Structural Study and Upgrading of Kazakhstan Oil Sands

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Abstract

In the paper separation methods of organic part from oil sands were investigated at experimentally. For the determination of organic part (liquid fraction) of oil sands the extraction methods was used in Soxhlet apparatus by solvent. Thermal processing was carried out with a monotonic heating of oil sands from room temperature to 500 ºC. As showing results, organic part of Beke and Munayli-Mola oil sands studied by extraction method were 12.0 wt.% and 16 wt.%. Thermal processing results showed, that the organic part of Beke and Munayli-Mola oil sands were 9.6 wt.% and 13.5 wt.%. Physical and chemical characteristics of liquid fraction are established by standard methods.

1. Introduction

The terms "oil" and "petroleum" are sometimes used interchangeably. Technically, the term petroleum only refers to crude oil, but sometimes it is applied to describe any solid, liquid or gaseous hydrocarbons. Crude oil is a mixture of hydrocarbons that exists as a liquid in natural underground reservoirs and remains liquid when brought to the surface. Petroleum is the broad category that includes both crude oil and petroleum products. Petroleum products are any petroleum-based products that can be obtained by refining and comprise refinery gas, ethane, liquefied petroleum gas, distillate fuel oil, naphtha, gasoline, aviation fuel, lubricants, white oil, grease, wax, asphalt, as well as coke. A reserve of the total world conventional oil is 30% and most of the world's oils are unconventional as shown at Fig. 1 [1-4].

As time passes, reserves of fossilized carbon are being depleted for use as energy and more attention is being focused on alternate energy sources. One such energy source is oil sand. The largest deposits of the world oil sands are located in Canada and Venezuela. This valuable resource also can be found in several locations in the world such us USA, Russia, China, Cuba, Indonesia, Brazil, Trinidad, Tobago, Jordan, Madagascar, Colombia, Albania, Romania, Spain, Portugal, Nigeria and Argentina. Over 50 fields of oil sands have been discovered in Kazakhstan [5, 6].

Oil sands have different terms in the world, for example: oil-bituminous sands, tar sands, extra heavy oil, oil-bituminous mineral (rock). These oil sand resources are called unconventional oil to distinguish them from oil, which can be extracted using traditional oil well methods. Because compared to conventional crude oil, heavier crude oils from oil sands have too much carbon and not enough hydrogen, these processes generally involve removing carbon from or adding hydrogen to the molecules, and using catalytic cracking to convert more complex molecules in the oil to the shorter, simpler ones in the fuels [7-11].

Well known extraction methods of oil from oil sands are hot water extraction, solvent extraction and retorting. Main industrial technologies of the extraction of oil from oil sand use a hydrodynamic, thermal and chemical influence. With the goal of processing heavy oil, bitumen, and residue to obtain gasoline and other liquid fuels, an in-depth knowledge of the constituents of these heavy feedstocks is an essential first step for any technological advancement. Compared to conventional oil (obtained from traditional, easily accessible sources), however, synthetic crude from bitumen is expensive and complicated to produce [9, 12-14].

The surface mining extraction method is sim-

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ilar to many coal mining operations. Traditional extraction methods are not suitable for bitumen recovery so, when the Canadians started to extract oil sands from their deposits, they had to remove the layer of ground that is over the wanted ore. However, more modern extraction methods have been developed to overcome this problem such as "in situ" extraction methods that are more environmentally friendly and avoid the need to remove the upper layer of the ground. Steam Assisted Gravity Drainage (SAGD) and Cyclic Steam Stimulation are the two major methods used nowadays as in situ extraction methods [15, 16].

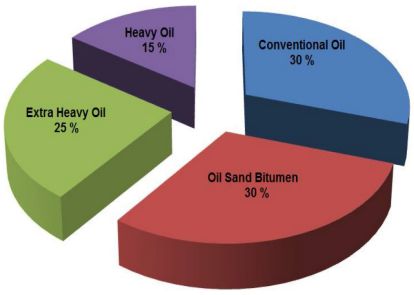

Fig. 1. Total world oil reserves.

