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Supercritical Solvent Extraction of Oil Sand Bitumen

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Abstract. The supercritical solvent extraction of bitumen from oil sand studied with organic solvents. The experiments were performed in autoclave reactor at temperature above 255 °C and pressure 29 atm with stirring for 6 h. The reaction resulted in the formation of coke products with mineral part of oil sands. The remaining products separated into SARA fractions. The properties of the obtained products were studied. The supercritical solvent extraction significantly upgraded extracted natural bitumen.

INTRODUCTION

Currently, among the problems facing the science are the most pressing environmental and energy that are directly related to the chemistry and unconventional sources of hydrocarbons processing technology. Nowadays coal, oil shale, natural bitumen, heavy oil, and their residues are used for energy with a small extent and mainly low efficiency and high environmental risks. Therefore in the near future, the need arises for a widely and rational using these raw materials not only for energy purposes, also as source of valuable chemical products.

Tendency to reduce stocks and prices of light oil, which focused on many processing refineries (refinery) with increasing in the share of hydrocarbon production related to heavy and extra heavy oil. Feature of heavy oil as natural bitumen, oil residues and other heavy hydrocarbon feed is the high content of high molecular components (resins, asphaltenes), which makes them difficult to processing by traditional method in petroleum refineries [1-3].

Deep processing and efficient use of heavy oil must be solved by develop of new methods of complex processing of petroleum residues and heavy oil feedstock. Currently, in the western countries are worked and proposed about processes for the processing of natural bitumen obtained from oil sands and oil shales. Proposed methods were used thermal methods with inject variety of "cracking additives" to raw material, but their implementation technologies has need to be further improved, because has not sufficient information about the composition of the heavy oil feedstock components and reactions characteristics under different temperature conditions [1-4].

Prospects for development of complex processing new methods of heavy hydrocarbon raw materials (bitumen, heavy oil, heavy oil residues) is associated with the use of supercritical fluid (SCF) extraction or formation supercritical fluids in oil processing [5]. One of the most perspective and environmentally safety ways of recycling of solid or viscous fossil fuels is the thermal decomposition using supercritical fluid. Based on the properties of SCF being developed new technologies including the production of motor fuels [6].

Using SCF for extraction of natural bitumen from oil sands (OS) has a number of advantages. First the combination of high density and low viscosity characteristic of the supercritical fluids makes it possible to easily separate the fine particles from organic substance. Second, higher solubility of hydrocarbons in SCF comparing with

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conventional solvents could increase liquid and gaseous products conversion of raw materials. Thus, in reaction systems supercritical conditions change thermodynamic and transport properties, which leads to qualitative and quantitative nature changes and mechanism of organic matter destruction process flow. Furthermore, using of supercritical fluid as solvent provides additional opportunities to extract natural bitumen from oil sands, supercritical solvents at varying time and pressures to allow changing the reaction rate.

Beke field located 53 km north-west from the Zhanaozen town and 40 km from the Zhetybai village (Figure 1). In tectonically oil sand field is confined to the most elevated areas Bekebaskuduksk vault, which is usually referred to Karasyaz-Taspas anticline [7].

FIGURE 1. Geological description of oil sand from Beke field

Associated industrial productive stratum deposits of natural bitumen in the Beke area presented sands, sandstones and clays. Morphologically described deposit tabular shape is elongated from north-west to south-east, it traced length 1300 meters and width from 50 to 840 m. Reservoir capacity area irregularly varies from 2.5 to 20.5 m^2. The amount of bitumen in the oil sands on various samples varies from 7.2 to 20.6 wt. %. Physical-chemical studies of these bitumens has shown that their composition in the intermediate position between liquid and viscous bitumen, only at surface portion zone of bitumen modified to asphalt and occasionally to asphaltite.

MATERIAL AND METHODS

Materials

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. 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. The oil sand composition was found to be 11.7 ± 0.5 wt. % bitumen, 88.3 ± 0.5 wt. % solids, and 0.4 wt. % water. The asphaltenes content of the bitumen was found to be 5.9 ± 1.5 wt. %. Oil sand composition and asphaltenes content analyses were based on three replicates each.

