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Cracking of Vacuum Residue in the Presence of Nanoscale Tungsten Carbide and Nichrome Powders

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Abstract

The cracking of vacuum residue from the Novokuibyshevsk refinery was investigated. The yields of gas, liquid, and solid products were determined at a temperature of 500 °C and a process time of 10–30 min. The composition of oils of vacuum residue cracking products was explored. It was demonstrated that the addition of nanoscale WC/Ni-Cr powder increased the yield of fractions with the boiling point up to 360 °C by 66.4 mass % and 40.4 mass % compared to the initial vacuum residue and cracking without nanoscale powder, respectively. The effect of nanoscale WC/Ni-Cr powder on changes in molecular structures of high-molecular-mass heteroatomic components (resins and asphaltenes) was examined.

Keywords: vacuum residue, cracking, hydrocarbons, resins, asphaltenes, molecular structure

INTRODUCTION

Extra-heavy crude oil and natural bitumen are becoming an important source of raw materials in the course of exhausting light and middle oil reserves. World heavy oil and natural bitumen resources are much higher than the reserves of light ones and are assessed at more than 810 billion t [1]. Canada and Venezuela, and also Mexico, the USA, Russia, Kuwait, and China have significant reserves of natural bitumen. According to different estimates, from 30 to 75 billion t of heavy oil and natural bitumen are concentrated in the territory of the Russian Federation [1]. The development of light and medium oil fields pre-determines the increasing involvement of heavy oil raw materials in the processing [2]. No less important is an increase in the depth of oil refining due improving the efficiency of the processing of secondary oil raw materials (fuel oil, vacuum residue, cracking residues, etc.) [3].

Currently, the processing of heavy oil residues (HORs) used at the Novokuibyshevsk refinery is based on hydro and coking processes. In the future, with greater involvement in the process of super heavy oils and natural bitumens and an increase in the fraction of HORs, procedure cost would inevitably increase due to tightening conditions (pressure, temperature, new catalysts, and a large amount of hydrogen) [4–8].

Thus, the processing of vacuum distillates and residual fractions is complicated by high contents of resin-asphaltene materials, heteroatomic compounds, and metal-containing components therein [9, 10]. The development of thermal decomposition methods for resin-asphaltene components with the production of additional amounts of light fractions without using hydrogen would allow significantly improving the efficiency of thermal processes of heavy hydrocarbon raw materials processing and consequently obtaining oil products with lower contents of high-molecular-

mass and heteroatomic compounds and a high content of distillate fractions [11–15].

In order to develop efficient methods for processing and further using HORs conversion products, information regarding the effect of the temperature and nature of catalysts on various functional groups in the structure of molecules of resins and asphaltenes leading to their decomposition is required. They are important for deeper understanding changes that proceed in resins and asphaltenes in thermal and catalytic cracking processes, selection of optimum schemes for modernization of plants and determination of modes of heavy hydrocarbons raw materials processing by oil processing enterprises [16–19].

The purpose of the research was to increase the yield of light fractions due to the decomposition of resin-asphaltene components during cracking vacuum residue from Novokuibyshevsk refinery in the presence of nanoscale WC/Ni-Cr powder without using hydrogen.

EXPERIMENTAL

Research object

Vacuum residue from the Novokuibyshevsk refinery was the research object. Transformations of high-molecular-mass vacuum residue components were investigated during high-temperature cracking at 500 °C and lengths of 10–30 min.

According to the data in Table 1, the initial vacuum residue is characterised by a high content of resin-asphaltene components, mass %: resins 33.6, asphaltenes 5.7, and oils 60.7. Raw materials are high-sulphur (3.04 % by mass of sulphur). The low H/C atomic ratio (1.56) testifies high cyclicality of the components contained in the vacuum residue. The initial boiling point (IBP) is high and equals to 343 °C; the content of the IBP 360 °C fractions is only 1.4 mass %. Vacuum residue produced by distillation of commercial oil at the Novokuibyshevsk refinery is heavy hydrocarbon raw materials with high thermal stability, as it has already been thermally treated.

