IRSTI 61.53.15

CATALYTIC CRACKING OF NATURAL BITUMEN OF BEKE FIELD

Alina Khasanova[2], Yerbol Tileuberdi[2*], Aliya Beisekova[2], Ganimat Kyzyr[3]

[1]Individual Entrepreneur "Malina Agency", Astana, Kazakhstan
[2]Faculty of Natural Sciences and Geography, Abai Kazakh National Pedagogical University, Almaty, Kazakhstan
[3]Kazhybek Bek Secondary School, Almaty region, Kazakhstan

[*]Corresponding author's e-mail: *er.tileuberdi@gmail.com*

Abstract.

In this study, the catalytic cracking of natural bitumen derived from the Beke oil sands was investigated in order to enhance the production of light hydrocarbon fractions and synthetic liquid fuels. Catalytic cracking experiments were carried out in reactors at 450 °C under steady-state conditions. Natural zeolite from the Taizhuzgen deposit was used as a catalyst due to its high adsorption capacity, ion-exchange properties, and catalytic activity. Prior to use, the zeolite catalyst was acid-treated and thermally activated to improve its surface acidity and catalytic performance. The material balance of the cracking process, as well as the group and fractional compositions of the obtained products, was analyzed. The results demonstrate that the use of natural zeolite significantly improves the efficiency of the cracking process by increasing the yield of liquid products while reducing coke formation. The yield of liquid hydrocarbons increased from 67.7 wt.% during non-catalytic cracking to 79.9 wt.% in the presence of the zeolite catalyst. Additionally, the catalytic process promoted the formation of lighter fractions and reduced the content of heavy residues. These findings confirm the potential of natural zeolite catalysts to upgrade heavy hydrocarbon resources and produce valuable liquid fuels from the natural bitumen of domestic oil sands.

Keywords: Catalytic Cracking, Oil Sands, Natural Bitumen, Beke deposits, Natural zeolite.

1. Introduction

The primary trends in the growth of the modern oil refining industry are caused by the need to enhance the depth of petroleum conversion and the more strict ecological standards imposed on oil refining processes and products [1-2]. A decline in light oil reserves and a rise in the percentage of heavy petroleum wastes and oil sands produced and processed are the present characteristics of the global oil refining business. The development of raw materials for the production of petroleum products becomes a subject of growing current interest due to a decline in output and an increase in the prime cost of light oils [3-5].

A growing area of petroleum refining is the processing of oil sands, which should be viewed as a source of natural bitumens, promising hydrocarbon raw materials. The high concentration of high molecular weight compounds (resins and asphaltenes, whose molecules condensed a significant portion of heteroatoms present in the source material) in natural bitumens is one of the most significant issues associated with their processing. The aggregative stability of natural bitumens during thermolysis, as well as the characteristics of the dispersed phase and the dispersion medium, are influenced by the quantity of resins and asphaltenes [3–5]. These compounds have high molecular weights; they are prone to condensation and coke production following processing, and they deactivate catalysts. The primary issue of processing heavy hydrocarbon raw materials will be resolved by the development of techniques for the thorough destruction of the resin-asphaltene components of heavy oils and natural bitumens, which will also lessen the future shortage of hydrocarbon fuel [5-6].

The thermal destruction processes of heavy hydrocarbon raw materials make it possible to increase the yield of low-boiling liquid products with the formation of coke and gas as byproducts. Cracking processes in the presence of different catalysts are of special interest. The thermocatalytic

conversion of heavy hydrocarbon raw materials with iron oxide additives is a promising method to produce synthetic oil. Microspheres, which can initiate the deep destruction of high molecular weight components, exhibited high efficiency in the processes of cracking [1, 4-6].

Heavy oil contains a high proportion of impurities such as sulfur and nitrogen. These impurities not only reduce product quality during processing, but also easily react with catalysts, causing catalyst poisoning, seriously affecting catalytic efficiency, and causing equipment corrosion problems. Polycyclic aromatic hydrocarbons and asphaltene in heavy oil are easily decomposed to form coke under high-temperature cracking conditions. A large amount of coke is deposited on the reactor surface and in the catalyst pores, which not only hinders the diffusion of reactants, but also causes reactor coking, reduced thermal efficiency, and ultimately leads to rapid catalyst deactivation [1, 7-8].

