

Changing the Structure of Resin-Asphaltenes Molecules in Cracking

Ye. Imanbayev^{1,2*}, Ye. Tileuberdi^{1,2}, Ye. Ongarbayev¹, Z. Mansurov^{1,2}, A. Batyrbayev²,
Ye. Akkazin¹, E. Krivtsov³, A. Golovko³, S. Rudyk⁴

¹Al-Farabi Kazakh National University, 71 al-Farabi ave., Almaty, Kazakhstan

²Institute of Combustion Problems, 172 Bogenbay batyra st., Almaty, Kazakhstan

³Institute of Petroleum Chemistry, 4, Akademichesky ave., 634021, Tomsk, Russia

⁴Sultan Qaboos University, Al Khoudh, Muscat 123, Oman

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Abstract

In the paper, structural changing of resin-asphaltene molecules in cracking process of oil sand bitumen are investigated. Cracking process to natural bitumen carried out in an open-to-air reactor, which extracted from oil sand by organic solvent. Reaction temperature was 450 °C and process duration was 60 min. The reactor was heated at a rate of 10 °C/min up to the desired temperature. Di-tert-butyl peroxide was used as radical formation additive. When limiting oxygen, it can be used catalyst molecule supplies as the oxidizer. The thermal destruction processes of heavy hydrocarbons with the catalyst make it possible to increase the yield of low boiling liquid products with the formation of coke and gas as by-products. High temperature leads to increase the oil content, and decrease the total resin-asphaltene components in bitumen. Monte Carlo method used for construction the molecular structure of resin-asphaltene components. The calculations data determined the most stable conformation of resins and asphaltene molecules, that the stability of the molecules affect structural characteristics such as the number of structural blocks, their size and spatial arrangement of atoms with respect to each other. Microscopic images showed that the asphaltene have around 40–50 nm of particle size, which large monolithic switching, weakly focused on a major surface, provided with amorphous carbon.

1. Introduction

Currently, international oil refining industry characterized by a decreasing light oil reserves and an increase the fraction of the production and processing of heavy oil, heavy petroleum residues and oil sands. Because of a decrease in the production and an increase in the prime cost of light oils, the production of raw materials for the manufacture of petroleum products becomes a problem of increasing current interest. The thermal destruction processes of heavy hydrocarbon raw materials make it possible to increase the yield of lowboiling liquid products with the formation of coke and gas as by-products. Cracking processes in the presence of different catalysts are of special interest. The thermocatalytic conversion of heavy hydrocarbon raw materials with iron oxide and other organic radical

formation additives are a promising method for the production of synthetic oil. Microspheres, which can initiate the deep destruction of high-molecular-weight components, exhibited high efficiency in the processes of cracking [1–3]. Organic radical formation additives allows to promotion the birth of radicals in the system, which reduces the rate of coke formation. These radical-forming additives can be related to an anti-coking agent. DTBP has a relatively weak RO–OR bond and readily undergoes dissociation at higher temperatures to two RO• radicals and it is widely used as a radical source, reaction initiator [4].

Asphaltene is the most refractory and often the heaviest component that containshighly aromatic and polar of hydrocarbon. Because of these fundamental characteristics, it considers an important factor that causes hindrance in many petroleum

*Corresponding author. E-mail: erzhan.imanbayev@mail.ru

operations, production, transportation, refining, even wax crystallization, crude oil emulsification, and de-emulsification [5]. Though many of these claims are not fully proved or understood, asphaltene does have a negative effect on many of the above operations. The term asphaltene does not imply any particular molecular structure or molecular weight. It is natural to attribute these negative impacts to particular molecular and thermodynamic properties associated with asphaltene [6]. Additionally, asphaltenes are known to be a complex mixture containing thousands of distinct molecular formulas. Despite this scrutiny, some fundamental aspects of asphaltene chemistry are still debated. Asphaltenes are a group of molecular species, whose exact molecular weight is still unknown and varies from 500 to 15000 depending on the analytical technique used [7, 8].

In nature, asphaltenes are hypothesized to be formed as a result of oxidation of natural resins. Asphaltenes comprise a heterogeneous fraction consisting of largely polycondensed aromatic rings and cyclic naphthenes, containing most of the heteroatoms (S, N, and O) and metals of the bitumen [9]. Almost all of the heteroatoms and the metals in the asphaltenes are present in five- or six-member ring structures, in a layer of blocks lying one after another. At temperature of 300–400 °C the asphaltene does not melt, only 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 that are not properly peptized [8, 10].

