

Catalytic Hydrogenation of Oil Sand's Natural Bitumen

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Abstract. In the paper catalytic hydrogenation of natural bitumen (NB) of Kazakhstan oil sands were investigated. The process provided under 350 bar of H₂ pressure and a temperature of 430 °C. At the experiment activated carbon supported catalyst was used. It has 699.807 m²/g of surface area and 0.0635 nm of medium pore size. In the processes the yield of hydrogenated natural bitumen was 91%, including 1st fraction is 13.12 wt.%; yield of 2nd fraction increased, that the temperature range from 216 to 316 °C formed in amount of 45.68 wt.%; vacuum residue of the distillation takes the 41.20 wt.% in natural bitumen.

1 Introduction

Well known the oil sands contain mixtures of bitumen, sand, water, small amounts of metals and other contaminants. Compared to conventional crude oil, natural bitumen of oil sand contains more carbon, too little hydrogen and denser with higher viscosity. For obtaining light petroleum fractions is necessary to process the hydrogenation of natural bitumen, which allows improved characteristics and simplify of the obtained product. The processing of heavy crude in the presence of hydrogen is a major step in the upgrading of heavy oil or bitumen. Because bitumen is highly deficient in hydrogen and contains high concentrations of heteroatoms and metals, it is imperative to improve the quality of the upgraded product by removing the impurities; this is done by means of adding hydrogen [1-4].

As it was written before [1, 4], 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.

Hydrogenation is a chemical reaction of great importance to the petrochemical and fine chemical industries. Usually hydrogenation refers to the addition reaction of molecular hydrogen with an unsaturated carbon-carbon double bond. There are first compound - alkene converted into the corresponding alkane [3, 5]. It illustrate as following:

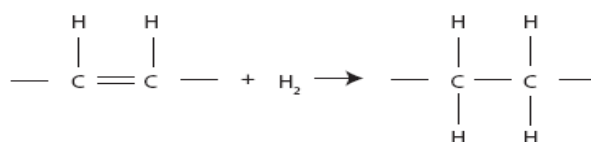


Figure 1. Typical hydrogen reaction [5]

All hydrogenation reactions are highly exothermic. The heat released hydrogen consumed about 65 ± 5 kJ/mol. Well known the importance of catalyst on the hydrocarbon processing. A number of metal catalysts are available for hydrogenation reactions, such as nickel, chromium, tungsten, molybdenum, palladium, cobalt, iron, and copper. The catalysts get poisoned easily in the presence of sulfur and nitrogen [6, 7].

Therefore, the catalytic hydrogenation was tested to natural bitumen recovered by extraction with hexane. Hydrogenation process was carried out to natural bitumen of oil sands on the apparatus "Autoclave" with molybdenum based catalyst.

2 Materials and methods

The object of research was oil sand of deposits Beke, which located Mangistau region (Western part of Kazakhstan). Natural bitumen of oil sand was separated by extraction methods in apparatus Soxhlet with organic solvents.

The hydrogenation experiments of natural bitumen extracted from oil sands were carried out in a "Autoclave". Around 200-300 g of NB was charged into the reactor together with active coal supported catalyst. The process provided under 350 mbar of H_2 pressure and a temperature of $430^\circ C$. After loading the sample, the reactor was sealed and flushed 3 times with hydrogen followed by tuning the system to the desired initial pressure of H_2 . The reactor agitated at 120 rpm, which had been heated to the desired temperature and maintained for 40 min. After the processes the hydrogenated products in the reactor were removed out.

For the purpose of adding to hydrogenation process, the active coal supported catalysts were prepared. At first, 10 ml of distilled water added in flask and 3 g of molybdenum oxide (MoO_3) added to water and stirred them for 2-3 minutes by magnetic mixer. Then 25% of ammonia solution added slowly (drop by drop) till all catalyst solved. At last, 10 g of active coal were added to mixture and heated until water evaporation. Finally, prepared catalyst dried in oven under vacuum.

Fractional compositions of hydrocarbons were performed using the ARN-LAB-03 by gradually heating and condensed vapors in receiving special containers at atmospheric pressure. Density is important properties of petroleum and petroleum products. At experiment pycnometer was used for the determination of density of oil samples. Ash content of oil samples tested in the muffle furnace "Nabertherm". It installed maximal temperature at $815^\circ C$.