Kazakhstan's oil producing sector is quickly developing. Crude oil production grew from 40 in 2001 to 80 million tons in 2014 i.e. for two times. Oil production growth and large oil-fields development of Caspian Sea offshore demand appropriate infrastructure [17]. Figure 2 shows the oil production amount in near 20 years of Country.

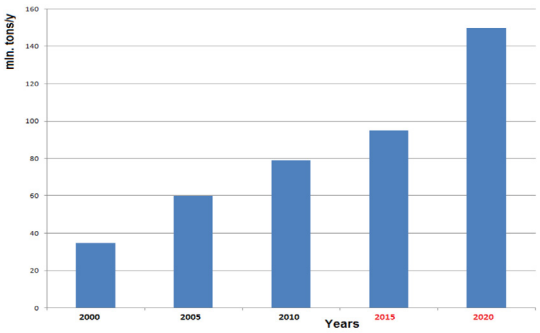

Fig. 2. Oil productions in Kazakhstan.

As it was written before, in Kazakhstan discovered huge amount of oil sands, its reserve more than conventional oil of Republic. They are accumulated in three region of Kazakhstan (Western part). Namely, Aqtobe, Atyrau and Mangistau regions (Fig. 3). According published dates that the in West Kazakhstan at depths up to 120 m occurs more than 1 billion tons of natural bitumen and over 15-20 billion tons of oil sands. Pioneer of complex study on processing oil sands was in 80-90s of last century. The problem of development of Kazakhstan oil sand in 1980-1985 was conducted in four main areas: investigation of geology and geochemistry of mineral and organic components of the oil sand deposits; development of technologies of oil sand and tools for use in road construction; study of organic mineral constituents of the oil sand as an additional source of energy and chemical resources [8].

Fig. 3. Oil sands located area in Kazakhstan.

Compared to Canadian oil sands, the Kazakhstan oil sand deposits are situated far from water source. Therefore, the traditional extraction methods are not suitable for processing this "black gold". So, it is actually problem that the study oil extracting methods and producing fuel and other petrochemical products from oil sands.

2. Materials and Methods

2.1. Oil sand samples

The objects of research were oil sands from two deposits. One of the samples is oil sand of deposits Munayli-Mola, which located in Atyrau region. LLP "Dortechnika" supported us Munayli-Mola oil sands for experiment. Second sample is oil sand of deposits Beke. Beke oil sands located Mangistau region. It was supported to research by LLP "Altyn KDT".

2.2. Description of the laboratory setup for processing of oil sands

Separation of organic substances from oil sand's mineral part provided by two methods in this paper. First one is solvent extraction. Extraction was carried out in Soxhlet apparatus till termination of solvent coloring. The hexane, toluene, ethanol and

benzene mixture (the ratio of ethanol: benzene was equal to 1:4) was used as a solvent.

Thermal method was used for separating organic part from oil sands, also. Thermal processing (Fig. 4) was carried out with a monotonic heating of oil sands from room temperature to 500 ºC. Feedstock heating rate was varied from 6 to 16.7 ºC per minute. The average duration of processes was 45 min.

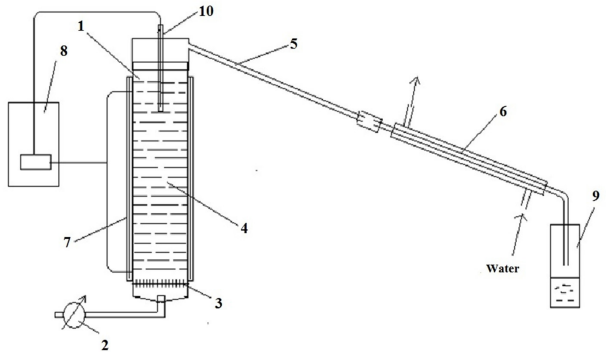

Fig. 4. Scheme of apparatus for the thermal processing of oil sands: 1 – cylindrical reactor, 2 – tube, 3 – Perforated diaphragm, 4 – raw material, 5 – connecting pipe for output gas and products, 6 – refrigerator, 7 – electric furnace, 8 – thermoregulator, 9 – receptacle.

