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THERMOCATALYTIC CRACKING OF KAZAKHSTAN'S NATURAL BITUMEN

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ABSTRACT. The article shows the results of thermal cracking of natural bitumen of Kazakhstan's two deposits. The variation of the chemical and the fractional composition of the cracking products are determined depending on the process conditions. A comparative analysis of the influence of the catalyst is carried out to composition of natural bitumen.

***Key words**: Cracking, natural bitumen, microspheres, di-tert-butyl peroxide, molecular weight*

INTRODUCTION

The main trends for the oil refineries is due to the need to increase the depth of oil refining and tightening environmental requirements for refinery processes and products [1]. The worlds refining is currently characterized by destocking light oils, increase the share of mining and processing of heavy oil residues and oil sands. Due to a reduction in production and appreciation of light crude matter of getting raw materials for the production of petroleum products every year becomes more urgent.

One of the growing trends in refinery residues is processing petroleum bitumen rocks. Petroleum bitumen rock should be considered as a source of natural bitumen and hydrocarbon compounds. One of the major problems associated with the processing of natural bitumen, is the high content of high-molecular compounds - resin and asphaltene molecules which concentrates most of the heteroatoms present in the feedstock [2, 3]. Number of resins and asphaltenes determines the properties as a dispersion medium, and the dispersed phase, and natural bitumen aggregate stability under thermolysis

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process [4, 5]. These compounds have a high molecular weight, tend to condense and the formation of coke during the processing, deactivate the catalyst. Creating ways to deep destruction of resin-asphaltene components of heavy oil and natural bitumen will solve the basic problem of conversion of heavy hydrocarbon compounds and hydrocarbon fuels will reduce the deficit in the future [6].

Particularly noteworthy are cracking processes followed by the addition of a catalyst. One of the most perspective catalysts for cracking is microspheres, which can initiate the degradation of macromolecular components. According to the patent it is known that catalysts based on iron oxide, both synthetic and man-made origin or ore to be active in the process steam and hydrocracking of heavy petroleum feedstock [7].

The goal of the work was to conduct catalytic thermal cracking of natural bitumen of Kazakhstan and the establishment of the group and fractional composition of cracking products.

RESULTS AND DISCUSSION

One of the perspective methods for producing synthetic oil is thermocatalytic conversion of heavy hydrocarbons in the presence of catalytic additives such as iron oxides [8-10]. In thermal degradation processes of heavy oil can increase the yield of low-boiling liquid products with the formation of coke.

The object of investigation was selected sample of bitumen Munaily Mola and Beke deposits. Extracting 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: ρ – 1.112 g/cm^3; congelation point is 18 °C; coking content – 30 %; ash content – 0.35 wt. %; sulfur content – 1.5%; elemental composition was C – 84.79 %; H – 11.68 %; N – 0.58 %; O – 2.02-4.04 %. Organic content of the sands from Munaily Mola deposit was 16 wt. %, It is characterized by high densities (0.992 g/cm^3), viscosity (26.0 cSt at 80 °C) and coking (35 %) [11, 12].

As seen from Table 1, the cracking of natural bitumen and liquid products formed amount of coke and gas appeared. Yield of cracking liquid products from Munaily Mola deposits was higher than in the processing of bitumen from Beke deposits for 6 wt. % and coke content was lower 4.7 wt. %. Cracking has led to increased yield of oil components and the amount of high molecular weight components of bitumen decreases: resin content was decreased. Apparently, this is caused by an increase in coke formation and destruction of resinous components to lighter products. The content of oils in the composition of the liquid cracking products from Munaily Mola deposit is more for 22 % than the bitumen of Beke deposits and content of resin is less for 15 %, asphaltenes content is lower 7 %. These number shows that the bitumen from Munaily Mola deposit more acceptable for cracking than the bitumen from Beke deposit.

