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Natural Bitumen Cracking in the Presence of Nanosized Fe_2O_3 and Ni Powders

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Abstract. Catalytic cracking process (CC) of natural bitumen, containing high sulfur (4.7 wt. %) and high-boiling fractions ($>360^\circ\text{C}$), was studied in the presence of Fe_2O_3 and Ni nanosized catalysts under static conditions (autoclave) at 450°C . Both thermal and catalytic cracking experiments were carried out in order to identify CC details and for the reference. Liquid products composition and properties correlation with the process conditions, catalyst nature and quantity have been studied. It is defined that Ni catalyst application in CC result in a higher yield of light fractions in liquid products compared to another thermal cracking, but contributes to increased generation of coke and gas products, which causes reduced liquid products yield. CC in the presence of Fe_2O_3 produces low-viscous semi synthetic oil with low resin and asphaltene content of 8.5 and 3.9 wt. % respectively. Study of high-molecular weight components in bitumen has shown that resin and asphaltene molecules decrease as a result of aliphatic molecules break off and reduction of aromatic cycles.

INTRODUCTION

Heavy oils and natural bitumen play an increasing role in meeting global energy needs for hydrocarbon resources. At the present time, heavy oil and bitumen, are subject to conversion into “synthetic oil”, which then can be used for light oil and industrial chemicals production [1]. One of the major challenges associated with the heavy hydrocarbons processing is high content of high-molecular heteroatomic compounds, such as asphaltenes and resins, which can cause coke build up and catalysts poisoning [1, 2].

To develop effective methods of processing heavy oils and natural bitumen, as well as further products application, it is necessary to understand how the process temperature and nature of catalyst affect various functional groups in resin and asphaltene molecular structures [3–5]. These data are important for in-depth understanding of the changes that occur in resins and asphaltenes during thermal and catalytic cracking, for selecting preferred modernization designs of equipment units and determine processing modes for heavy hydrocarbon feeds at the refineries [6, 7].

EXPERIMENTAL

Natural bitumen from the Ashalchinsky (AB) deposits (Tatarstan, Russia) has been studied, its physicochemical properties are shown in Table 1. High sulfur bitumen ($S_o = 4.7\%$) is shown to have low content of distillate fractions (32.5% of fractions boiling up to 360°C) and high content of resin-asphaltene compounds (over 30 wt. %).

TABLE 1. Bitumen characteristics

Content, wt. %										
C	H	N	S	O (difference)	Oil cut	Resins	Asphaltenes	IBP– 200°C	$200\text{--}360^\circ\text{C}$	$>360^\circ\text{C}$
82.1	10.4	1.0	4.7	1.8	67.6	26.2	6.2	4.6	27.9	67.5

TABLE 2. Fe₂O₃ and Ni nanosized powders characteristics

Catalyst	Specific surface, m ² /g	Average particle size, nm
NSP Fe ₂ O ₃	6.7	114.0
NSP Ni	34.8	20.0

The atomic H/C ratio is 1.52, which is quite low value indicating significant amount of cyclic and aromatic compounds in the bitumen. Nitrogen and oxygen content is also high and is 1.0 and 1.8 % wt. respectively.

Nanosized iron oxide and nickel powders (NSP) were used as catalyst systems. Specific surface area and average size of iron oxide and nickel NSP particles are shown in Table 2. Iron oxide NSP has a specific surface area 6.7 m²/g, which is 5 times less than that of nickel NSP. The average particle size of iron oxide NSP is greater than nickel NSP almost 6 times.

THE EXPERIMENTAL CONDITIONS AND PRODUCT ANALYSIS

Material composition. To isolate asphaltenes, a weighed sample was diluted with a 40-fold excess of hexane and held for a day. The precipitate was filtered, 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. Followed asphaltenes removal, samples were absorbed on silica (ASK, particles size 0.05–0.07 mm) and gradually extracted in Soxhlet extractor using n-hexane for hydrocarbons removal and benzene: ethanol mix (1 : 1) for resins removal.

Fractional composition. Fractional composition of the liquid products from cracking was analyzed by gas-chromatography (GC) using chromatograph “Crystal-2000” equipped with a flame ionization detector (FID) and quartz capillary column 25 m × 0.22 mm, with a stationary phase SE-54, carrier gas-helium. GC analysis was programmed from 80 to 290°C, with 15 °C/min heating rate. The identification and separation of the hydrocarbon chromatograms into gasoline (IBP–200°C) and diesel (200–360°C) fractions were carried out based on the retention times of n-alkanes (hexane and hexadecane), pristane and phytane.