The thermal apparatus consists of a cylindrical reactor (1) with a length of 20 cm and an inner diameter of 8 cm. At the bottom of the reactor has a tube for supplying bubbling gas (2). Gas from the air reservoir fed to the reactor through a perforated diaphragm (3) upwards by the raw material (4). Then gases and vapors enter through tube (5) in the refrigerator (6) being cooled with water. The reactor is heated by an electric furnace (7). The process temperature was controlled by thermoregulator (heat controller) (8). The condensed liquid products flow from the refrigerator to the receptacle (9).

3. Results and Discussion

3.1. Microscopic study of oil sand structure

Most deposits of oil sands contain mixtures of bitumen (organic part), coarse sand, water, fine solids, small amounts of heavy metals and other contaminants. Oil sands solids or mineral parts are mostly silica but include smaller amounts of kaolinite, illite, chlorite and smectite (montmorillonite) [7-9, 14]. Surface structure of oil sand was studied at modern microscopic techniques. Figure 5 shows the comparing of oil sand with after solvent extracted sand grain surface appearance and morphology.

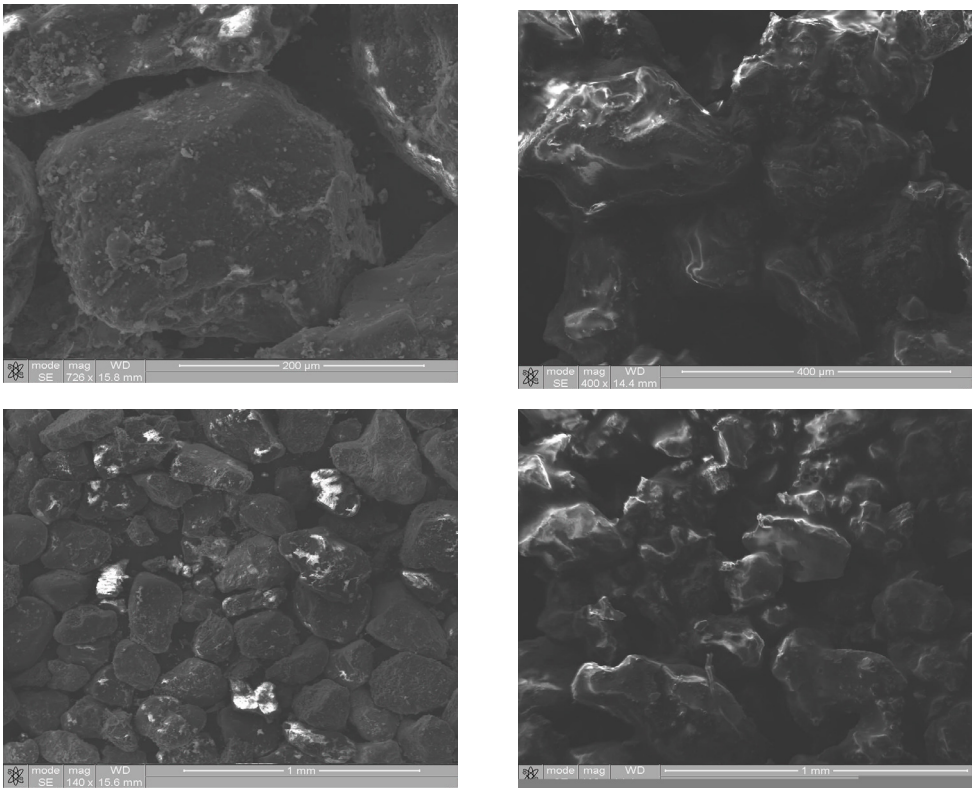

Fig. 5. SEM image of oil sand and after thermal extracted sand.