One of the earliest descriptions of asphaltenes in crude oil suggested that the asphaltenes behaved as solid particles. Very fine particles a few microns in diameter or smaller dispersed in a continuous phase are commonly called colloids. This model portrayed that the asphaltenes as a molecular cluster with polar aromatic compounds (called resins) adsorbed on the surface. These resins maintain the asphaltenes in suspension in the oil, which consists of less polar materials such as n-alkanes. However, the ease of dispersing asphaltenes in aromatic solvents is proof that the resins do not play a special role in solubility. More direct evidence for

the behavior of asphaltenes as colloids comes from measurements of aggregation in solution. These measurements show that at least a portion of the asphaltene fraction is found in multimolecular aggregates 2–20 nm in size, both in crude oils and in solvent solutions. These aggregates also readily account for the controversy regarding the true molar mass distribution of the asphaltene fraction [11].

The asphaltenes comprise the heaviest part of the heavy oil resin and play a negative role in bitumen recovery, in transportation, and, most important, in the upgrading and refining processes. Asphaltene plays a threefold role in the fouling process [7]:

- first, it has the tendency of precipitating out in the presence of lighter paraffinic hydrocarbon fractions, making the crudes mobility restricted. This creates fouling in the production well during the recovery process, as well as in the pipeline during the transportation of bitumen;
- second, once the structure of the asphaltene is disturbed, the fouling tendency increases (e.g., thermally cracked asphaltenes foul at a higher rate than unprocessed asphaltenes);
- finally, an increase in asphaltene concentration in the feedstock results in a high rate of fouling on furnace walls.

The high density and high viscosity of bitumen are also attributed to its asphaltene content. Asphaltenes are so complex that no single research group can complete a study or answer all the questions about them. Scientists are still debating the molecular weight of asphaltenes, which can vary from hundreds to millions in some cases. It is still debated whether the physical nature of asphaltenes presents as an aggregate, a colloid, or an association with resins. Asphaltenes are a contentious area among researchers, with long-standing battles still raging [10, 12]. Asphaltenes are very sensitive to atmospheric oxygen. It has been observed that just the handling of asphaltenes in the atmosphere oxidizes the sample rapidly enough that its characteristics change. Visually, one can observe the asphaltene color change rapidly with the time of exposure, and any chemical properties measured will be influenced by the length of time of exposure to air [13].

Resins are the polar components that remain after asphaltenes are precipitated. They are higher in heteroatoms and have higher concentrations of aromatic carbon, whereas the asphaltenes have the highest molar mass and contain most of the polar compounds. The resins are portion of the maltenes

in a solution in n-pentane that are adsorbed by a column of silica gel, alumina or by attapulgus clay (alumino-silicate clays). The resin fraction contains more than twice the Conradson carbon residue (CCR) and metals as compared to the de-asphalted oil (DAO) fraction. Resin divided two types by density: low-density resin is a dark-colored liquid (yield 75–80% of the total resin), whereas the high-density resin (yield 20–25% of the total resin) obtained as a dark-colored crystalline semisolid. The resins are components of an intermediate structure located between the asphaltenes and the oil that serves to keep the aggregates dispersed in the oil. Understanding the role of resins is still important for understanding the causes of aggregation [7, 11].

The aim of this work was to perform the thermocatalytic cracking of the natural bitumen of Kazakhstan under varied conditions and to determine the group and fractional composition of the cracking products.

2. Experimental

2.1. Materials

Natural bitumen (organic part) obtained from an oilsand of Western Kazakhstan was used in this research work. Some important characteristics of this field are shown in Table 1.

Table 1
Physical and chemical characteristics
of the organic part of oil sand

Parameters	Oil sand from Beke field
Content of organic part, wt. %	12.0
Total sulfur content, %	1.5
Density, kg/m ³	958.1
Kinematic viscosity at 80 °C, sSt	26.0
Carbon residue, wt. %	30.1
Ash content, wt. %	1.1
Softening temperature, °C	20.0

The extraction of natural bitumen from oil sand was performed in a Soxhlet apparatus with chloroform as a solvent. All of the experiments on processing oil sand and its product analyses were repeated at least three times, in the tabulated dates chosen average value. The amounts of natural bitumen extracted from the oil sand of the Beke field were 12% (Table 1). The residual concentrations of organic matter in the oil sand of the Beke depos-

it were about 1.1%. The carbon residue of organic matter was 30.1%.

