

UDC 665.7.032.57:665.775

DOI: 10.15372/KhUR20170111

Destruction of Resins and Asphaltenes of Natural Bitumen on a Nickel-Containing Catalyst

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Abstract

The effect of the catalytic addition of mesoporous aluminosilicate on the composition of the cracking products of natural bitumen on the Ashalchi deposit with a content of IBP-200 °C fractions of 4.6 mass % in the autoclave reactor was studied. It was demonstrated that the addition of 5 % catalyst increased destruction of resins and the yield of low-boiling fractions. It was determined that the catalyst modification with nanoscale nickel powder slowed down coke formation. At cracking of bitumen employing mesoporous aluminosilicate modified with nickel, the yield of IBP-360 °C fractions per 35.2 mass % was increased, and destruction of resins and asphaltenes was 48 % in comparison with the initial bitumen.

Key words: natural bitumen, catalyst, resins, asphaltenes, nanoscale nickel powder

INTRODUCTION

Heavy oils and natural bitumens will play an increasingly important role in satisfying the global demand for hydrocarbon energy resources. Currently, heavy oils and bitumens, as a rule, are initially subjected to conversion to synthetic oils that can then be used to produce light petroleum products, as well as industrial chemicals [1]. One of the major problems associated with processing of heavy hydrocarbon raw materials is a high content in its composition of high molecular mass heteroatomic compounds, such as asphaltenes and resins prone to coke formation and poisoning of catalysts [2–5].

To elaborate effective processing methods of heavy oil or natural bitumen the knowledge on the effect of the temperature and the nature of catalysts on various functional groups in the structure of resins and asphaltenes [6–9] molecules leading to their destruction are required. These data are important for deeper understanding of changes that occur in resins and asphaltenes in thermal and catalytic cracking

processes and selecting optimum modernization schemes of units and determining modes for processing of heavy hydrocarbon raw materials by refineries [10–12].

This paper presents the results regarding the effect of the content of nanoscale nickel powder in mesoporous aluminosilicate on the yield and composition of the products of natural bitumen in the catalytic cracking process.

EXPERIMENTAL

Research object

A research object is natural bitumen on the Ashalchi deposit; major physicochemical characteristics are given in Table 1. High sulphur bitumen ($S_o = 4.66\%$) is characterized by a low content of distillate fractions (boiling away up to 360 °C – 32.5 %) and a high content of resinous-asphaltene substances (over 30 mass %). The atomic H/C ratio is 1.52, which is a relatively low value and testifies the content in the

TABLE 1
Characteristic of bitumen on the Ashalchi deposit

Indicators	Values
Elemental composition (mass %):	
carbon	82.10
hydrogen	10.41
sulphur	4.74
nitrogen	1.05
oxygen	1.78
H/C	1.52
Componential composition (mass %):	
oils	67.6
resins	26.2
asphaltenes	6.2
IBP, °C	109
Contents of fractions (mass %) with IBP, °C:	
200	4.6
200–360	27.9
360–500	41.6
Residue >500	24.9

composition of bitumen of a significant amount of cyclic and aromatic compounds.

Catalytic system

Mesoporous aluminosilicate (MP) synthesized at the Institute of Petrochemistry and Catalysis, Ufa Scientific Centre, RAS (Ufa) with a pore size of 50 nm was taken as a carrier [13]. Nanoscale powder of nickel (NSP Ni) with an average pore size of 20 nm was the active catalytic component. The carrier modification with nickel was carried out in a vibrating mill by mixing. The availability of a mesoporous structure in the synthesized aluminosilicate ensures the accessibility of its active centres situated in the volume for large molecules of resins and asphaltenes where they are subjected to destruction. Metal nickel particles contribute to

disproportionation and hydrogen redistribution from high molecular mass compounds to components of gasoline and diesel fractions. The amount of the modifier (NSP Ni) was varied from 0.5 to 5.0 mass %. Characteristics of a mesoporous catalyst (MP) and nanoscale powders of nickel (NSP Ni) are given in Table 2.