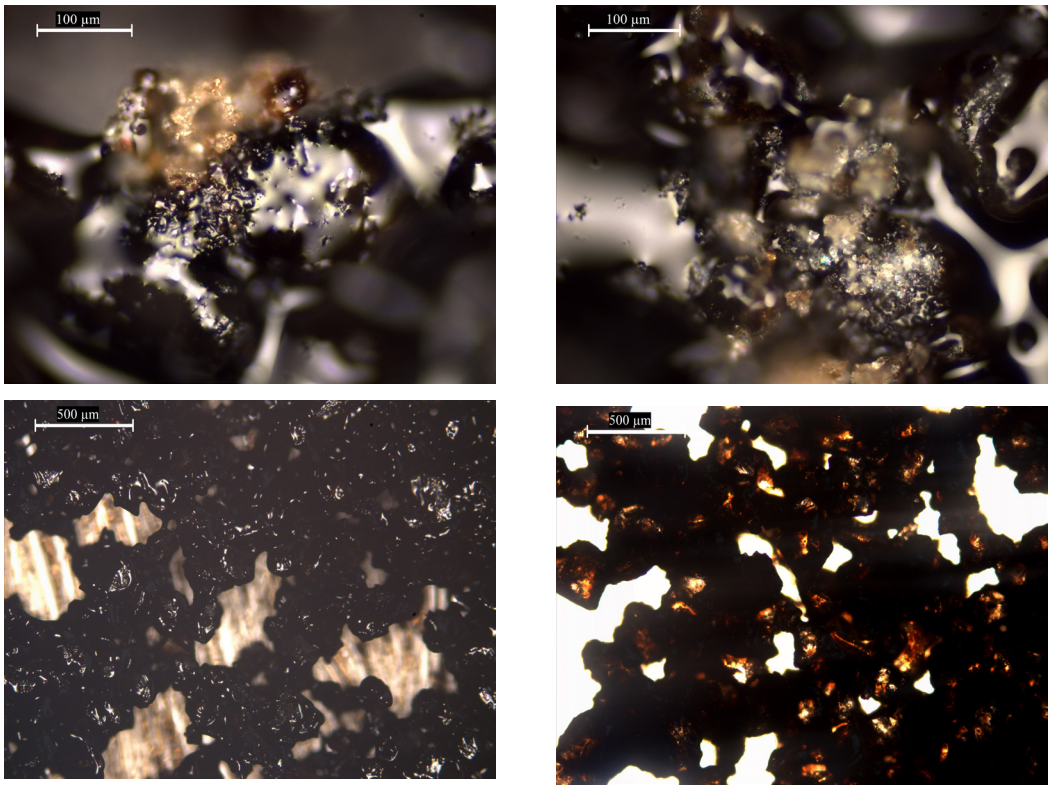

Fig. 6. Optical microscopic images of Beke oil sands.

As present Fig. 5, sand grains of oil sand surrounded by natural bitumen and wetted water. There are Fig. 6 a and c sand particles of oil sand, which organic part extracted by solvents. Whereas Fig. 6 b and d are original oil sand's surface images. It was published that the thin layer of water between the quartz and bitumen is around 10 nm across [18]. This layer makes the oil sands water-wet, which shows figure 6 a and b. It should be noted, there are air avoid between sand particles without bitumen covered (Fig. 6 c and d).

Study of linkage between natural bitumen and sand grains in oil sand is important. This phenomenon is more useful at processing and developing of oil sand. Thus, structure of oil sands can be concluded as Fig. 7.

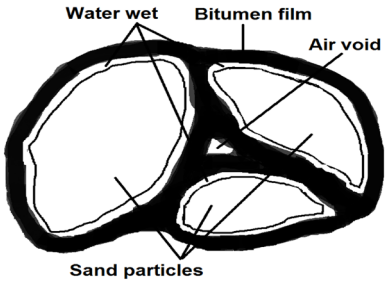

Fig. 7. Composition and structure of oil sands.