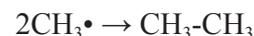
2.2. Cracking apparatus and cracking conditions

The reactor consists of a stainless steel cylindrical vessel (inner diameter – 10 mm and height – 140 mm). The experiments were done in an open-to-air reactor. The reactor is heated by an electric furnace, which is coupled with a temperature control unit. The temperature was monitored with a thermocouple placed in the reactor. The experiments were started by adding about 7 g of sample to the reactor. The reactor was heated at a rate of 10 °C/min up to the desired temperature. After a series of the prescribed heating times the reactor was quenched in cold water, then the liquid products and solid residue was removed from the reactor. Reaction temperature was 450 °C, process duration were 60 min.

2.3. Preparation of catalyst and radical additives

The narrow fractions of magnetic microspheres, which were isolated from fly ash after the combustion of coals at heat and power plants by a set of separation and hydrodynamic and granulometric classification processes, were used as an initiator of the cracking of bitumen [9]. The formation of a metal oxides structure is a result of the thermochemical transformation of mineral coal form droplets to reaction complex of iron melts (FeO-CaO-MgO-SiO₂-Al₂O₃) macroelements partial oxidation and crystallization phases separated on cooling. Amount of microspheres in cracking process was 10 wt.% by weight of bitumen sample.

The peroxide bond undergoes homolysis at temperatures >100 °C. For this reason, di-tert-butyl peroxide is commonly used as a radical initiator in organic synthesis and polymer chemistry. The decomposition reaction proceeds via the generation of methyl radicals.



Di-tert-butyl peroxide was added 3 wt.% by weight of sample. This organic peroxide initiates the reaction to the destruction of macromolecular compounds, and provides a higher yield of light products.

2.4. Precipitation of asphaltene from bitumen

During the experimental work the precipitation of asphaltenes from oil sands of Beke field were carried out. The extracted natural bitumen and liquid cracking products were added a 40-fold amount of n-hexane 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 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.

2.5. Separation of resin from bitumen

On the separation of maltenes in oil and resin was used Soxhlet method with activated silica gel. Activation of silica gel carried out at 350 °C temperature for 4 h. Activated silica gel wetted with hexane and prepared maltenes transferred to this silica gel in Soxhlet. Apparatus have been placed on a water bath and extracted oil with 200 ml of hexane until the flask was not drain pure hexane. After extraction of oil, flask replaced to a clean flask with 200 ml benzene-alcohol mixture, which ratio is 1:1. Adsorbed resins on silica gel desorbed by alcohol-benzene mixture. After the separation of oil and resins, all solvents were distilled off on a rotary evaporator. Then the samples were dried at 60 ± 4 °C temperature until a constant weight (STP SZhShI 1217-2005 procedure, Institute of Petroleum Chemistry).

2.6. Microscopic study of asphaltene

The microstructures and microanalysis of asphaltene were investigated with a transmission electron microscopy (TEM). TEM uses an electron beam to interact with a sample to form an image on a photographic plate or specialist camera. In addition, the study was performed on a transmission electron microscope JEM 100CX, at an accelerating voltage of 100 kV (vacuum, a small temperature). Samples were prepared by dry preparation.

3. Results and Discussion

In the cracking of natural bitumen were formed liquid product, coke and small quantities of gas appeared (Table 2). The yield of the liquid products

of the cracking bitumen was 67.7%, however the yield of liquid products after addition catalysts is 63%. The experimental data show that the di-tert-butyl peroxide positively affected to bitumen with formation lower content of gases, coke and higher content of liquid products.

The presence of microspheres has a negative effect on the amount of liquid products of the cracking of bitumen; the yield of coke increased by 5% (Table 2). Catalysts intensify the condensation reactions of bitumen cracking products, which occur on the surface; this was confirmed by the greatest coke formation in these experiments. In results of experiment, organic peroxide initiates the degradation reactions of the high-molecular-weight compounds of natural bitumen and ensures the yield of light cracking products. The peroxide additive favorably influenced the thermal destruction process.