Cracking method. Cracking experiments were carried out in 12 cm³ volume autoclave. Bitumen weight in the experiment was 7 g, the amount of nickel and iron oxide varied from 0.01 to 0.10 wt. % from bitumen weight. Experiments were performed at a temperature 450°C for 100 min in the air. Weights of the empty reactor and reactor with sample load were recorded prior the experiment. After conducting natural bitumen heat treatment the gaseous products yield was determined by the weight loss of the reactor with sample after gas products were removed from the reactor.

After sampling the liquid products, the reactor was washed with chloroform and weighed. The difference between the mass of the reactor before and after the experiment was described as condensation products (coke).

Structural group analysis. Resins and asphaltenes, extracted from the original bitumen samples and bitumen cracking products, were studied with application of the structural group analysis methodology developed at the Institute of Petroleum Chemistry, SB RAS [8]. With the use of the elemental composition, average molecular mass and NMR-spectroscopy data, the structural group analysis allow calculation of the average atom distribution between the structural elements of resins and asphaltenes. This distribution provides information on the molecular structure and composition, as well as the amount and composition of various structural groups.

Elemental composition. Elemental composition of the original bitumen and cracking products was studied using Vario EL Cube CHNS-Analyzer, oxygen is determined by the difference (Table 1).

RESULTS AND DISCUSSION

Bitumen cracking in the presence of nanosized nickel and iron oxide powders leads to a significant degradation of resins and asphaltenes, which is reflected in the data shown in Table 3. When NSP reduced from 0.10 to 0.01 wt. % as generation increases from 5.8 to 9.4 wt. % and condensation products increase from 3.2 to 4.4 wt. %. Asphaltene content in the liquid products of bitumen cracking is 5.8 wt. % in the presence of 0.10% nickel NSP, and 7.1 wt. % in the presence of 0.05% nickel NSP. Asphaltenes yield dropped slightly to 6.8 wt. % in the presence of 0.01% Ni NSP, this is probably due to increased generation of condensation products. Reduction of the nickel NSP amount is found to be leading to acceleration of the oil degradation reactions producing gaseous products, as well as condensation reactions producing resins and asphaltenes. Thus, the most efficient amount of Ni NSP is 0.10%. In

this case the lowest yield of by-products (gas and coke) is observed and not more than 9 wt. %, resins yield is 11.2 wt. %, asphaltenes—5.8 wt. % and the highest yield of oil components is 74.0 wt. %.

The use of iron oxide catalyst in the natural bitumen cracking is changing the direction of its components conversion and as a result the composition of the final products. Reducing the amount of Fe_2O_3 NSP from 1.0 to 0.1%, in contrast to nickel NSP, inhibits generation of gas and coke from 5.8 to 3.1 and from 3.1 to 0.6 wt. % respectively. The asphaltene content is reduced in the products of cracking with iron oxide NSP compared with the content in the initial bitumen. Maximum reduction of 2.3% is observed when 0.10 wt. % of NSP added. Change in asphaltene concentration upon reduction of the added iron oxide NSP is similar to experiments in the presence of Ni NSP: an increase in asphaltene content from 3.9 to 4.5 with NSP reduction from 0.10 to 0.05%, when Fe_2O_3 NSP reduced to 0.01% the amount of asphaltenes is reduced to 4.4 wt. %.

Various amounts of metal NSP's used in the range from 0.10 to 0.01% do not change oil fraction yields, accounting 77.5–78.7 wt. %, which is 10% higher than that in the initial bitumen. The lowest oil yield of 77.5 wt. % is observed in the bitumen cracking products generated with 0.05 Fe_2O_3 NSP. It is most likely due to acceleration of condensation reactions of oils, which produce increased resin content of 8.5 to 11.0 wt. %. When the smallest amount of Fe_2O_3 NSP was used, the resin content reached 13.8%. The high yield of oil fraction in this case is probably caused by the delayed gas generation from oils and condensation products from asphaltenes. Based on the data obtained (Table 3) the most efficient amount of iron oxide NSP used for cracking was 0.10 wt. %.

Fractional composition shown in Table 3 indicate that addition of 1.0 wt % Ni NSP provide with an extra 26.9% of the fractions boiling up to 360°C, and the total yield of gasoline and diesel fractions amounted to 59.4 wt %. Nickel NSP reduction from 0.10 to 0.05 and 0.01% leads to an increased yield of gasoline fractions at 3.1 and 6.3 wt. %, and also to reduction of diesel fractions at 8.9 and 14.3 wt. % respectively.