In the form of microspheres of the catalyst chosen and for cracking process was given 10 % weight mass of the catalyst. Microspheres are ferrospheres energy ashes with a high content of iron oxides. Selection ferrospheres due to the fact that they contain the iron oxide phase, represented mainly hematite and spinel ferrite, which can initiate the degradation of high molecular weight components. Ferrospheres are one of the most common types of microspheres in volatile ash from pulverized coal combustion in thermal power stations. The formation of a globular structure is a result of the thermochemical transformation of mineral coal forms droplets to form complex high-iron melts ($FeO-CaO-MgO-SiO_2-Al_2O_3$) macroelement of partial oxidation and crystallization phases separate on cooling.

Table 1. Material balance and composition of cracking products of natural bitumen

Cracking conditions	S_{total} in oil, wt. %	Yield, wt. %			Composition of liquid products, wt. %		
		Gas	Liquid	Coke	Oil	Resin	Asphaltene
Natural bitumen from Beke deposit							
Natural bitumen	0.30	0.0	100.0	0.0	49.17	44.89	5.94
450 °C, 60 min.	0.43	1.4	67.7	30.9	61.29	28.27	10.44
450 °C, 60 min. with catalysis	0.34	1.3	63	35.7	60.05	32.24	7.71
450 °C, 60 min. with DTBP	0.35	1.1	70.3	28.6	63.27	24.81	11.92
Natural bitumen from Munaily Mola deposit							
Natural bitumen	0.7	0.0	100.0	0.0	47.58	46.37	6.05
450 °C, 60 min.	0.57	0.2	73.6	26.2	83.61	13.39	3.0
450 °C, 60 min with catalysis	0.64	0.5	64.8	34.7	77.53	14.39	8.08
450 °C, 60 min. with DTBP	0.65	1.5	87.6	10.9	77.07	15.23	7.71

Presence of a catalyst in a cracking process had a negative impact on the yield of liquid products and content of oil components: for bitumen both of deposits yield of liquid products decreased, and yield of coke increased for 4-8 %. Oil content decreased, while the total amount of resin-asphaltene components increased for 1 and 6 %, respectively, for the bitumen from Beke and Munaily Mola deposits. Catalyst intensified condensation and consolidation reaction in cracking products.

One of the methods to achieve a more profound transformation of resin-asphaltene components to target products and as a consequence, increase the yield of distillate fractions in the cracking process is a radical-additive component, which are the initiators of radical chain processes of low-temperature cracking. Di-tert-butyl peroxide (DTBP) was added 3 wt. % as the radical-additive addition. This organic peroxide initiates the reaction to the destruction of high-molecular compounds and provides to yield of light products.

The addition of peroxide favorably influenced the cracking process: the yield of liquid products is increased; especially in the case of cracking bitumen increasing was 14 % from Munaily Mola deposit. Yield of coke is reduced; in this case the decrease was 15 %. In part of the liquid cracking products of bitumen from Beke deposits content oil components increased for 2 %, the amount of resin content decreased for 3.4 %. However, the processing of natural bitumen from Munaily Mola deposits despite the significant increase yield of liquid products is showed a decrease the amount of oil and the increase content of resin-asphaltene substances. It appears that the cracking with radical-additive addition involved not only resins and asphaltenes for degradation processes, but also the oil molecules.

After the thermal and catalytic thermal processing of natural bitumen of oil sands from Munaily Mola and Beke deposits were investigated fractional composition of the obtained products. Results of the analysis on the fractional composition of the obtained products are major importance for the study, as the basis of these data we can judge the depth of processing of the bitumen.

Analysis of the fraction composition of the bitumen cracking products (Table 2) showed that a reduction the boiling point fractions under cracking as compared with the initial bitumen. The cracking of bitumen from Beke deposits elevation of boiling point – 360 fractions observed in the case of the catalyst, while the number of fractions of B.p.-200 °C increased for 11 %, the fraction in the range of 200-360 increased for 6.6 %. Cracking bitumen from Munaily Mola deposits in all cases leads to the increase the B.p.-200 fractions, indicating an increase in the proportion of destructive processes in the reaction medium. Here, the maximum increase in the content of light fractions occurred during the cracking of bitumen without addition of catalyst and peroxide: the fraction of B.p.-200 increased for 7.1 %, and the fractions 200-360 increase for 18.6 %. The presence of a catalyst and an initiator additive resulted to higher contents of such light fractions.