SCE Unit

Supercritical solvent extraction of natural bitumen from oil sand was carried out by supercritical hexane and isopropanol. These solvents transition to critical condition parameters are shown in Table 1. Extraction process conditions by supercritical solvents are shown in Table 2.

TABLE 1. Critical condition parameters [6]

Solvent	Temperature, °C	Pressure, atm	Critical density, g/cm^3
Isopropanol	235	47	0.274
Hexane	234	29	0.234

Installation for SCF extraction (Figure 2) provides modes under the following conditions: the maximum pressure is 100 atm and an operating temperatures range of the reactor to 600 °C. This process temperature is automatically maintained, the raw materials given supply speed to the reactor, the possibility of sampling of gaseous and liquid products after process.

TABLE 2. SCF extraction process conditions

Parameters	Solvent	
	Isopropanol	Hexane
Temperature, °C	297.0	255.0
Pressure, atm	54.8	29.6
Time, hour	6.0	6.0
Solvent flow rate, ml/min	1.0	1.0
Volume of solvent, ml	320.0	320.0

As seen from Tables 1 and 2, the comparison process conditions SCF extraction with critical parameters of solvents shows that the critical conditions are reached in the case of both solvents.

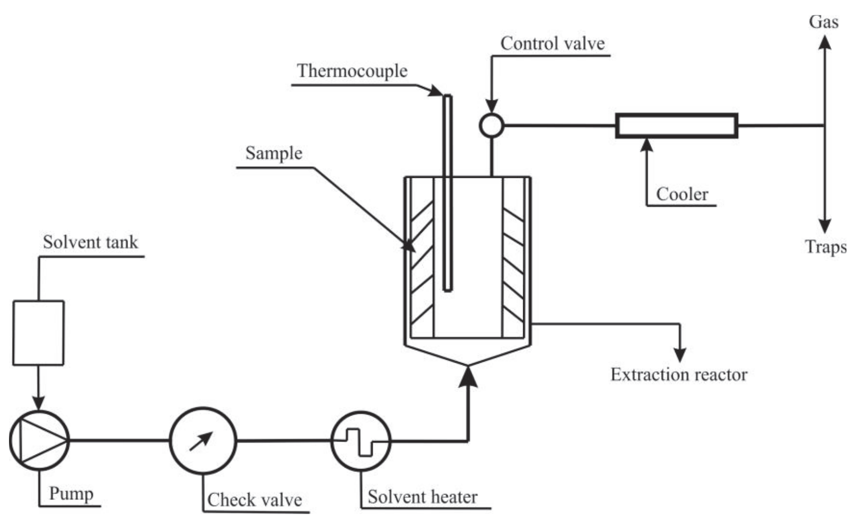


FIGURE 2. Setup for SCF extraction of natural bitumen

Autoclave Engineers in Novosibirsk (Russia) built the SCF extraction system. A schematic of the SCF extraction system is presented in Figure 2. The system consisted of four major subsystems: the supercritical fluid supply system, the extractor, the separator assembly and the data acquisition system. The fluid supply system consisted of a liquid cylinder (solvent tank). The separator assembly consisted of a separator vessel, a backpressure control valve, a flow meter. In each experiment, a known quantity of bitumen was charged to the extractor and a measured quantity of the heated solvent was transferred into the extractor using the positive displacement pump. Temperature and pressure control of the system achieved using the controllers provided with the system. After the initial solvent charge, the positive displacement pump used to supply replacement solvent during the continuous extraction experiments. The extract phase from the extractor flowed to the separator through the backpressure control valve and the cooler. The major pressure reduction occurred at the backpressure value before the extract phase flashed in the separator, which operated at the ambient pressure. Liquid samples collected from the separator for every 1 hour of solvent vented through the system. Six samples have been collected during the course of each experiment. The residual fraction in the extractor collected at the end of the experiment.