Zeolite, as an important type of solid acid catalyst, has a unique pore structure, adjustable acidity, and good thermal stability. It can promote the efficient cracking and conversion of heavy oil molecules, reduce coke formation, and improve the yield and quality of light oil products [1, 9]. Previous studies show that zeolite catalysts effectively catalyze the cracking of heavy hydrocarbons and waste oils into liquid fuels. This process occurs in laboratory-scale distillation reactors, where factors like catalyst loading, temperature, and residence impact efficiency and product distribution. The physicochemical properties of the resulting liquid products are key indicators of fuel suitability. GC–MS analysis is employed to assess the chemical composition of the cracked products. Research indicates that zeolite catalysts made from local clay enhance cracking and increase fuel yields, with optimal conditions at around 380 °C and 8 wt.% catalyst loading, highlighting the importance of zeolite acidity and structure in promoting hydrocarbon breakdown and the formation of lighter fuel fractions [10].

The aim of this work was Processing of heavy oils of the Republic of Kazakhstan in the presence of zeolite catalyst by the thermocatalytic cracking method and obtaining its light oil products.

2. Experimental Section

The natural bitumen of oil sands from the deposits Beke (Mangystau region) were used as heavy hydrocarbons. Beke Field is located 53 km away from northwest side of the town Zhanaozen and 40 km from Zhetybai. In tectonic oil, the sand deposit is concentrated in the most elevated areas of the Beke baskuduk crypt, which usually refers to the anticlinal Karasiaz-Taspas. Associated industrial productive strata of natural bitumen in the Beke district were sands, sandstones and clays. Morphological explanations of the field extends from the northwest to the southeast, the length is 1300 meters, and the width is from 50 to 840 m. The area of the reservoir varies irregularly from 2.5 to 20.5 m^2. The amount of bitumen in oil sands on different samples varies from 7.2 to 20.6% by weight. %. Physicochemical studies of these bitumens showed that their composition in the intermediate position between liquid and viscous bitumen is only in the area of the bitumen surface, which modified to asphalt, and sometimes to asphaltite.

As a catalyst we employed zeolite (figure 1) from Taizhuzgen deposit. Zeolite is a unique natural mineral that has the property of absorbing and firmly holding in its structure particles of diverse substances. In addition to several natural mineral compounds, natural zeolite is an efficient and less expensive alternative to artificial zeolite. Therefore, the utilization of natural materials is crucial in such technological processes where the use of manufactured zeolites is not profitable. The presence of distinct molecular and catalytic capabilities resulting from crystal-chemical features, the capacity for cation exchange, and the loss and absorption of water and other molecules without disrupting the structural framework determine the economic worth of natural zeolite. Zeolites are materials with an ever-widening variety of compositions, structures, and applications. Numerous zeolite deposits in Kazakhstan have been investigated; the primary indicators of these deposits are the same as those found in Russia (Kholinskoye, Kulikovskoe, Vanginskoye), Georgia (Tedzamskoye), and Ukraine (Sokirnitskoye). Map of the explored deposits of natural zeolites in the CIS nations Two significant zeolite deposits are known in Kazakhstan: the Taizhuzgen.

Figure 1– Natural zeolite catalyst

Table 1 shows texture characteristics of used catalyst samples. As the tabulated data show, the specific surface area of natural zeolite (BET) is 7.2 m^2/g, and the total pore volume (BJH, desorb.) is 0.02 cm^3/g. The average pore diameter (BJH, desorb.) is 104.1 Å.