3.2. Characteristics of oil sand's natural bitumen

Separation of organic part from oil sand was carried out by extraction method at apparatus Soxhlet. To verify the accuracy of the results the variety of organic solvents are used. Table 1is presenting the content of oil sand (OS).

Table 1
Organic content of oil sands extracted by variety of solvents

Samples	Extracted by hexane, wt. %	Extracted by toluene, wt. %	Extracted by ethanol and benzene mixture, wt. %	Medium organic content of OS, wt. %
Munayli-Mola oil sand	15.5	16.5	15.9	16
Beke oil sand	10.6	11.3	11.2	11

Including three kinds of samples, organic substances extracted by toluene has higher content. However, due to the toluene have higher boiling point, after process the remove solvent from oil was more difficult. In this case, on solvent extraction using hexane was more suitable. The medium content of organic part in oil sands of Munayli-Mola depos-

its are 16 wt.%. Whereas, it is determined that the Beke oil sand has 11 wt.%. of organic substances. Other parts (without organic part) of oil sands are consists solid and sand mixture.

Depending on the concentration of bitumen, the oil sands are usually divided into three main classes [18], as follows:

• Low-grade oil sands – bitumen content 6-8 wt%

• Medium-grade oil sands – bitumen content 8-10 wt%

• Rich oil sands – bitumen content >10 wt%.

As experimental results, Munayli-Mola and Beke oil sands consists more than 10 wt% of bitumen content. It allows conclude that the both oil feedstock are rich oil sand. It was reported that the percentage of bitumen in oil sand can range until 30%. It is depended deep level of feedstock.

Organic part of oil sand is black with glitter, characteristic viscous oil road bitumen. And it is natural raw material. Therefore it called "natural bitumen" (NB), also called as "bitumen". Some characteristics of NB are presenting in the Table 2.

Table 2
Physical and chemical properties of natural bitumen of oil sands

Oil sand samples	Characteristics	NB extracted by hexane	NB extracted by toluene	NB extracted by the ethanol and benzene mixture
Munayli-Mola OS	Density, g/cm^3	0.997	1.090	0.987
	Heating value, j/g	43006	42464	41857
Beke OS	Density, g/cm^3	0.917	0.925	1.002
	Heating value, j/g	42728	43264	42536

As tabulated dates, the results of density presented the object of research is heavy oil. Because of density of heavy oil produced from Munayli-Mola oil sand was 0.997 g/cm^3 and produced from Beke oil sand was 0.987 g/cm^3.

Medium heating value of natural bitumen produced from Munayli-Mola oil sand was 42442 j/g and produced from Beke oil sand was 42842 j/g. The heating value or calorific value of hydrocarbons is the amount of heat released during the complete combustion of a specified amount of them. Usually, the heat value of crude oil expected around 42-44 Mj/kg. Physical and mechanical characteristics of natural bitumen were determined as bitumen according to international standard 22245-90. They are presenting in Table 3.

Table 3
Physical and mechanical characteristics of Munayli-Mola natural bitumen

Characteristics	Results	Units
Penetration, at 0 ºC	20	0.1 mm
Softening point	28	ºC
Ductility, at 0 ºC	100	cm

As showing in Table 3, depth of needle penetration of natural bitumen at 0 ºC was 20·0.1 mm and softening point is 28 ºC. Ductility of NB at 0 ºC was 100 cm. At room temperature the bitumen characteristics could not determinate, because of more sticky. On physical and mechanical characteristics, the natural bitumen are not satisfaction to requirement of any mark of paving bitumen. However, the natural bitumen is high viscously hydrocarbons.

3.3. Producing synthetic oil from oil sands

Thermal processing of oil sand was conducted in the installation at temperature 450-500 ºC. The reactor is a cylindrical basin with a length of 20 cm and an inner diameter of 8 cm. The individual product yield and physical and chemical characteristics of the liquid distillate obtained from oil sand was defined (Table 4).