Fractional Analyses of Extraction Products

Fractional composition of obtained hydrocarbons were performed by using the ARN-LAB-03 (Russia), that gradually heating and condensed vapors in receiving special containers at atmospheric pressure. At temperatures up to 350 °C, the error of the method for such objects is not more than 1.0 %.

Bulk Composition of SCF Extraction Products

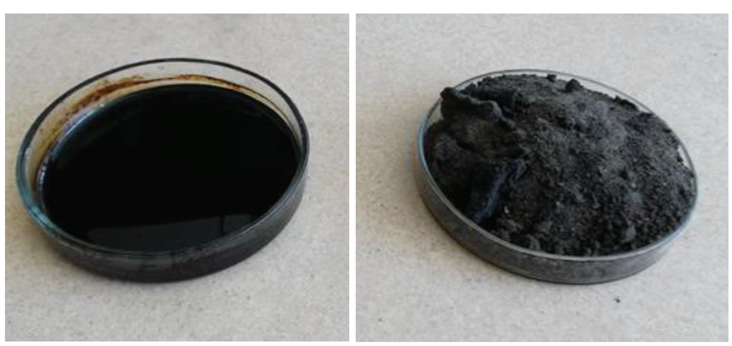
The group composition of the initial bitumen and the liquid products of SCF extraction have been determined in accordance with a traditional procedure: first, the asphaltene content of the sample was separated by the cold Holde method. The concentration of tars in the resulting oils was determined by an adsorption method: the analyzed product was applied to activated ASK silica gel; the mixture was placed in a Soxhlet extractor, and the hydrocarbon components (oil) and tars were sequentially extracted with *n*-hexane and an ethanol-benzene mixture in a ratio of 1:1, respectively (STP SZhShI 1217-2005 procedure, Institute of Petroleum Chemistry).

RESULTS AND DISCUSSION

SCF Extraction Results

Solvent extraction of natural bitumen from oil sands of Beke field was extracted by trichlorormethane as solvent. The content of natural bitumen in the oil sand is varies from 10 to 13 wt. %, and it is characterized by the following indicators: density – 0.958 g/cm^3; softening temperature – 20 °C; coking content – 30 wt. %; ash content – 0.05 wt. %. After SCF extraction process an organic part of oil sands, organic part represents a black color resinous, viscous mass. The yield of natural bitumen after extracted by SC isopropanol was 7.63 wt. %, and by hexane – 7.32 wt. %. A cold extraction organic part from oil sand by chloroform was 11.0 wt. %, hence the degree of extraction of organic part by SCF solvent extraction is 65-70 %.

Supercritical isopropanol unique properties show ability to hydrogenate double bonds of organic compounds in the natural bitumen and conduct hydrogenolysis by single bonds, such as C-N, C-O, C-P, C-S. It has been found that the SCF alcohols differ greatly in reactivity with respect to the same substrate, for example, in the hydrogenation order are arranged in the following line: $(CH_3)_2CHOH > C_2H_5OH > CH_3OH$ [8]. At the end of the extraction process, the remaining amount of mineral part was disassembled and unloaded. Solvents from the organic part were distilled off. Photos of obtained products after extraction are shown in Figure 3 and Figure 4.



a b

FIGURE 3. SC-isopropanol extraction products:

a – the organic part of oil sand, b – the mineral part of oil sand

The viscosity of the bitumen recovered by different solvents are different, in particular, the bitumen extracted by hexane has a low viscosity compared to the bitumen extracted by isopropanol. Perhaps during the process the organic part of oil sand undergoes a small destruction. Usually, isopropanol is taken as a donor. Isopropanol decrease the viscosity by giving off the hydrogen.

a b

FIGURE 4. SC-hexane extraction products:

a – the organic part of oil sand, b – the mineral part of oil sand

Fractional Analysis of Products

Fractional composition of obtained hydrocarbons was performed using the special apparatus. The mass loss of natural bitumen from the effect of temperature (Figure 5) and its fractional composition (Table 3) were determined. The obtained data were compared with natural bitumen extracted by the conventional extraction method.

