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Hydrogenation of Kazakhstan's natural bitumen

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Қазақстанның табиғи битумдарының гидрогенизациясы

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Гидрогенизация природных битумов Казахстана

The results of hydrogenation of Western Kazakhstan Beke and Munaily Mola natural bitumens in the presence of MoO_3/C nanocatalyst are presented. The changes of the fractional composition of natural bitumens are established. The characteristic differences of the composition of the liquid products of hydrogenation are determined. The temperature and pressure profiles of hydrogenation process on time are registered. It is shown that the natural bitumen of Munaily Mola deposit is more susceptible to hydrogenation than the bitumen of Beke deposit. Hydrogenation can increase the yield of liquid products of processing of natural bitumen. A significant reduction in the initial boiling point of liquid products is observed during the hydrogenation process. The presence of the catalyst resulted in higher yields of light fractions and improvement of liquid hydrogenation products. Hydrogenation of the Beke natural bitumen passed at short time than the hydrogenation of the Munaily Mola natural bitumen.

Key words: natural bitumen; hydrogenation; nanocatalyst; oil sand.

Батыс Қазақстанның Беке және Мұнайлы Мола кен орындарының табиғи битумдарының MoO_3/C нанокатализаторы қатысында гидрогенизация нәтижелері берілген. Табиғи битумдардың фракциялық құрамының өзгерістері анықталды. Гидрогенизация сұйық өнімдерінің құрамының ерекшеліктері анықталды. Табиғи битумдардың гидрогенизация процесінің температура мен қысым профилдері уақытқа байланысты түсірілді. Мұнайлы Мола кен орнының табиғи битумы Беке кен орнының табиғи битумына қарағанда гидрогенизация өткізуге қолайлы екендігі анықталды. Гидрогенизация процесін өткізу табиғи битумдарды өңдеудің сұйық өнімдерінің шығымын көбейтуге мүмкіндік береді. Гидрогенизация процесін өткізгенде сұйық өнімдердің қайнауы басталу температурасының айтарлықтай төмендеуі байқалады. Катализатордың қатысында жеңіл фракциялардың шығымы артады және гидрогенизация процесінің сұйық өнімдерінің құрамы жақсарады. Беке кен орнының табиғи битумының гидрогенизациясы Мұнайлы Мола табиғи битумымен салыстырғанда қысқа уақытта өтетіндігі анықталды.

Түйін сөздер: табиғи битум; гидрогенизация; нанокатализатор; мұнайбитумды жыныс.

Представлены результаты гидрогенизации природных битумов месторождений Беке и Мунайлы Мола Западного Казахстана в присутствии нанокатализатора MoO_3/C . Установлены изменения фракционного состава природных битумов. Выявлены характерные отличия состава жидких продуктов гидрогенизации. Сняты профили температуры и давления процесса гидрогенизации природных битумов в зависимости от времени. Показано, что природный битум месторождения Мунайлы Мола более приемлем для проведения гидрогенизации, чем битум месторождения Беке. Проведение гидрогенизации позволяет увеличить выход жидких продуктов переработки природных битумов. Наблюдается существенное снижение температуры начала кипения жидких продуктов при проведении гидрогенизации. Присутствие катализатора привело к повышению выхода легких фракций и улучшению состава жидких продуктов гидрогенизации. Установлено, что гидрогенизация природного битума месторождения Беке проходит за короткое время по сравнению с природным битумом Мунайлы Мола.

Ключевые слова: природный битум; гидрогенизация; нанокатализатор; нефтебитуминозная порода.

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HYDROGENATION OF KAZAKHSTAN'S NATURAL BITUMEN

Introduction

Today a complex conversion and rational use of hydrocarbon raw materials for the production of the valuable chemical materials and high quality petroleum products are one of the primary ways of representing the Republic of Kazakhstan within the market economies. Petroleum products play an important role in economic development of any nation. At present Kazakhstan is one of the large world oil exporters and oil producing sector takes a leading position in the structure of national economy of Kazakhstan. As time passes, reserves of fossilized carbon are being depleted for the use as energy and more attention is being focussed on alternate energy sources. One such energy source is oil sand. This valuable resource can be found in several locations in the world such as Canada, Venezuela and other. In the Western part of Kazakhstan there are more reserves of oil sand, currently over 50 fields of oil sands have been discovered.