Table 1. Texture characteristics of catalyst samples

Catalyst	Specific surface area (BET), m^2/g	Total pore volume (BJH, desorb.), cm^3/g	The average pore diameter (BJH, desorb.), A°
Zeolite	7.2	0.02	104.1

Zeolite was manufactured by preliminarily grinding and filtering the particles through molecular sieves with a size of 0.25 mm. Ion exchange of the zeolite was carried out with 0.1 M HCl solution in a quartz column in a stirring mode in a boiling in-water bath for 6 hours. Following acid treatment, the zeolite was filtered, cleaned of chlorine ions using distilled water through a reaction with silver nitrate, and then dried in the air at 100 °C until its weight remained constant. After that, they underwent a 3.5-hour thermal treatment in an air current at a temperature between 100 and 500 degrees Celsius. A 0.25 mm particle size was achieved by crushing the catalyst. The IRS method of adsorbed CO was used to identify the catalysts' acid characteristics based on the amount of bands in the spectrum that corresponded to the different types of Lewis and Brunsted adsorption centers. The concentration of Lewis centers was measured from the integrated intensity of bands of adsorbed CO:

$$N\ [\mu mol / g] = A / A_0 \quad (1)$$

where A is the integrated intensity of the band of adsorbed CO; A_0 is the coefficient of integral absorption.

Determination of the specific surface area of the catalyst samples was carried out on a ASAP 2400 Micrometrics (USA) specific surface area analyzer by low-temperature nitrogen adsorption using the BET method.

Thermocatalytic cracking of heavy under steady-state conditions was carried out in autoclave reactors with a capacity of 12 ml. The reactor was filled with 7 g of bitumen. The studies were carried out in the air environment, which did not lead to substantial changes in the composition of the resultant products due to their modest volume, at a temperature of 450 °C and a period of 60, 100 and 120 minutes. During the experiments, the reactor's mass was initially fixed without a sample, and then it was fixed with a sample that had been prepared for cracking. After thermal processing of natural bitumen, the yield of gaseous products was evaluated by the loss of mass of the reactor with the sample after removal of the gas products from the reactor. After separate products, the reactor

was rinsed with chloroform and weighed. Solid products (coke) were calculated as the difference between the reactor mass before and after the experiment. Ferrosphere-induced cracking was also tested in 12 cm3 autoclaves with a 7 g bitumen admixture charged to the reactor and a 10% weight addition of ferrospheres. With the exception of filtering the cracking products to separate the liquid portion from the ferrosphere, the experiments were conducted as previously described. The filtered ferrospheres were weighed following the breaking. The sum of the discrepancies found between the weight of the reactor and the ferrospheres before and after the experiment was determined as solid products.

The pre-bitumen was homogenized with the catalyst and placed into an autoclave. The bitumen charge was 7 g, while the catalyst content was 0.5, 1.0, and 1.5 wt.%. Figure 2 shows a diagram of the general view of thermal installation.

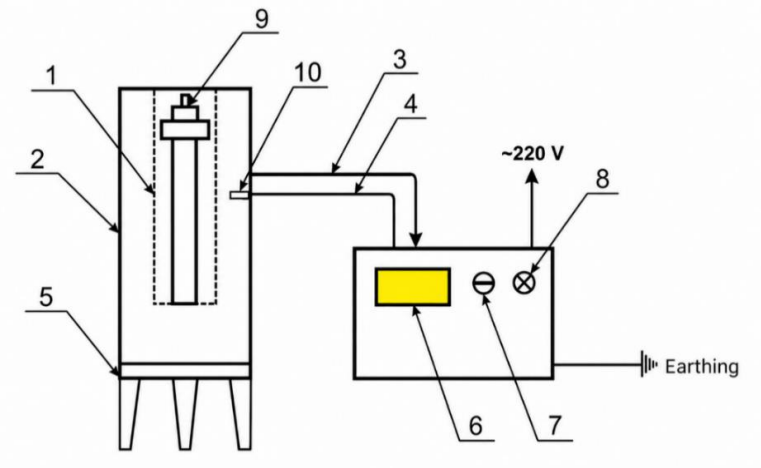

Figure 2 – Diagram of the installation for thermal catalytic cracking of natural bitumen: 1 - place for the reactor, 2 - electric heater, 3 - cord for connection to the network (220 V), 4 - thermocouple, 5 - legs of the heater, 6 - furnace temperature sensor, 7 - process temperature controller, 8- installation switch, 9 - autoclave, 10 - tap for thermocouple.