Bitumen cracking

The cracking of bitumen was carried out in autoclaves with a volume of 12 cm³ at a temperature of 450 °C and duration of 100 min in air. Preliminarily bitumen with a catalyst was homogenized and placed in the autoclave, the sample weight of bitumen was 7 g, and the catalyst amount was 5 mass % from the mass of bitumen.

When conducting experiments the reactor mass and the reactor mass above the sample prepared to cracking were registered. After conducting the thermal treatment of natural bitumen, the yield of the gaseous products was determined according to the loss of the reactor mass with the sample after the removal of the gas products from the reactor. After separating the products, the reactor was washed with chloroform and weighted. The resulting difference between the reactor mass before and after the experiment was determined as solid products (coke).

Determination of the fractional composition of liquid products

The fractional composition of liquid products was carried out by the gas-liquid chromatographic method. Gas-liquid chromatography (GLC) was carried out using a Crystal-2000M chromatograph with a quartz capillary column 25 m × 0.22 mm with a stationary phase SE-54, the carrier gas is helium. The device is equipped with a flame ionization detector (FID),

TABLE 2
Characteristics of mesoporous catalyst (MP) and nanoscale powders of nickel (NSP Ni)

Catalysts	Pore size, nm	Specific surface, m ² /g	Silicate module	Average pore size, nm
MP	50	600	20	–
NSP Ni	–	34.8	–	20.0

TABLE 3

Fractional and componential composition of the thermal cracking bitumen products (cracking temperature: 450 °C)

Cracking time, min	IBP, °C	Contents of products, mass %				
		Liquid			Solid	Gas
		Fractions with IBP, °C				
		<200	200–360	>360		
60	113	7.7	31.0	59.8	1.1	0.4
100	106	7.7	30.1	59.4	1.8	1.0
120	103	8.3	29.6	56.1	3.4	2.6

linear temperature increase ranged from 80 to 290 °C, the heating rate of the column thermostat 15 °C/min. The identification of hydrocarbons and separation of chromatogram segments for petrol (IBP-200 °C) and diesel (200–360 °C) fraction was carried out by the retention times of *n*-alkanes (hexane and hexadecane), pristane and phytane.

Determination of the material composition of the liquid products

The content of resins and asphaltenes in natural bitumens and the resulting liquid cracking products was determined according to the standard technique. To highlight asphaltenes a sample weigh was diluted with a 40-fold volume of hexane, by ageing during a day and

filtering out the precipitate. The resulting precipitate was placed in a paper cartridge and washed out in a Soxhlet apparatus with hexane from oils and resins, further, asphaltenes were washed from the cartridge with chloroform. Deasphaltenated samples were applied on silica gel ASM, and then successively extracted in a Soxhlet apparatus for hydrocarbon components (oils) by *n*-hexane and resins allocable by benzene/ethanol (1 : 1) mixture.

Determination of sulphur in cracking liquid products

The determination of sulphur content in the samples under study was carried out using a Spectroscan S energy-dispersive X-Ray fluorescent analyser (State Standard GOST R

