришћен природни битумен изолован из нафтног песка поља Beke (Казахстан). Термичка обрада природног битумена доводи до промене укупног хемијског састава и повећања удела неких фракција. Одређени су садржај нафте, катрана и асфалтена и процењен елементални састав катранско-асфалтенских једињења. Молекулске структуре катранских и асфалтенских компоненти природног битумена пре и после крековања су дефинисане на основу података елементалне анализе, НМР спектроскопије и релативних моларних маса. Једињења високих релативних моларних маса су била присутна у виду огромних молекула који садрже мала ароматична острва, од који су нека повезана алифатичним ланцима, што је доказано инфрацрвеном спектроскопијом.

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