3. RESULTS AND DISCUSSION

One of the perspective methods for producing synthetic oil is catalytic conversion of heavy hydrocarbons in the presence of catalytic additives. In thermal degradation processes heavy oil can increase the yield of low-boiling liquid products with the formation of coke [3, 10].

In the work, for the comparison the cracking process of heavy oil studied with the addition of catalyst and without catalyst addition. Table 2 illustrates the number of three different processes as well as the number of contents of these processes. It is noticeable that the number of liquid products after cracking with natural zeolite is strikingly higher than the other percentage if disregard the number of first state of given natural bitumen of oil sands.

Table 2. Material balance of the process of thermal catalytic cracking of Natural bitumen of the Beke deposit in steady state

Process	Content, wt. %		
	Gas	Coke	Liquid products
Initial bitumen	0	0	100.0
Cracking	1.4	30.9	67.7
Cracking with natural zeolite (2%)	1.0	19.1	79.9

According to table 2 the amounts of gas products after usual cracking and cracking with the catalyst show nearly the same level with 1.4 and 1.0, respectively. Nevertheless, number of coke

products after cracking shows wild decrease from 30.9 to 19.1 percent. It is clear that catalyst gives positive results of liquid products, here is a sharp increase with different in 12.2 percent.

Using natural zeolite catalysts significantly influenced the distribution of cracking products and improved the efficiency of the conversion process. The reduction in coke formation indicates that the catalyst promotes secondary cracking reactions and suppresses excessive carbonization during thermal decomposition of the natural bitumen. At the same time, the increased yield of liquid products suggests enhanced breakdown of heavy hydrocarbon molecules into lighter fractions. This behavior may be associated with the porous structure and acidic active sites of natural zeolite, which facilitate hydrocarbon chain scission reactions. The obtained results demonstrate that catalytic cracking is a promising approach for improving the conversion of Beke oil sands bitumen into valuable liquid hydrocarbons.

Table 3 gives information about group components (figure 3) of products of catalytic cracking of Natural bitumen of the Beke deposit in steady state. Overall, it is clear from the chart that the percentage of oils and asphaltenes showed an upward trend and the percentage of tars dipped down.

Table 3. Component composition of products of catalytic cracking of Beke bitumen in steady state.

Process	Content, wt. %		
	Oils	Resins	Asphaltenes
Initial bitumen	49.2	44.9	5.9
Cracking	61.3	28.3	10.4
Cracking with natural zeolite	77.0	14.4	8.6

The findings in Table 3 indicate that catalytic cracking using natural zeolite significantly modifies the group composition of Beke bitumen. The most notable alteration is evident in the oil fraction, which rose from 49.2 wt.% in the original bitumen to 77.0 wt.% following catalytic cracking. This signifies improved conversion of high-molecular-weight resinous compounds into lighter hydrocarbon fractions. Concurrently, the resin concentration diminished significantly from 44.9 wt.% to 14.4 wt.%, validating the catalyst's efficacy in facilitating breakdown and transformation reactions. Despite a modest rise in asphaltene concentration following thermal cracking, its value diminished in the presence of natural zeolite compared to non-catalytic cracking. This behavior indicates that the catalyst inhibits excessive polycondensation and the generation of coke precursors. The acquired data validates that natural zeolite enhances the upgrading efficiency of natural bitumen and facilitates the generation of more valued light hydrocarbon products appropriate for subsequent refining and fuel production.

Figure 3 – Picture of asphaltenes, oils and resins

Table 4 shows fractional composition of cracking products of natural bitumen of the Beke deposit. As can be seen from the chart cracking with natural zeolite improved light fraction and middle fraction and decreased heavy fraction of given natural bitumen of oil sand.

