CRACKING OF NATURAL BITUMEN IN THE PRESENCE OF NANOSIZED POWDERS Mo AND CuO

Nikita N. Sviridenko[1], Evgenii B. Krivtsov[1], Anatolii K. Golovko[1], Nadezhda I. Krivtcova[2]*

[1] *Institute of Petroleum Chemistry, Siberian Branch of the Russian Academy of Sciences, Tomsk, Russia*
[2] *National Research Tomsk Polytechnic University, Russia*

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Abstract

The analysis of the bitumen deposits Ashalchinskoye cracking products (content of fractions boiling up to 360 °C – 32.5 % wt., respectively) has been conducted. It shows the impact of nanosized powders of molybdenum and copper oxide on the cracking process. It has been found that the presence of nanosized molybdenum powder leads to the formation of large amounts of gas and oil degradation due to the resins compared with nanosized copper oxide powder.

Keywords: Natural bitumen; cracking; resins; asphaltenes, nanosized powders.

1. Introduction

In the future, heavy oil and natural bitumen will play an increasingly important role in meeting the global demand for energy hydrocarbon resources. Currently, heavy oil and bitumen are generally initially subjected to transformation into "synthetic" oil, which can then be used to produce light oil [1-2]. One of the main problems associated with the processing of a heavy hydrocarbon feedstock, is the high content in its composition of high-molecular heteroatomic compounds – asphaltenes and resins, are prone to the formation of coke and catalyst poisoning [3-4].

In order to develop effective ways of recycling and further use of heavy oil conversion products or natural bitumen the knowledge about the influence of the process temperature and the nature of the catalysts used in the transformation of a variety of functional groups in the molecular structure of asphaltenes and resins is required. These data are important for a better understanding of the changes that occur in resins and asphaltenes in the processes of thermal and catalytic cracking process, selection of optimal schemes of the modernization and the definition of technological conditions for the processing of heavy hydrocarbon feedstocks refineries [5-6].

2. Experimental

Bitumen Ashalchinskoye (AB) oil field in the Republic of Tatarstan was the object of investigation (Tab. 1).

Table 1. Bitumen characteristic

Characteristic	Content, % wt.	Characteristic	Content, % wt.
C	82.1	Resins	26.2
H	10.4	Asphaltenes	6.2
N	1.0	fractional composition, ºC	
S	4.7	IBP–200	4.6
O difference	1.8	200–360	27.9
Oils	67.6	>360	67.5

High sulfur bitumen (S_o= 4.7 %) is characterized by a low content of disti-llate fractions (fractions boiling up to 360°C - 32.5 %) and high content of resin-asphaltene substances (over 30 % wt.). The atomic ratio H/C amounts to 1.52, which is quite a low value and it indicates that the bitumen contains significant amounts of cyclic and aromatic compounds. Nitrogen and oxygen content is also high and is 1.0 and 1.8 % wt. respectively.

Brief characteristics of nanosized powders (NSP) of molybdenum and copper oxide is shown in Table 2 (specific surface and the average particle size). NSP copper oxide has a specific surface area of 6.8 m^2/g, which is two times higher than the rate of NSP molybdenum. The average particle size of molybdenum is greater than 6 times the copper oxide.

Table 2. Nanosized powder of Mo and CuO characteristics

NSP	Specific surface, m^2/g	Average particle size, nm
CuO	6.8	80.0
Mo	3.3	500.0

2.1. The experimental conditions and product analysis

Elemental analysis of the natural bitumens was performed by the microanalytical method using CHNS Vario EL Cube analyzer, oxygen was defined by differences (Tab. 1).

The amount of resins and asphaltenes in natural bitumens and their liquid cracking products was determined according to the standard procedure. To isolate asphaltenes, a weighed sample was diluted with a 40-fold excess of hexane and held for a day. The precipitate was filtered off, placed in a paper cartridge, and washed with hexane in a Soxhlet extractor to remove hydrocarbons and resins; then, asphaltenes were washed out of the cartridge with chloroform. The deasphalted samples were applied to ASK silica gel and then successively extracted in a Soxhlet apparatus with hexane and a 1:1 benzene-ethanol blend to isolate the hydrocarbon components and resins, respectively.

Fractional composition of liquid cracking products was carried out by gas-liquid chromatography. Gas-liquid chromatography (GLC) was performed on a chromatograph "Crystal-2000M" with quartz capillary column 25 m × 0,22 mm, with a stationary phase SE-54, carrier gas-helium. The device is equipped with a flame ionization detector (FID) was a linear increase in temperature from 45 to 290°C, column oven heating rate - 15 deg/min. The identification and separation of the hydrocarbons to gasoline chromatograms segments (IBP–200ºC) and diesel (200-360ºC) fraction were carried out according to the retention times of n-alkanes (hexane and hexadecane), pristane and phytane.