Main industrial technologies of the extraction of oil from oil sand use a hydrodynamic, thermal and chemical influence. Well known, hot water extraction is used for the commercial bitumen recovery from oil sand. The effects of several factors on the bitumen recovery have been investigated, including solid-liquid ratio, NaOH concentration, stirring time. The solvent extraction is only used in the experimental work. Not every solvent extraction process is commercialized in the world at present because of the difficulty of solvent recovery and solvent loss. Retorting is a process in which oil sand is heated to around 500 °C under the condition of oxygen to produce oil. After retorting, oil sand bitumen is thermally cracking process. Alberta Taciuk Process was invented for oil sand retorting, but it is now used for oil shale retorting. 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 [1-5].

The goal of the work was to study the process of conversion of hydrocarbons in the hydrogenation of natural bitumen and determine the optimal conditions of the process.

Experiment

The object of investigation was selected samples of bitumen Munaily Mola and Beke deposits. Extraction of natural bitumen was carried out in the Soxhlet apparatus by chloroform solvent. Content of natural bitumen in the rock was 12 wt. % from Beke deposit. And it is as follows: $\rho = 1.112 \text{ g/cm}^3$; congelation point is 18°C ; coking – 30%; ash content – 0.35 wt. %; sulfur content – 1.5%; elemental composition was N – 0.58%; C – 84.79%; H – 11.68%; O – 2.02–4.04%. Organic content of the rocks from Munaily Mola deposit was 16 wt.%, it is characterized by high densities (992.0 kg/m^3), viscosity (26.0 cSt at 80°C) and coking (35%).

For the purpose of adding to hydrogenation process, the active coal supported catalyst was prepared. At first, 10 ml of distilled water was added in flask and 3 g of molybdenum oxide (MoO_3) was added to water and was stirred for 2-3

minutes by magnetic mixer. Then 25% of ammonia solution was added slowly (drop by drop) till all catalyst was dissolved. At last, 10 g of active coal were added to mixture and heated until water evaporation. Finally, prepared catalyst dried under vacuum and oven.

The hydrogenation experiments of natural bitumen extracted from oil sands were carried out in an «Autoclave» (Figure 1). Around 200-300 g of natural bitumen was loaded into the reactor together with active coal supported catalyst. The process was carried out under 350 mbar of H_2 pressure and a temperature of $430\text{--}460^\circ\text{C}$. 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 40-160 min. After the processes the hydrogenated products in the reactor were removed.

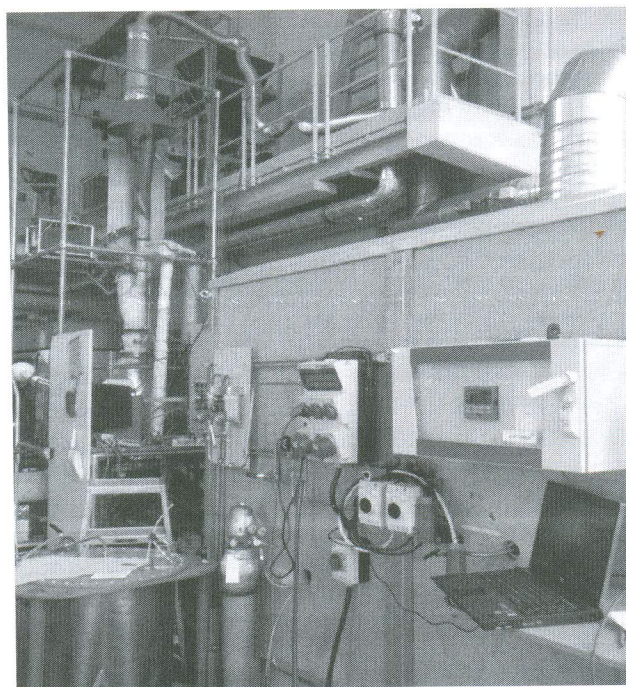


Figure 1 – Installation for hydrogenation of natural bitumen

Results and discussion

For obtaining light petroleum fractions it is necessary to process the hydrogenation of natural bitumen, which leads to improved characteristics and simplification 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 [6].

Munayli-Mola oil sands processed by hydrogen at a temperature 460°C , hydrogen pressure of

350 bar and the process time of 2 h 40 min. At the experiment, 2 g of activated carbon supported catalyst – molybdenum oxide (MoO_3) was used. It has $699.807 \text{ m}^2/\text{g}$ of surface area, 0.0635 nm of

medium pore size. Microscopic structure of catalyst is presented in Figure 2. SEM image of catalyst showed that the catalyst consists of different sizes agglomerates of plate-like structure.