Table 4. Fractional composition of cracking products of Beke natural bitumen

Process	Content, wt. %		
	<-200ºC	200-360 ºC	>360 ºC
Initial bitumen	5.1	20.2	74.7
Cracking	2.3	18.9	78.8
Cracking with natural zeolite	14.3	34.1	51.6

According to the tabulated results, the catalytic treatment significantly influenced the physicochemical properties of the resultant compounds. The rise in lighter hydrocarbon fractions signifies that the catalyst improved the cleavage of long-chain and condensed aromatic structures seen in natural bitumen. This transition is crucial for diminishing viscosity and enhancing the processability of heavy hydrocarbon feedstocks. The comparatively low coke production noted during catalytic cracking further substantiates that natural zeolite creates advantageous circumstances for selected cracking reactions instead of unregulated thermal disintegration. The conversion efficiency is linked to the acidic surface centers and porous structure of the catalyst, which promote the diffusion and fragmentation of heavy molecules. The findings indicate that catalytic cracking using natural zeolite is an efficient method for enhancing Beke oil sands bitumen and producing more value hydrocarbon fractions suitable for fuel and petrochemical uses.

The catalytic cracking mechanism of Beke oil sands bitumen is significantly affected by the acidity and pore architecture of the natural zeolite catalyst. In the reaction, heavy hydrocarbons, such as resins and asphaltenes, are first adsorbed onto the Brønsted and Lewis acid sites of the zeolite surface, where protonation facilitates C–C bond cleavage and β-scission reactions. The porous structure of zeolite promotes the diffusion of hydrocarbon intermediates and improves the conversion of big aromatic molecules into lighter fractions [1]. Recent studies indicate that hierarchical and mesoporous architecture enhances the accessibility of bulky molecules to active areas and mitigates diffusion restrictions during heavy oil cracking. Moreover, the modest acidity of natural zeolite mitigates excessive secondary condensation and polyaromatic growth processes, thereby restricting the synthesis of coke precursors. The reduction of coke formation can be ascribed to enhanced molecular diffusion and reduced residence time of reactive intermediates within the catalyst pores. Thus, the catalyst facilitates selective cracking of liquid hydrocarbons while reducing carbon accumulation and catalyst deactivation. The findings affirm that the structural features of zeolite and the distribution of acidity are pivotal in improving cracking efficiency and product selectivity in the catalytic upgrading of natural bitumen.

4. CONCLUSION

The present study investigated the catalytic cracking of natural bitumen obtained from the Beke oil sands using natural zeolite as a catalyst. The increasing demand for light petroleum products and the gradual depletion of conventional crude oil resources make the processing of heavy hydrocarbon feedstocks an important technological and economic challenge. Natural bitumen, which contains a significant amount of high-molecular-weight components such as resins and asphaltenes, requires effective upgrading methods in order to convert it into lighter and more valuable hydrocarbon fractions.

The experimental results demonstrated that the application of natural zeolite significantly enhances the efficiency of the cracking process. Compared with thermal cracking without catalyst, catalytic cracking in the presence of zeolite resulted in a higher yield of liquid products and a considerable reduction in coke formation. In particular, the yield of liquid hydrocarbons increased from 67.7 wt.% to 79.9 wt.% when the zeolite catalyst was introduced, while the formation of coke decreased from 30.9 wt.% to 19.1 wt.%. At the same time, the amount of gaseous products remained relatively low and showed only minor variations.

The analysis of group composition revealed that the catalytic process promotes the transformation of heavy resin-asphaltene components into lighter oil fractions. The proportion of oils

in the products increased significantly, while the content of resins decreased. Furthermore, the fractional composition analysis showed a notable increase in light and middle distillate fractions (<200 °C and 200–360 °C), accompanied by a reduction in heavy fractions (>360 °C). These changes indicate the effective breakdown of high-molecular-weight hydrocarbons during catalytic cracking.