High temperature leads to increase oil content and decrease the total resin-asphaltene components of bitumen. Figure 1 represents other additives as catalysts and organic initiator increase in the formation of coke and the destruction of asphaltene components with the formation of lighter products. Oil concentration after cracking with di-tert-butyl peroxide reached to maximum 63.27%.

The net concentration of aromatics in liquid product kept going higher with removal of aliphatic as fragments in the gas fraction. Aromatic in liquid product can be created either from naphthenes or from side chains in aromatic compounds of bitumen. The olefins from cracked side chains can build aromatics by free-radical additions followed by rearrangements.

The molecular weight of asphaltenes and resins immersed in a great dilemma by different research groups. The main discrepancies are due to the experimental technique employed for its measurement and, in some cases, the conditions for the analysis, such as solvent or temperature.

Table 2

Material balance of cracking products of bitumen

Cracking conditions	Total sulfur content in oil, wt. %	Yield, wt. %		
		Gas	Liquid	Coke
Natural bitumen	0.30	0.0	100.0	0.0
450 °C, 60 min	0.43	1.4	67.7	30.9
450 °C, 60 min with catalysis	0.34	1.3	63.0	35.7
450 °C, 60 min with DTBP	0.35	1.1	70.3	28.6

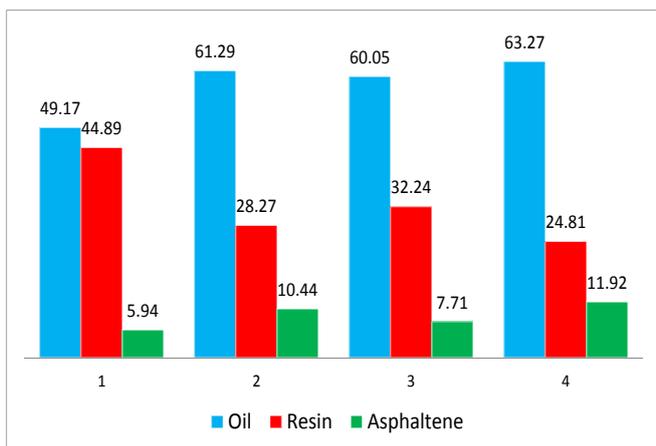


Fig. 1. Diagram of bulk composition of cracking products: 1 – initial bitumen; 2 – after cracking; 3 – cracking with catalysts; 4 – cracking with DTBP.

Molecular weight of asphaltenes and resins measured at Cryoscopes in naphthalene by "Kryon" apparatus. Heat treatment these compounds lead to a change of the structural characteristics of averaged molecules within lower mass components. Asphaltene molecules more destroyed by addition of catalyst to formation products such as gas and liquid products (Table 3).

Table 3

Changing the molecular weight of resin-asphaltene components

Sample	Asphaltenes, Dalton	Resins, Dalton
Natural bitumen	2044	751
After cracking	1304	499
With catalysis	1003	550
With DTBP	1042	564