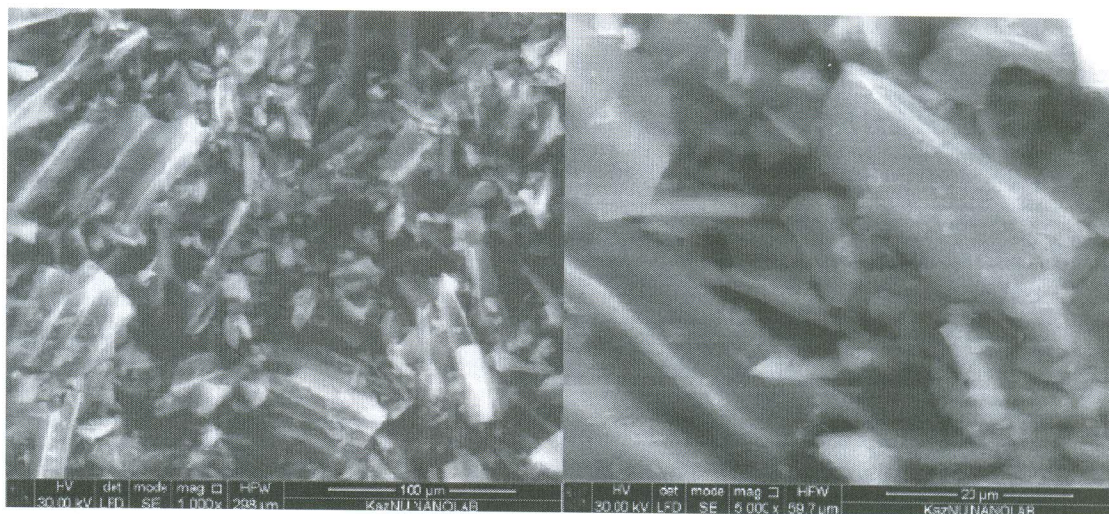


Figure 2 – SEM image of active carbon supported catalyst

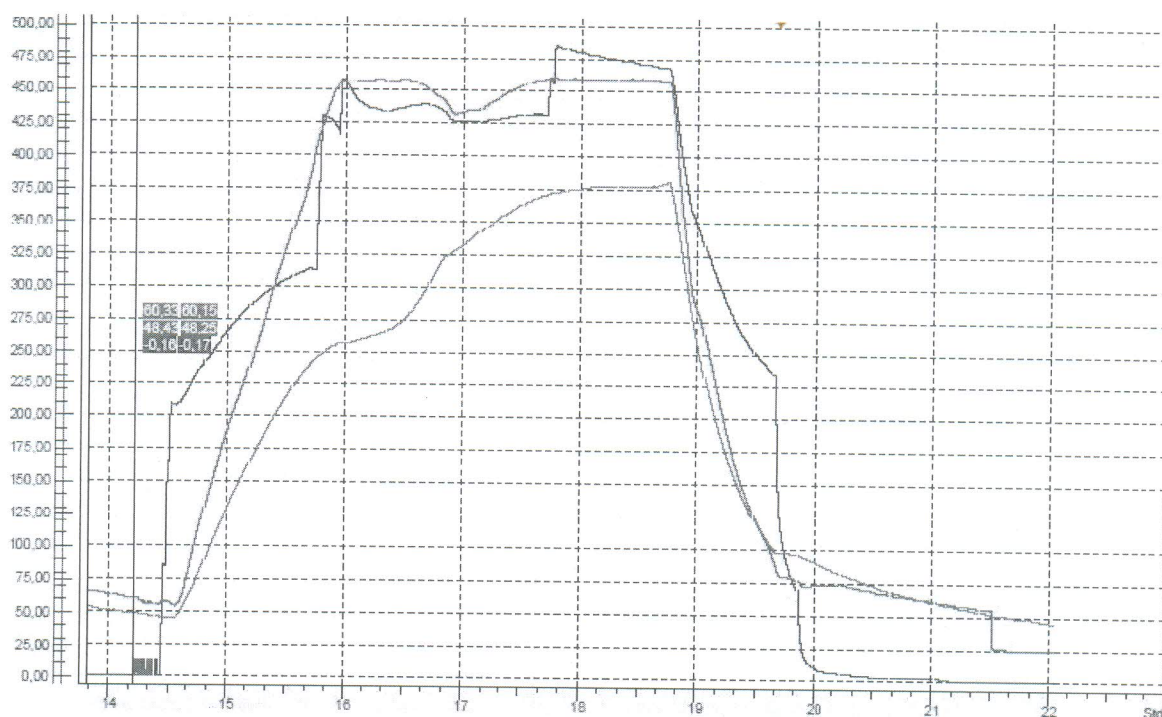


Figure 3 – Profiles of temperature and pressure over time hydrogenation process of Munayli-Mola natural bitumen

Figure 3 shows the profiles of temperature and pressure over the time of the hydrogenation process of natural bitumen. We can see from the figure, the temperature of reactor was raised gradually to

450°C , then stabilized at this temperature and after 2 hours and 40 minutes begins to decline. The hydrogen pressure in the reactor (lower line) increases until the end of the process, and reaches 375 bar. Thus

during the hydrogenation the pressure of hydrogen ranges from 250 to 375 bar.