Overall, the results confirm that natural zeolite from the Taizhuzgen deposit is a promising and economically attractive catalyst for upgrading natural bitumen from the Beke oil sands. The use of such catalysts can improve the conversion efficiency of heavy hydrocarbon resources and contribute to the production of synthetic fuels. The findings of this study provide a scientific basis for the further development of catalytic technologies for processing oil sands and other unconventional hydrocarbon feedstocks in Kazakhstan.

Acknowledgments

The research undertaken was made possible by the equal scientific involvement of all the authors concerned.

Author Contributions

Conceptualization: Alina Khasanova, Formal analysis: Yerbol Tileuberdi, Investigation: Ganimat Kyzyr, Methodology and Supervision: Alina Khasanova, Writing – original draft: Alina Khasanova, Writing – review & editing: Yerbol Tileuberdi.

Funding: Not applicable.

Conflict of interest: The authors declare no conflict of interest.

Data availability statement: The data presented in this study may be obtained on request from the corresponding author.

References

1. Wei, L.;Wang, H.; Dong, Q.; Li, Y.; Xiang, H. A Review on the Research Progress of Zeolite Catalysts for Heavy Oil Cracking. Catalysts 2025, 15, 401. DOI: https://doi.org/10.3390/catal15040401
2. Joshi, J.B., Pandit, A.B., Kataria, K.L., et al., Ind. Eng.Chem. Res., – 2008, – vol. 47, – №. 23, – p. 8960.
3. Ongarbayev Y.K., Golovko A.K., Krivtsov E.B., Imanbayev Y.I., Tileuberdi E., Tuleutaev B., Mansurov Z.A. Thermocatalytic Cracking of the Natural Bitumens of Kazakhstan // Solid Fuel Chemistry. – 2016. – Vol. 50, No. 2. – P. 81-87.
4. Yerbol Tileuberdi, Yerdos Ongarbayev, Yerzhan Imanbayev, Ainura Yermekova, Frank Behrendt, Akmaral Ismailova, Khairulla Zhanbekov, Ainur Seilkhan, Zulkhair Mansurov. Studying Characteristics of Natural Bitumen of Oil Sand with Comparison to Heavy Crude Oil. ES Materials and Manufacturing. 2023, 22, 1035, DOI: https://dx.doi.org/10.30919/esmm1035.
5. L.Ya. Kizil'shtein, I.V. Dubov, A.L. Shpitsgluz, S.G. Parada. Komponenty zolishlakov TES (Thermal Power Plant Ash and Slag Components), –Moscow: Energoatomizdat, – 1995, –p. 210.
6. Imanbayev Ye., Tileuberdi Ye., Ongarbayev Ye., Mansurov Z., Batyrbayev A., Akkazin Ye., Krivtsov E., Golovko A., Rudyk S. Changing the Structure of Resin-Asphaltenes Molecules in Cracking // Euras. Chem.-Techn. J. – 2017. – Vol. 19, No. 2. – P. 147-154.
7. Corma, A. Inorganic solid acids and their use in acid-catalyzed hydrocarbon reactions. Chem. Rev. 1995, 95, 559–614.
8. Ding, L.; Sitepu, H.; Al-Bogami, S.A.; Yami, D.; Tamimi, M.; Shaik, K.; Sayed, E. Effect of zeolite-Y modification on crude-oil direct hydrocracking. ACS Omega 2021, 6, 28654–28662. DOI: https://doi.org/10.1021/acsomega.1c03029.
9. G. R. Bikbova, G.I. Mannanova, I.M. Gubaydullin. Catalysts of the catalytic cracking process and development of a fourteen-component kinetic model. Journal of Physics: Conference Series, 2021, 1745, Doi:10.1088/1742-6596/1745/1/012052.
10. Temofeh P.T., Korode T.B., Akpeji B.H. Application of Zeolite in the Catalytic Cracking of Waste Vegetable Oil for the Production of highly Volatile Liquid Fuel, British Journal of Multidisciplinary and Advanced Studies: Engineering and Technology, 2024, 5(2), 22-39. Doi: https://doi.org/10.37745/bjmas.2022.0467.