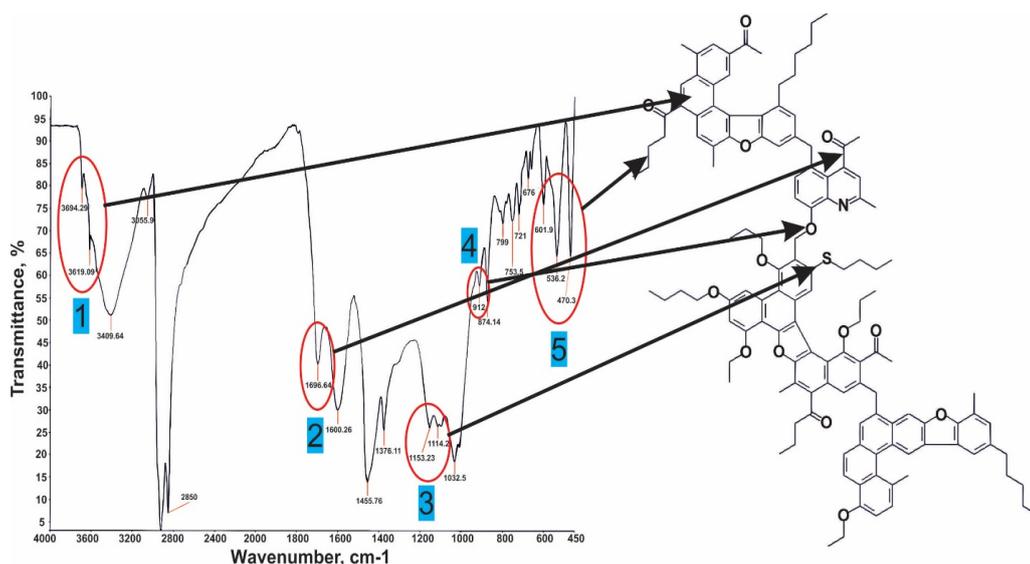


Fig. 2. Infrared spectrum and hypothetical molecular structures of asphaltene.

As the Table 3, high temperatures within the molecular cyclization, recombination with benzyl and heterocyclic radicals, dehydrogenation, condensation – all of these processes lead to increase in the degree of condensation and aromaticity of system. We found that the thermal cracking of bitumen leads to a decrease in molecular weights of asphaltene components by 30%, as compared with the initial data. Upon the cracking in the presence of microspheres, the molecular weights of tars and asphaltenes are somewhat lower than with the use of radical-forming additives.

Monte Carlo method was used for construction the molecular structure of resin-asphaltene components. Constructing molecular structure program is written in Compaq Visual Fortran 6.6. The developed program for the construction of molecular structure used as input parameters of analytical data and calculated using the structural-bulk composition analysis, which describes the structural fragments of average molecular structure resin and asphaltene. In the constructing program expanded polycyclic structures library, which used in the construction of high molecular weight components of bitumen by comparison with similar published scientific literature procedures and has been included distribution of heteroatoms into functional groups of molecules (Figs. 2 and 3).

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

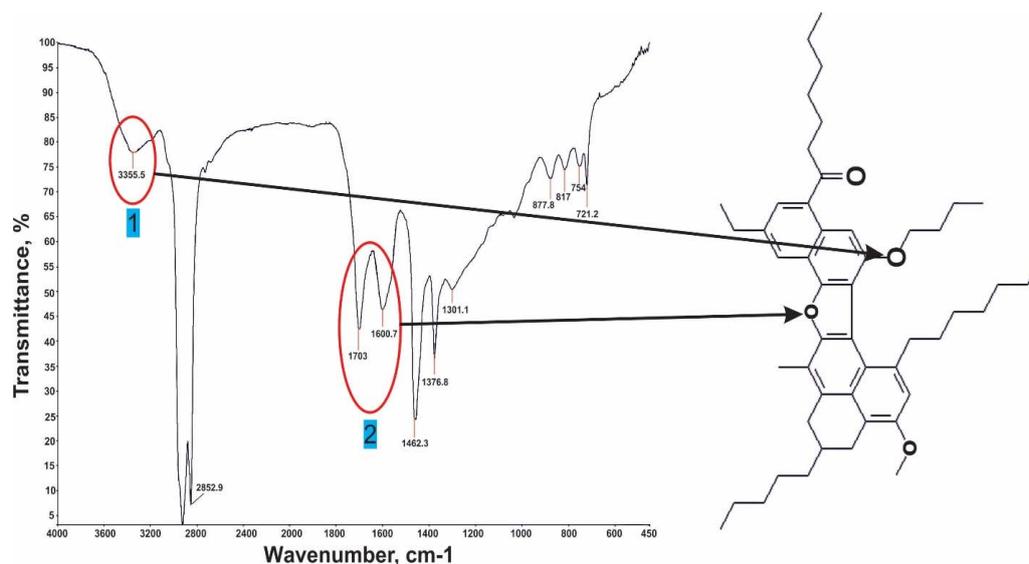


Fig. 3. Infrared spectrum and hypothetical resinmolecular structure.