To separate out synthetic oil from heavy residue with catalyst, the products of hydrogenation underwent vacuum distillation. Results of fractional composition of hydrogenated natural bitumen (hydrogenated oil) of vacuum distillation are presented in table 1. As can be seen from table 1, the yield

fraction of hydrogenated oil from Munayli-Mola bitumen, which boiled out from the start of boiling to 215 °C is 40,8 wt.%. Fraction of hydrogenated oil at the temperature range from 216 to 316 °C formed in an amount of 36,9 wt.%. These data confirm the positive effect on the hydrogenation process of the natural bitumen, resulting in an increased yield of volatile petroleum products.

Table 1 – Fractional composition of hydrogenated oil from Munayli-Mola, while vacuum distillation

Characteristics	1 st fraction	2 nd fraction	vacuum residue
Temperature interval, °C	I.B. – 215°C	216 – 316°C	316°C – E.B.
Pressure, mbar	808	805 – 60	60 –
Mass of fraction, g	80,4	72,7	43,9
Yield of fraction, %	40,8	36,9	22,3

Table 2 shows the comparative characteristics of natural bitumen extracted from oil sand before and after the hydrogenation process. As seen from the tabulated data, after hydrogenation process there 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 is significantly increased compared to the original natural bitumen. This shows the need in hydrogenation process for expanding the range of products derived from oil sands. The only limiting factor may be the high cost of the process in connection with the use of hydrogen.

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

Characteristics	Natural bitumen	Hydrogenated natural bitumen
Density, g/cm ³	0,992	0,883
Ash content, wt. %	0,5	0,07
Yield of fraction, %		
I.B. – 180°C	-	50,0
180 – 240°C	1,39	20,0
240 – 300°C	0,96	12,6
300°C – E.B.	97,68	17,4

Hydrogenation process was examined on natural bitumen of Beke oil sand as Munayli-Mola feedstock. The process was carried out using the same installation method on the apparatus «Autoclave». There is some change of experimental condition in comparison with hydrogenation of Munayli-Mola bitumen: has lower process temperature (460°C) and short time, only 40 minutes (not 2 h 40 min). For the experiment, 1.5 g of activated carbon supported catalyst – molybdenum oxide (MoO₃) was used. The H₂ pressure didn't change, process occurred under 350 bar as before. The yield of hydrogenated natural bitumen was 91%.

The profiles of temperature and pressure over the time of the hydrogenation process of natural bitumen show that the temperature of reactor was raised gradually to 430 °C, and then stabilized at this temperature. The hydrogen pressure in the reactor increases until the end of the process, and reaches 350 bar and the hydrogen pressure didn't decrease. It means in the process there is no more consumption of hydrogen for saturating the hydrocarbons. In this reason, process time prolonged only for 40 minutes. Upon the end of vacuum distillation to hydrogenation products of Beke bitumen, the fractions were obtained.

As shown in table 3, the yield of first fraction of hydrogenated product of Beke bitumen is 13,1 wt.%. It is lower than sample of Munayli-Mola.

Yield of 2nd fraction was increased such that at the temperature range from 216 to 316°C it was formed in amount of 45,7 wt.%.

Table 3 – Fractional composition of hydrogenated oil from Beke, while vacuum distillation

Characteristics	1 st fraction	2 nd fraction	vacuum residue
Temperature interval, °C	I.B. – 215°C	216 – 316°C	316°C – E.B.
Pressure, mbar	808	805 – 60	60 –
Mass of fraction, g	24,6	85,8	77,4
Yield of fraction, %	13,1	45,7	41,2

The fact that 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. There are a number of mechanisms proposed for the initiation step of the cleavage of strong C-C bonds. It is also difficult, because several reactions occur simultaneously

(e.g., the removal of S, N, O, and metals, along with the saturation of aromatics and olefins).

Above 400 °C, the coking reaction competes with the hydrogenation reaction, and the availability of hydrogen and the reaction pressure defines the dominance of a particular reaction [6].

Thus, results indicate the possibility of using oil sands not only as a raw material for road-construction materials (bitumen, asphalt mixture), but also useful for producing synthetic oil or light petroleum products.

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