Brunauer-Emmett-Teller (BET) surface area of catalyst was determined by nitrogen adsorption at $-196^\circ C$ using a sorbtometer-M adsorption analyzer. Total pore volume was calculated from the amount of nitrogen adsorbed at a relative N_2 pressure (P/P_0) of 0.99. The average pore size was assumed to be $4V/BET$. All the samples were degassed at $150^\circ C$ for 12 h before the measurement. The microstructures and microanalysis of catalyst were investigated with an scanning electron microscopy (Quanta 3D 200i) at an accelerated voltage of 20 kV and a pressure of 0.003 Pa.

3 Results and discussion

At the experiment 1.5 g of activated carbon supported catalyst - molybdenum oxide (MoO_3) was used. It has $699.807\text{ m}^2/\text{g}$ of surface area and 0.0635 nm of medium pore size. Microscopic structure of catalyst is presenting at figure 2. Scanning electron microscopy (SEM) images of catalyst showed that the catalyst consisting different sizes agglomeration of plate-like structure.

The H_2 pressure provided under 350 bar and yield of hydrogenated natural bitumen was 91%. Figure 3 is presenting the profiles of temperature and pressure over time the hydrogenation process of natural bitumen.

The figure 3 shows the temperature of reactor was raised gradually to $430^\circ C$ (red line), and then stabilized at this temperature. The hydrogen pressure in the reactor (blue line) increases until the end of the process, and reaches 350 bar. As seen this picture, the hydrogen pressure didn't decrease. It means in the process don't more consumption hydrogen for saturating of hydrocarbons. In this reason, process time prolonged only 40 minutes.