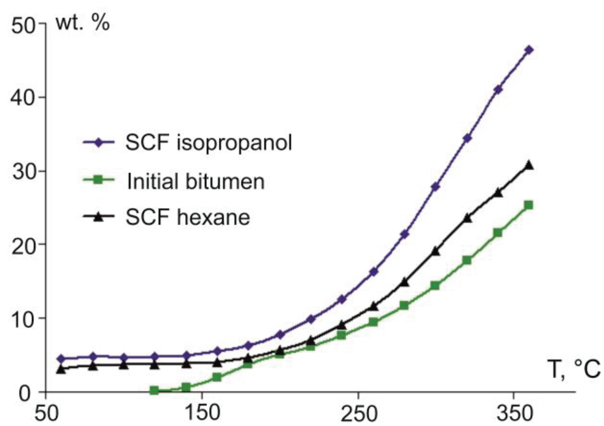


FIGURE 5. Fractional composition of bitumen extracted by different SC solvents

Bitumen samples obtained in different extraction has different fractional composition. In the samples obtained by SC isopropanol and hexane extraction increases the content of distillate fractions by 21.1 and 5.6 wt. %, respectively. The yield increasing of fractions is due to diesel distillates (200-360 °C) by isopropanol total content is 38.7 wt. %, and by hexane is 25.2 wt. %. As can be seen from Table 4, the boiling point of the bitumen extracted by SCF extraction is significantly lower than the bitumen extracted by conventional extraction. This is explained by the process of destruction of high-molecular structures (resins, asphaltenes) during SCF extraction. More complete conclusions can be drawn after determining the bulk composition of the extracted bitumens.

Thus, research studies have been shown that the extraction of natural bitumen from oil sand can be achieved by the SCF extraction method, but it can also impact the properties of the obtained products. The bitumen properties can vary depending on the SCF extraction solvent, because bitumen components in thermal processes undergo changes. An increasing the yield of distillate fractions can be explained by the destruction of high molecular weight components and reactions with the extraction solvent.

The natural bitumen extracted from oil sand is characterized a higher yield of light fractions than the bitumen which extracted by conventional extraction. This makes it possible to use these products as a raw material for obtaining for oil products, binding for road building materials and other types of productions.

TABLE 3. Fractional and bulk composition of bitumen extracted by different SCF solvents

Fractional composition, wt. %	**Sample of bitumen**		
	Conventional extraction	**SCF extraction by isopropanol**	**SCF extraction by hexane**
Boiling point, °C	116.8	80.2	77.1
B.p. – 200 °C	5.11	2.93	1.80
200 – 360 °C	20.18	38.71	25.24
> 360 °C	74.71	58.36	72.96
Bulk composition, wt. %			
Asphaltenes	5.94	11.32	4.49
Resin	44.89	27.14	45.11
Oil (hydrocarbons)	49.17	61.54	50.40

The hydrocarbon oil contents of the residual fractions were significantly higher than the oil contents predicted on a prorated basis for initial bitumen. This trend was due to the extraction of solubilizing components that kept the resin compounds in suspension in the bitumen. It concluded that solute polarity played a significant role in the extraction yields of the bitumen. The experimental data show that the SC isopropanol positively affected to bitumen with formation lower total content of resin-asphaltene compounds (38.46 wt. %). Hexane is not explosed to destruction under supercritical condition, this is presented from the bulk composition of bitumen, therefore is closer to the initial composition of bitumen.

CONCLUSION

The SCF extracted natural bitumen has a higher yield of light fractions than the bitumen extracted by conventional extraction. This confirms that degradation process of natural bitumen, which leads decomposition of high molecular components (resins, asphaltenes) in bitumen. The few of asphaltene content covered mineral part during the extraction process, therefore makes it difficult to extract bitumen. A reasonable match between predicted and experimental values obtained.

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