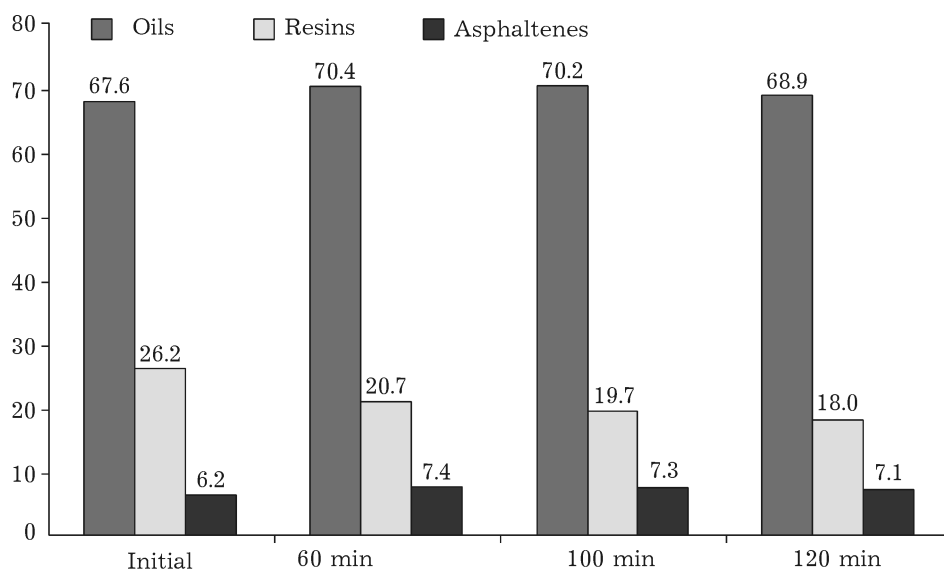


Fig. 1. Material composition of the initial bitumen and the products of thermal cracking.

TABLE 4

Fractional and componential in the presence of mesoporous aluminosilicate (cracking temperature: 450 °C, time: 100 min)

Ni contents in sample of MP, mass %	IBP, °C	Contents of the products, mass %				
		Liquid			Solid	Gas
		Fractions with IBP, °C				
		<200	200–360	>360		
0	51	18.4	35.1	37.6	3.9	5.0
0.5	43	22.3	39.8	31.3	1.1	5.5
1.0	42	24.8	42.9	27.0	0.4	4.9
3.0	42	22.4	36.9	33.4	0.6	4.8
5.0	40	20.5	34.3	41.3	0.8	3.1

51947–2002) of sulphur in oils and oil products. Measurement range of the sulphur mass fraction is from of 0.0002 to 5 %.

RESULTS AND DISCUSSION

Cracking bitumen

Analysis results of the fractional composition of the initial bitumen and liquid cracking products are presented in Table 3.

According the fractional composition data, one can see that when increasing the duration of cracking a slight monotonic increase of gasoline fractions is observed. Thus, at the crack-

ing duration of 60 min, the content of IBP-200 and 200–360 °C fractions is increased by 3.1 and 3.1 mass %, respectively, and the temperature of start of liquid products boiling increases by 4 °C. Cracking for 100 min leads to a decrease in the temperature start of liquid products boiling by 3 °C and the increment of fractions boiling up to 360 °C by 5.3 mass %. At cracking of bitumen for 120 min no significant change in the fractional composition is observed. The yield of by-products (gaseous and solid) is increased from 60 to 120 min of the process from 1.5 to 6.0 mass %.

On the assumption of the material composition data presented in Fig. 1, one should note