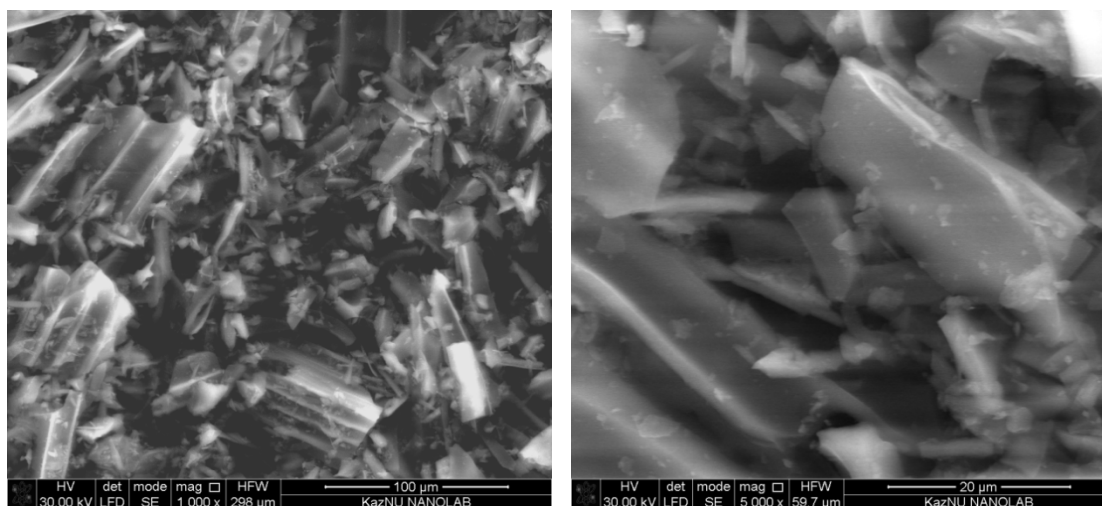


Figure 2. SEM image of active carbon supported catalyst

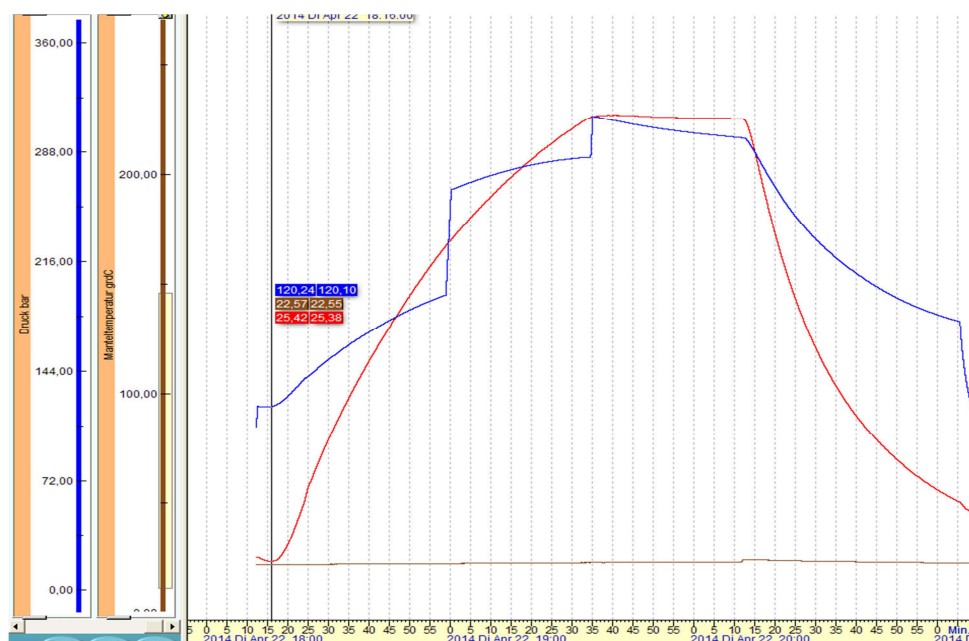


Figure 3. Profiles of temperature and pressure over time hydrogenation process of Beke natural bitumen

Due to separate out synthetic oil from heavy residue and catalyst, the products of hydrogenation provided vacuum distillation. Results of fractional composition of hydrogenated natural bitumen (hydrogenated oil), while vacuum distillation are presenting in table 1.

Table 1. Fractional composition of hydrogenated oil from Beke, while vacuum distillation

	1st fraction	2nd fraction	Vacuum residue
Temperature, °C	I.B. – 215 °C	216 – 316 °C	316 °C – E.B.
Pressure, mbar	808	805 - 60	60
Mass of fraction, g	24.64	85.78	77.37
Yield of fraction, %	13.12	45.68	41.20

As shown table 1, the yield fraction of hydrogenated products of Beke bitumen, which first fraction is 13.12 wt. %. Yield of second fraction increased, that the temperature range from 216 to 316 °C formed in amount of 45.68 wt. %. Third fraction, which vacuum residue of the distillation takes the 41.20 % in natural bitumen. The divided vacuum distillation products of hydrogenated oil are showing at figure 4.



Figure 4. Fraction of hydrogenated natural bitumen

The 1st and 2nd fractions are extremely light hydrocarbons, their mix called hydrogenated oil and 3rd fraction estimated as vacuum residue (after 320 °C under vacuum). Table 2 shows the comparative characteristics of natural bitumen extracted from oil sand before and after the hydrogenation process.

Table 2. Comparative characteristics of natural bitumen extracted from oil sand before and after the hydrogenation process

Characteristics	Natural bitumen	Hydrogenated NB
Density, g/cm ³	0.948	0.887
Ash content, wt. %	1.09	0.2
Yield of fraction, %		
I.B. – 180 °C	8.9	47.4
180 – 240 °C	10.7	20.1
240 – 300 °C	26.9	13.3
300 °C – E.B.	53.5	19.2

As seen from the tabulated data, after hydrogenation process decreases the density and ash content of natural bitumen, which also confirms the change in the fractional composition of the bitumen. The yield of light fractions of hydrogenated natural bitumen significantly increased compared to the original natural bitumen. This shows the need to hydrogenation process for expanding the range of products derived oil sands. The only limiting factor may be the high cost of the process in connection with the use of hydrogen.

The fact thermal hydroprocessing of bitumen and heavy oils can be accomplished at a much lower temperature and a relatively high conversion indicates that the cleavage of C-C bonds is not a rate-determining step. The initiation step may involve cleavage of the C-S bond, or the breakage of the C-C bonds must be accomplished by a mechanism other than homolytic cleavage due to several reactions occurs simultaneously [3-6].

4 Conclusion

Experimental results showed that the light fractions of hydrogenated oil sand bitumen significantly increased compared to the original natural bitumen. SEM image of catalyst showed that the catalyst consisting different sizes agglomeration of plate-like structure. The only limiting factor may be the high cost of the process in connection with the use of hydrogen. Thus, results indicate the possibility of using oil sands not only as a raw material for road-construction materials (bitumen, asphalt mixture), but also for producing synthetic oil as light petroleum products.

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