The chemical composition of resin and asphaltene of bitumen were studied by Fourier transform infrared spectroscopy (FTIR). Broad absorption bands in asphaltenes at 3694 and 3619 cm^{-1} (Fig. 2) are characteristic for polycyclic aromatic hydrocarbons, like phenanthrene compounds (peak #1). Figure 2 (peak #2) absorption band at 1696 cm^{-1} is due to stretching vibrations C=O groups that actively involved in the formation of intermolecular hydrogen bonds. These hydrocarbons are at the ends of free functional groups (carboxyl, carbonyl, and hydroxyl) which forming hydrogen bonds. Stretching and deformation vibrations CH_2 and CH_3 groups (peak #5) presented at absorption bands of 601, 536 and 470 cm^{-1} . As shown presence intensity bands of stretching vibrations Ar-O-C (peak #4) in the region 912 cm^{-1} is combined with intense aromatic structure (at 753.5, 799, 874 cm^{-1}) captured most clearly in asphaltenes spectrum. These absorption bands are included aromatic compounds and due to the presence of hydrocarbons C=O groups. The absorption band in the spectrum 1153 cm^{-1} has given information about functional group S-C, and organic form R-S-R group (peak #3) expresses it. Low intensity peaks present oxygenates (at 1100–1300 cm^{-1}) is not clearly allocated at this spectrum, indicating that oxygen content is higher as fluctuations stretching benzene ring presented at 874 cm^{-1} band.

FTIR spectrum of resins (Fig. 3) peaks at absorbance bands 754, 817, 877.8, 1600.7 cm^{-1} provides information condensed aromatic hydrocarbon resin structure. Spectrum observed absorption band 721.2 cm^{-1} , characteristic of the alkyl substituent groups (CH_3 , CH_2) with long branched structures.

It should be noted Fig. 3 a rather high intensity of the band at 1376.8 cm^{-1} belongs to the compound of methylbenzene. Absorption band at 3355.5 cm^{-1} (peak number 1) clearly indicated the bonds between from aromatic ring and oxygen molecules, absorption spectra bands of 1600.7 and 1703 cm^{-1} give information stretching vibrations C-O-C and C-OH (peak number 2) in conjunction carbonyl groups. At spectrum 1462.3 cm^{-1} absorption bands belong to the stretching vibrations of methylene groups and characterize the degree of branching of paraffin compounds.

The calculations data determined the most stable conformation of resins and asphaltenes molecules. It was found that the stability of the molecules affect structural characteristics such as the number of structural blocks, their size and spatial arrangement of atoms with respect to each other. Consisting of more structural blocks of smaller size molecules are more thermodynamically stable in compared with monoblock structure.

Scanning electron microscopy does not give us complete information about the processes of aggregation of asphaltenes [8, 15, 16], and therefore in the paper studied by transmission electron microscopy. Results of the TEM analyses of the asphaltene surface precipitated from natural bitumen were shown at Fig. 4.

Asphaltene samples consist mainly of fragments sufficiently dense film (Fig. 4a). For some annealing of the sample occurs thinning of the film and occasionally there are sample substance of formation, having a crystal lattice. At the edge of the film may be dense large and thin particles (Fig. 4b).