Gas composition of cracking products was determined by gas adsorption chromatograph. The main gaseous cracking products include methane, that its content greater than 30 wt. % of Beke deposit and another deposit from

Munaily Mola deposit is more 10 wt. % of methene, in addition has ethane, propane, iso-butane and hydrogen (Table 3). Hydrogen content after cracked gases is 2.5-4.5 wt. %.

Table 2. Fractional composition of cracking products of natural bitumen

Sample	$T_{b.p.}$, °C	Composition, wt. %		
		B.p.-200	200-360	> 360
Natural bitumen of Beke deposit				
Natural bitumen	116.8	5.1	20.2	74.7
After cracking	77.9	2.3	18.9	78.8
With catalysis	73	16.1	26.8	57.1
With DTBP	77.4	4.9	14.6	80.5
Natural bitumen of Munaily Mola deposit				
Natural bitumen	96.5	2.2	15.6	82.2
After cracking	92	9.3	34.2	56.5
With catalysis	75	7.1	23.3	69.6
With DTBP	82.7	6.5	21.4	72.1

Table 3. Gas composition of cracked products

Gas	Composition, wt. %					
	Munaily Mola			Beke		
	After cracking	With catalyst	With DTBP	After cracking	With catalyst	With DTBP
H_2	4.53	4.16	4.1	2.71	2.97	2.53
O_2	3.43	3.59	5.69	3.86	4.84	3.19
N_2	13.43	15.81	24.57	22.78	22.38	15.55
CH_4	24.39	24.93	21.97	30.28	35.87	33.14
C_2H_6	17	13.33	9.16	10.14	11.62	8.12
CO_2	24.79	28.56	19.18	23.77	14.22	16.99
C_3H_8	8.88	7.15	6.8	5.16	6.34	5.26
i-C_4H_{10}	2.05	1.41	7.93	0.76	0.97	14.53
n-C_4H_{10}	0.08	0.05	0.04	0.03	0.04	0.03
i-C_5H_{12}	0.96	0.69	0.32	0.3	0.36	0.4
n-C_5H_{12}	0.46	0.32	0.24	0.19	0.32	0.18

Molecular weight of asphaltenes of natural bitumen and cracking products was measured by method cryoscopies in naphthalene in installation "Kryon" that is created in IPC SB RAS. The thermolysis is lead to a deep changing of the structural characteristics of average molecules of asphaltenes than in subcritical conditions (Table 4). Asphaltene molecules more destroyed by addition of a catalyst to produce lighter products such as: coke, gas and resin compounds.

Table 4. Molecular weight of asphaltenes of natural bitumen (NB) and cracking products

Sample	Asphaltenes of NB from Munaily Mola deposit	Asphaltenes of NB from Beke deposit
Natural bitumen	1803	2044
After cracking	677	1304
With catalysis	1045	1003
With DTBP	869	1042

CONCLUSIONS

The heat treatment bitumen of Beke deposit leads to deterioration fraction and composition of liquid cracking products, and quality of products from cracking bitumen of Munaily Mola deposits – conversely improved (increasing the amount of oil is increased to three times the amount of gasoline fraction and 10 wt. % diesel fraction). In both cases there was a decrease resin and coke formation.

Microspheres addition, as a catalyst for the cracking of natural bitumen coke formation led to an increase, and decrease in the amount of oil and reduce the start of boiling point of liquid products (compared with the composition of products of thermal cracking). The total content of distillate fractions (B.p.-360) as part of the cracking products of bitumen with the addition of microspheres does not differ from gasoline fraction, with increasing amounts of gasoline fractions of 2-5 wt. %. The amount of oils is increased by 3 to 6 wt. %.