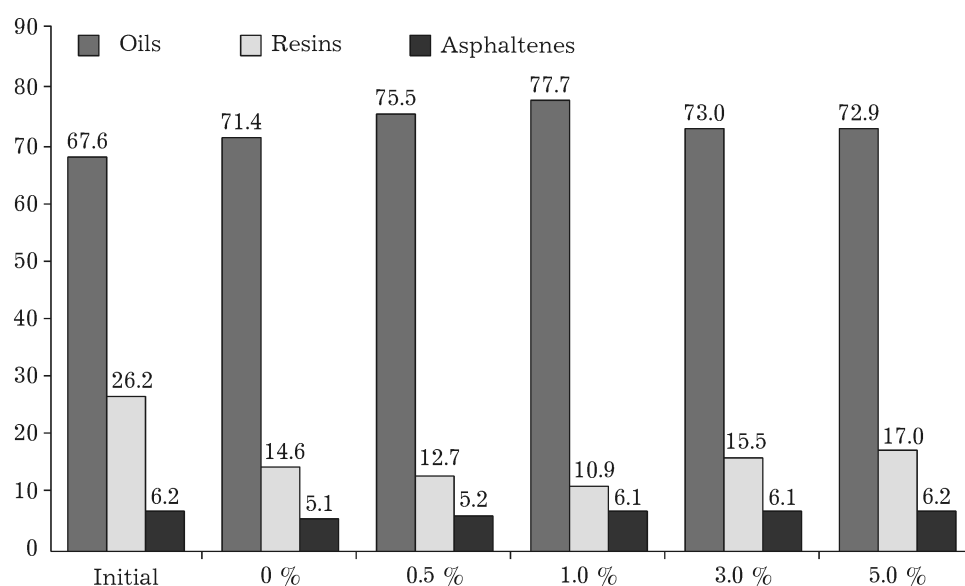


Fig. 2. Material composition of the initial bitumen and the products of catalytic cracking of raw materials with a mesoporous aluminosilicate, modified with NSP of nickel.

that when increasing the cracking time an increase in destruction of resinous components up to 8.2 mass % is observed, however, herewith, oils begin to disintegrate.

Catalytic cracking of bitumen

Data on catalytic cracking of natural bitumen at 450 °C and the duration of 100 min at this temperature are presented in Table 4 and Fig. 2, the maximum yields of light fractions at the minimum yields of gas and coke are observed at this temperature. From these data, it can be seen that cracking in the presence of 5 % mass catalyst leads to an increase in the cracking level. The yields of the gaseous and solid products increased in 5 and 2 times, respectively, in comparison with cracking without a catalyst. Herewith, the yield of the gaseous products is higher, than solid, while the yields were reverse at thermolysis. According to fractional analysis, a decrease in temperature of the reaction start to 51 °C is seen. The yield of low boiling fractions increased by 21.0 mass % due to the increase of petrol fractions by 13.8 and diesel fractions by 7.2 mass %. Destruction of resinous components amounted to 11.6 mass % (by 5 mass % more than at cracking), the content of resins increased and amounted to 71.4 mass %, and the yield of asphaltenes amounted to 5.1 mass %, which is lower than in the initial bitumen.

The catalyst modification with nanoscale nickel powder leads to significant changes of the obtainable products. Already 0.5 % NSP Ni in the catalyst in comparison with an unmodified catalyst allows lowering yields of solid products from 3.9 to 1.1 mass %. The temperature of the boiling start of liquid cracking products amounted to 43 °C, which is by 66 °C lower in comparison with initial bitumen. The cracking of bitumen with a modified catalyst 0.5 % NSP Ni increases the yield of fractions boiling out before 360 °C due to the content of gasoline fractions by 17.7 % and diesel ones – by 11.9 mass %. Oil content increases by 4.1 mass % and amounts to 75.5 mass %, due to an increase in destruction of resinous components by 1.9 mass %.

An increase in NSP Ni to 1.0 mass % lowers the yield of solid products to 0.4 mass %, which is 4.5 times lower than at cracking and 10 times lower than at the cracking of bitumen with an unmodified catalyst. On the assumption of the fractional composition data, it can be seen that 1.0 mass % NSP Ni in the catalyst leads to the maximum increase of gasoline (by 20.2 mass %) and diesel fractions (by 15.0 mass %) and the total yield of light fractions boiling out before 360 °C amounts to 67.7 mass %. Destruction of resins in this case is maximum and reaches 58 rel. %, the content of oily components increases by 10.1 mass %. The content of asphaltenes remains at the level of the initial bitumen.

A further increase in the content of NSP Ni to 3 and 5 % in the catalyst leads to worsening