Application of iron oxide NSP leads to different yields of light fractions compared to cracking in the presence of nickel NSP. The highest yield of these fractions is observed with the addition of 0.10% Fe_2O_3 and amounts 66.0%, where 27.0 wt. % is gasoline and 39.0 wt. % is diesel fractions. When lowered the amount of added catalyst, the decrease in gasoline fraction yield to 17.8% is observed at 0.05% Fe_2O_3 and 10.1% at 0.01 Fe_2O_3 . Yields of the fractions boiling in the range 200–360°C increase up to 42.2 and 41.8% wt in the presence of reduced NSP amount. Thus, based on the fractional composition data the most efficient amount of NSP for both Fe_2O_3 and Ni is 0.10 wt. %. In these conditions, is observed the increase of light fractions (IBP–360°C) in the presence of Ni NSP is 26.9%, and in the presence of Fe_2O_3 NSP is 33.5 wt. %.

In order to define principal trends of the high-molecular weight components destruction, structural-group analysis of resins and asphaltenes in the initial bitumen and cracking products generated in the presence of most effective Ni and Fe_2O_3 NSP amount was carried out (Table 4). The data indicate that NSP addition reduces the size of the average molecules of resins and asphaltenes.

TABLE 3. Material and fractional composition of the bitumen cracking products in the presence of Ni and Fe_2O_3 nanopowders

Sample	Content, wt. %					Fractional composition, wt. %		
	oils	resins	asphaltenes	Gas	Coke	IBP-200°C	200–360°C	>360°C
Initial Bitumen	67.6	26.2	6.2	0	0	4.6	27.9	67.5
After cracking	70.2	19.7	7.3	1.0	1.8	7.7	30.1	59.4
Products of cracking with NSP								
In the presence of Ni NSP, wt. %:								
0.10	74.0	11.2	5.8	5.8	3.2	22.3	37.1	31.6
0.05	68.2	12.2	7.1	8.6	3.9	25.4	28.2	33.9
0.01	66.6	12.8	6.8	9.4	4.4	28.6	22.8	34.8
In the presence of Fe_2O_3 , wt. %:								
0.10	78.7	8.5	3.9	5.8	3.1	27.0	39.0	25.1
0.05	77.5	11.0	4.5	5.6	1.4	17.8	42.2	33.0
0.01	78.1	13.8	4.4	3.1	0.6	10.1	41.8	44.4

TABLE 4. Structural-group parameters of resin and asphaltene molecules of the Ashalchinskoye bitumen and the cracking products in the presence of Fe₂O₃ and Ni nanopowders

Sample	Content, wt. %	MW, amu	H/C	Structural parameters of average molecules			
				m_a	K_{ar}	K_{sat}	C_n
Resins*	26.2	640	1.29	1.7	4.1	3.0	13.4
Resins**	11.2	553	1.18	1.7	3.9	2.6	9.2
Resins***	8.5	429	1.12	1.5	3.3	2.7	3.5
Asphaltenes*	6.2	1285	1.11	2.9	9.7	9.9	6.5
Asphaltenes**	5.8	812	0.73	2.3	7.2	12.9	1.1
Asphaltenes***	3.9	781	0.72	2.3	7.3	11.1	1.0

* Initial, ** after cracking with 0.10 Ni NSP, *** after cracking with 0.10 Fe₂O₃ NSP; MW—molecular weight; m_a —average number of blocks in the molecule; K_{ar} and K_{sat} —the amount of aromatic and naphthenic cycles; C_n —amount of carbon atoms in the aliphatic portions

The following reduction is observed in resins: molecular weight (MW) reduces 87 and 111 amu, atomic ratio of H/C decreases 1.18 and 1.12, the amount of K_{ar} 0.2 and 0.8, K_{sat} reduces 0.4 and 0.3 and C_n 4.2 and 9.9 in the presence of Ni and Fe₂O₃ NSP, respectively. Greater reduction of these parameters in resins after cracking with Fe₂O₃ NSP is due to a deeper destruction of these components leading to oil generation.

Changes of the average asphaltene molecule's structure are generally similar to those observed for the resins. The main difference is that asphaltene molecules have increased amount of saturated cycles compared to resins. Asphaltene molecules in the liquid products generated using Ni NSP are noted to have the highest number of saturated cycles, which is probably due to a faster generation of asphaltenes from oils and resins.

CONCLUSION

It is found that cracking of bitumen in the presence of Ni and Fe₂O₃ NSP can significantly increase the yield of motor fuels and oil distillates compared to thermal cracking. Correlation of the liquid products of cracking composition and the amount of NSP has been defined. The most efficient amount of Ni and Fe₂O₃ NSP is 0.10%, when in the products of cracking the highest content of the fractions boiling up to 360°C is observed (59.4 and 66.0 wt. % for Ni and Fe₂O₃, respectively), and destruction of resin and asphaltene components reach 47.5 and 61.7%. Changes of resin and asphaltene structural parameters after cracking with the preferred NSP amount is defined, as well as the impact of selected NSPs on the resin and asphaltene structure.

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