The experiments were carried out in autoclave volume of 12 cm^3. Bitumen weight in experimentation was 7 g, nanopowders amount of molybdenum and copper oxide was varied from 0.1 to 1 % by wt. by bitumen weight. Experiments were conducted at a temperature 450ºC for 100 min in the air environment. The mass of the reactor was registered without a sample and with a sample prepared for thermolysis. After conducting natural bitumen heat treatment, the gaseous products yield was determined by weight loss of the reactor with sample after removing gas products from the reactor.

After selection of liquid products the reactor was washed with chloroform and weighed. The resulting difference between the mass of the reactor before and after the experiment was referred as coke.

3. Results and discussion

Products cracking bitumen composition under various conditions is shown in table 3. It has been found that the cracking of bitumen in the presence of nanosized powders molybdenum and copper oxide leads to a significant destruction of resins and increased yield of oils. Reducing the amount additive NSP of molybdenum with 1 to 0.1 % by wt. slows down the gassing (from 5.2 to 0.9 % wt.) and accumulation of solids (from 1.0 to 1.8 % wt.). Thus, the resins content is increased by 2 % (from 15.0 to 17.0 % wt.), probably due to the reduced amount of additive on the surface of which the destruction of components of bitumen takes place. Oil yield increases with a decrease in the amount of additives of molybdenum from 72.2 to 74.9 % wt. by slowing down the gasification reactions.

Table 3. Bitumen cracking products composition under different conditions

Conditions	Component composition, % wt.				
	Oil	Resins	Asphaltenes	Gas	Coke
AB	67.6	26.2	6.2	0.0	0.0
Cracking	70.2	19.7	7.3	1.0	1.8
The addition of nanosized powder Mo, % wt.					
1.0	72.2	15.0	6.6	5.2	1.0
0.5	74.7	15.2	7.0	2.0	1.1
0.1	74.9	17.0	5.4	0.9	1.8
The addition of nanosized powder CuO, % wt					
1.0	1.0	71.3	18.6	6.5	2.8
0.5	0.5	73.3	16.4	6.1	2.5
0.1	0.1	73.6	15.4	6.9	2.2

Adding NSP copper oxide changes the direction of the components of the cracking process of natural bitumen and the composition of the obtained products. Reducing the amount of additive NSP copper oxide (as in the case of additives NSP Mo) from 1.0 to 0.1 % wt. it slows down the formation of gas and coke increases. The main difference will decrease the resins content (3.1 % wt.) due to the seal reactions with the formation of asphaltene and solid products cracking. Yield oils at 0.1 % by wt. copper oxide is 73.6 % wt.

Fractional composition of liquid cracking bitumen products changes in the presence of NSP presented in table 4 have been shown. The use of additives helps to increase the depth of the thermal degradation of high-molecular components tar and a significant increase in content of distillate fractions (gasoline and diesel) in the composition of the liquid cracking products.

Table 4. Fractional composition of bitumen cracking products under different conditions

Conditions	Fractional composition, % wt.		
	IBP–200ºC	200–360ºC	>360ºC
AB	4.6	27.9	67.5
Cracking	7.7	30.1	59.4
The addition of nanosized powder Mo, % wt.			
1.0	23.9	37.4	32.5
0.5	27.4	36.5	33.0
0.1	28.8	34.0	34.5
The addition of nanosized powder CuO, % wt			
1.0	12.8	32.2	51.4
0.5	22.5	33.9	39.6
0.1	25.0	29.8	41.1

With increasing of the additive the content of the fraction IBP-200ºC is increased, and diesel, conversely, decreases. This is probably due to the change in the ratio of condensation reactions and the destruction of resin and asphaltene of the bitumen on the surface of the NSP Mo and CuO. It is found that the addition of 1.0 % molybdenum increases the yields of gasoline and diesel fractions by 9.5 and 19.3 % wt., respectively. Reducing the amount of additive allows to increase the yield of gasoline fractions at the expense of the components generated from the destruction of the resin.

Addition of 1.0 % copper oxide increases the content of fractions of IBP-200ºC and 200-360ºC in the cracking products by only 8.2 and 4.3 % wt., which is significantly less compared to additive of molybdenum. Reducing the amount of additives of NSP CuO from 1.0 to 0.1 % wt., allows to increase the content of petrol fractions in products, maximum formation diesel fractions is observed when CuO is 0.5 % - 33.9 % wt. It should be noted that bitumen cracking with nanosize powder molybdenum leads to considerable destruction of bitumen components boiling above 360ºC.

4. Conclusions

Thus high sulfur natural bitumen cracking in the presence of NSP of CuO and Mo allows to destroy a considerable amount of resins at not high gas and coke yields, enlarge low-boiling fractions output in the composition of liquid cracking products (containing more than 50 % rel. distillate fuel).

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**Corresponding author, address: Institute of Petroleum Chemistry, Siberian Branch of the Russian Academy of Sciences, 4, Akademichesky Ave., Tomsk, 634021, Russia, tel.: (+7-3822) 491-020; fax: (+7-3822) 491-879; e-mail: dark_elf26@mail.ru*