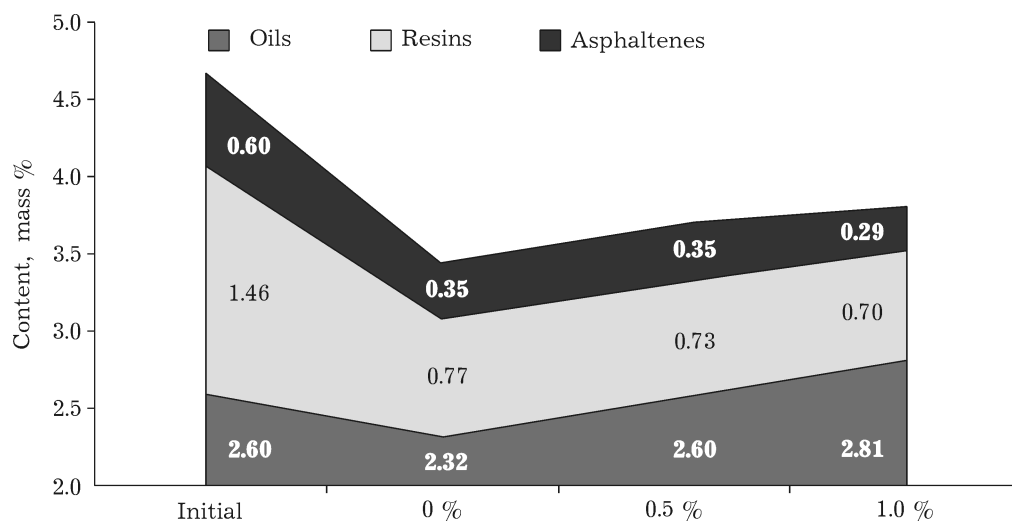


Fig. 3. Change of the sulphur content in components of liquid products of catalytic cracking.

the obtainable products. The yields of gaseous products are decreased and amount to 4.8 and 3.1 mass % for 3 and 5 mass % NSP Ni in the catalyst, respectively. The content of oily components in a row of 1, 3 and 5 mass % NSP Ni in the catalyst decreases from 77.7 to 73.0 and 72.9 mass %, respectively, while the amount of resins increases and amounts to 10.9 to 15.5 and 17.0 mass %. Changes of the material and fractional content have an identical dependence. The content of gasoline and diesel fractions is reduced.

The changed data of the sulphur content in the liquid cracking products of natural bitumen using a catalyst of modified by NSP Ni are given in Fig. 3. The use of an unmodified catalyst significantly reduces the sulphur content in resins, asphaltenes and oils by 0.69, 0.25 and 0.18 mass %, respectively. The addition of 0.5 mass % Ni into the catalyst leads to a lower yield of coke in 3 times (see Table 4), due to which reducing sulphur in liquid products is lower, than in a catalyst without Ni. The content of sulphur in asphaltenes does not change and remains equal to 0.35 mass %, very low reducing only by 0.04 mass % is observed in resins. Herewith, the content of sulphur in oils of the products is increased by 0.28 mass % most likely due to the degradation of resins by 2.0 mass % and the yield of oily components by 4 mass %. Apparently, sulphur-containing fragments of resin molecules because of destruction form sulphur-containing oil compounds due to destruction. The content of sulphur components in oils increases from 3.44 to 3.68 mass %, since the addition of nickel into a catalyst coke formation is low.

The use of a catalyst with 1 mass % NSP Ni reduces the amount of sulphur in resins and asphaltenes, in comparison with initial bitumen, by 0.76 and 0.31, the cracking products with a modernized catalyst by 0.07 and 0.06 and a mesoporous catalyst modified with 0.5 % Ni – by 0.03 and 0.06 mass %. The content of sulphur in oils also increases in this row by 0.49 and 0.21 %, respectively, and the total sulphur

content amounted to 3.80 mass %. This also confirms the conclusion that destruction products of resins are sulphur-containing compounds that remain in low-boiling fractions.

CONCLUSION

Thus, it was determined that the presence of mesoporous aluminosilicate at cracking of natural bitumen of the Ashalchi deposit allowed significantly increasing the yield of motor fuels and oil distillates. The content interconnection of NSP of nickel in the catalyst composition and the yield of the obtainable products was detected and demonstrated. It was shown that the optimum amount of NSP of nickel amounted to 1.0 %, herewith, the maximum increase in the content of fractions boiling out before 360 °C (35.2 mass %) is reached and coke formation slows down.

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