The presence of additives di-tert-butyl peroxide reduces coke formation in the cracking of bitumen (Beke deposits - 2.3 % Munaily Mola - 15.3 wt. %) compared to the thermal cracking products. The content of distillate fractions in products initiated cracking bitumen of Beke deposit minimally probably di-tert-butyl peroxide more initiates the condensation reaction of components of the bitumen. In the composition of liquid purged initiated cracking of bitumen from Munaily Mola deposits dominated oil. The number of fractions of B.p.-360 products initiated cracking bitumen from Munaily Mola deposits larger than the content in the initial bitumen and the cracking products from the microspheres, but less than at thermal cracking of bitumen. It should be noted that the reduction of coke formation has led to an increase of 20 wt. % of residual fractions (>360 °C), which are source for oil distillates.

EXPERIMENTAL SECTION

The scheme of the cracked experiment and analysis of the products is shown in Figure 1.

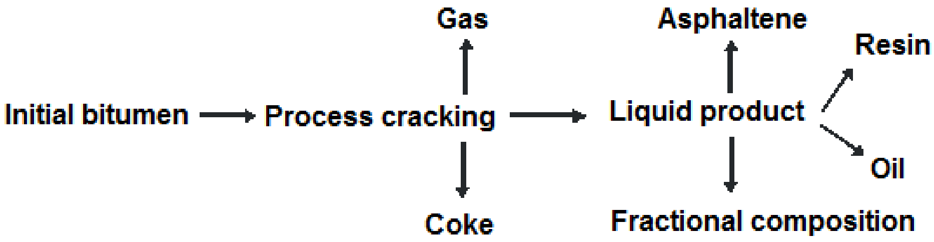

Figure 1. Scheme of the experiment

Both of natural bitumen was extracted from oil sands by chloroform solvent in Soxhlet apparatus. Then cracking process was carried out in bitumen autoclave reactor of 12 cm^3; the bitumen was weighed 7 g cracking duration of 60 minutes at a temperature of 450 °C. After the thermolysis samples from the reactor were quantitatively extracted, then yield of gas, liquid cracking products and content of coke were determined. Group composition of the initial bitumen and liquid cracking products installed on the traditional pattern: determine the content of asphaltenes in the sample by "cold" method Golde. Asphaltene sample solution in hexane settled for 16 hours in the dark at ambient temperature. In a conical funnel expose filter blue ribbon. The pooled sample solution in hexane without stirring carefully filtered through filter paper. For extraction of asphaltene compounds is carried out with filter paper extraction of benzene in a Soxhlet apparatus. The benzene extract was transferred into content of asphaltenes round bottom flask, and benzene is evaporated on a rotary evaporator. Content of asphaltenes with small amount of chloroform solvent transferred into a Petri dish and dried to solidness. Obtained asphaltene compounds should be brittle and shiny and black and brown color.

Maltenes, solution in hexane was placed in a round bottom flask and the hexane was distilled off. The concentrate maltenes small amount of hexane is applied at a Soxhlet apparatus with silica gel ASK marks. Apparatus was placed in a water bath and extracted oil (concentrate hydrocarbons) as long as in the flask of a Soxhlet apparatus will not drain the pure solvent hexane. Then replace the receiver flask with hexane solvent to pure ethanol-benzene mixture, the ratio of mixture was 1:1. Desorption from silica gel resins produced as long as there is no drain of pure ethanol-benzene mixture.

Extract of ethanol-benzene containing resin, solvent removed on a rotary evaporator. Resins with a small amount of the ethanol-benzene mixture was transferred to a Petri dish and dried to solidness (STF technique SZHSHI 1217-2005, IPC SB RAS).

Content of distillate fractions in the initial bitumen and cracking products was estimated by thermogravimetric analysis. Thermogravimetric analysis was performed in air derivatograph MOM (Hungary), which allows to fix the weight loss of the sample with the analytical sample with rising temperature till 350 °C at a heating rate of 10 degree/min.

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