Table 4
Physical and chemical properties of thermal processing products of oil sands

Parameters	Munayli-Mola oil sands	Beke oil sands
Yield of products, wt. %		
Gaseous	25	2.4
Liquid	13.5	9.6
Solid residue	84	88.0
Fractional composition, wt. %:		
Boiling point – 180 ºC	9.3	19.6
180-250 ºC	15.1	24.0
250-350 ºC	46.8	33.0
350- end of boiling	28.8	23.4

As seen from Table 4, the derived liquid part of Beke oil sand is 9.6 % by weight of oil sand and around 2.4 wt.% of gas products were separated out. Munayli-Mola oil sand has 13.5 wt.% of liquid hydrocarbon and 1.5 wt.% of gas. Due to the high temperature achieved inside the reactor, all the organic fractions of the bitumen boiled and just the inorganic sands will remain in the basin. The exhaust tube

of the reactor leads to a heat exchanger where the vapors are condensed and poured into an Erlenmeyer flask.

A liquid product of the processing seems synthetic oil, which has 0.862 g/cm^3 of density. It is less than density of solvent extracted NB (0.997 g/cm^3). As well as boiling end fraction after 350 ºC were 23.4 and 28.8 mass %. From the qualitative characteristics of wide fraction of products thermodestructive processing oil sand can be seen that it is in many physicochemical characteristics similar to petroleum fractions.

As indicators of Table 4, the values of fractional composition of the products, obtained by thermal method, allow to carry out further studies on the effect of heating rate factor of raw materials on the yield of light fractions. It must be note, in a little extent, the thermal method is also catalytic, the clay and the heavy metals present in the mineral phase of the oil sands act as catalyst so that heavy fractions of the bitumen react to form lighter parts.

Determining the detonation characteristics of fraction obtained from synthetic oil of Beke oil sands through thermal method at a semi-industrial apparatus were conducted. Characteristics of obtained products showed that their suitability as a motor fuel. The data are given in Table 5.

Table 5
Characteristics of synthetic oil produced from Beke bitumen

Parameters	The initial sample	Gasoline fraction 80-180 ºC	Diesel fraction 180-250 ºC	Gasoil fraction 250-320 ºC
Octane number	-	80	not defined	not defined
Cetane number	-	-	above 45	not defined
Flash, ºC	-	-	35-40	-
Density at 20 ºC, kg/m^3	0.870	0.754	0.817	0.864
Pour point, ºC	-40	not defined	-50-55	-45
Filterability temperature limit, ºC	above -35-40	not defined	above -40	above -25

Table 5 shows that the gasoline fraction correspond gasoline AI-80 and diesel fraction has a low melting point and a good indicator on the limiting filterability temperature, which is favorable for diesel in the winter time. Gasoil fraction can be used as furnace fuel. It follows from this that the synthetic oil was produced from Beke oil sand, it is also of interest for further investigations in this direction. Thus, experiment results showed that the thermal process is one way for producing synthetic oil from oil sands.

4. Conclusion

For the separation of organic part from oil sands the extraction method and thermal processing were used. It was determained that the organic part of oil sands produced by extraction more than thermal processing products. Also, Munaily-Mola oil sands have a higher amount of bitumen inside them than the Beke ones. Comparative fractional analysis of the organic part with thermal processing method increases the amount of low-boiling fractions and less heavy oil residue. The products of thermal processing have better properties as synthetic oil. Its density was 0.850 g/cm^3. The extracted products with solvents were highly viscous black substances as heavy oil residue. Its density was 1.012 g/cm^3 and ash content was 0.38%.

As it was shown in this study, oil sands are mainly formed by a mineral part, the most abundant one and, in a lesser extent an organic part. The organic part is the one that is actually valuable and the challenge is to extract it with the cheapest and most environmentally friendly way. While the extraction with solvents can give very high yields of extracted bitumen, the thermal method is faster and does not have the problem of using a dangerous and contaminant solvent. Besides, the thermo-contact method gives a lighter product more easily to refine and to transport via pipes.

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