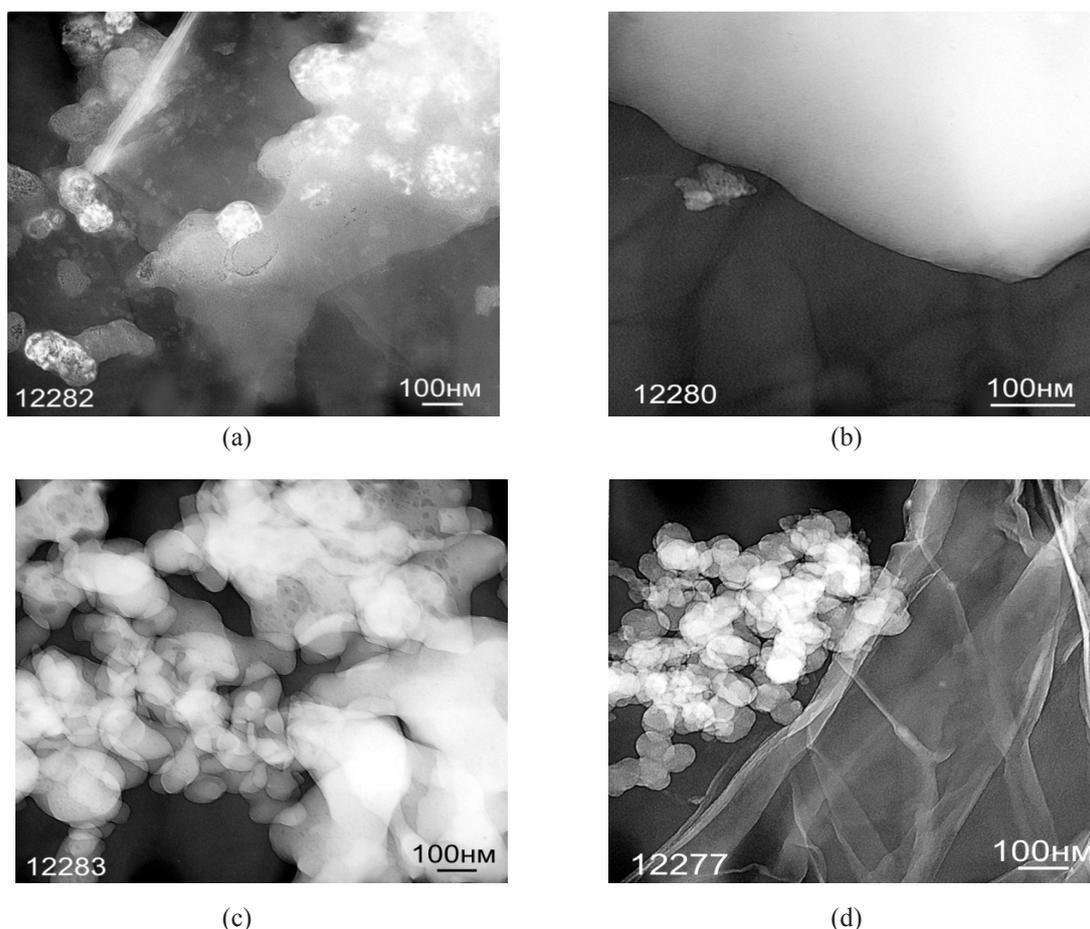


Fig. 4. TEM images of asphaltene.

Meanwhile on the figure C are present traces of the transformation of the particles. Microdiffraction image that reflect the crystalline order of the substance, give evidence of presented bulk amorphous material. As the TEM images, after annealing asphaltenes of oil sands natural bitumen going appearance two types of nano-dimensional structures: the capsule in the capsule and the ribbon-like structure. Sample submitted asphaltene is mainly composed of rounded particles, most of which are extremely small (Fig. 4c and d). The substance of the sample has no structural order – an amorphous structure. Single-crystal particles and traces the transformations of the particles observed.

4. Conclusions

In this paper, the cracking process of extracted natural bitumen from oil sands and the property of obtained liquid products were investigated. The averaged oil content of Beke oil sands was about 12 wt.%.

These oil sands are valuable resources and worthy of further development and upgrading. Based

on the analyses results of the bitumen and cracking products concluded that in the thermal cracking process, hydrocarbon generated free radicals, which leads to formation light gases and coke products.

Today, special catalysts have been developed for the cracking of heavy raw materials, with improved selectivity for coke yield. However, they are very expensive and the lifetime of the catalyst is not so much. Direct cracking of heavy oil is the simplest in a technical way. However, the presence of impurities in the heavy oils that deactivate the catalyst and promotes intense coke formation reduces the selectivity of the process, and impact to the quality produced products. Moreover, catalysts based on iron oxides do not aggregate with metal compounds in heavy oils. Therefore, cheap catalysts are of great interest and practical application. To solve the problem in oil refining and to reach heavy oil the deepening processes will determine processing to 85% in 2020, including catalytic cracking. A radical formation additive reduces the rate of coke formation. DTBP influence to reaction direction and inhibit condensation reactions in cracking of bitumen.

Reactions that contribute to this process are the cracking of side chains from aromatic groups, dimerization reactions, dehydrogenation of naphthenes (to form aromatics) and ring closure reactions (to form larger ring groups). When aromatic components reach a critical concentration, phase separation occurs to give a denser and more aromatic liquid phase. Aromaticity is the dominant factor that controls this phase separation. This observation suggests that increasing the molar mass is a significant factor in the formation of coke from bitumen. Microscopic images showed that the asphaltenes has large monolithic switching, weakly focused on a major surface, provided with amorphous carbon and asphaltene particle size around 40–50 nm.

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