Catalytic additive

In order to increase the cracking efficiency, nanoscale tungsten carbide and nichrome powders (WC/Ni-Cr) produced by mechanical treatment in a powder ratio of 1 : 3 were taken. They have high mechanical strength and resistance to

sulphur poisoning. In the nanoscale state, they are promising for use as catalysts for a wide range of reactions including hydrocarbon reforming and dehydrogenation [12]. Nickel and chromium are used for dehydrogenation reactions (if there is no hydrogen in the system) and C–C bond breaking. According to X-ray fluorescence and X-ray phase analysis, nanoscale powder contains 26.1 mass % of WC and 73.9 mass % Ni-Cr. The amount of the introduced additive experimentally determined earlier [20] is 0.10 mass %.

Cracking conditions

Vacuum residue cracking was carried in a 12 cm³ autoclave. The mass of vacuum residue loaded into the reactor was 7 g. Experiments were carried out at a temperature of 500 °C and lengths of 10, 20, and 30 min.

The mass of the reactor prepared to cracking, without a sample and with it was recorded during experiments. At the end of vacuum residue thermal treatment, the yield of gaseous products was determined according to reactor mass loss after removing from gas products. Afterwards, liquid cracking products were selected, and then the reactor was washed with chloroform and weighed. The resulting difference between reactor mass before the experiment and after was determined as solid products, *i.e.* coke.

Determination of the material composition of liquid products

Asphaltene content was determined as follows: the sample was diluted with *n*-hexane in a 1 : 40 volume ratio; the solution was kept for 1 day, the precipitate was filtered out, placed in a paper cartridge and washed with hexane from oils and resins in a soxhlet apparatus. Afterwards, asphaltenes from the cartridge were washed out with chloroform, the solvent was distilled off and asphaltenes were dried to constant weight.

The hexane solution was added to the deasphaltized sample, the solvent was removed and isolated maltenes were applied onto a layer of activated ASK silica gel (1 : 15 ratio). The resulting mixture of silica gel and adsorbed material was loaded into the soxhlet extractor and petroleum oils were sequentially washed out with *n*-hexane, while resins – with a mixture of ethanol and benzene (1 : 1) at boiling points of these solvents. The content of silica gel resins (SRT 1246-2011) in bitumen was determined after solvent removal.

Determination of the fractional composition of liquid products

The fractional composition of liquid cracking products was determined by gas-liquid chromatography using a Crystal-2000M chromatograph with a flame ionization detector (FID) in a quartz capillary column with SE-54 stationary phase, helium gas carrier. A chromatographic procedure was carried out under conditions of linear programming of temperature from 80 to 290 °C at the rate of heating of the thermostat column of 15 °C/min. Hydrocarbons were identified on chromatograms by the retention times of *n*-alkanes that were hexane and hexadecane (internal standard), and also by the typical exit time of pristane and phytane. After decoding chromatograms, the fractional composition of cracking liquid products was determined in accordance with GOST R 56720-2015.

Determination of group composition of oils

Group hydrocarbon composition of oils of initial raw materials and their cracking products were determined by liquid adsorption chromatography using activated Al₂O₃ (II Brockmann activity grade). A 75 × 1.8 cm chromatographic column was filled with a "wet" sorbent in a 1 : 80 sample/sorbent ratio (by mass). The sample was mixed with hexane and equally distributed along the entire surface of the sorbent. Fractions of saturated, mono- and biaromatic hydrocarbons (HC) were isolated by *n*-hexane; three aromatic hydrocarbons were eluted with a mixture of hexane/benzene (3 : 1 by volume) and polyaromatic hydrocarbons – with a mixture of alcohol/benzene (1 : 1 by volume). The separation of different HC was monitored according to electronic spectra of eluate absorption that were recorded using a Specord UV-VIS spectrometer. The losses during distilling off the solvents from eluates were not higher than 2.5 mass %.

Structural-group analysis of resin and asphaltene molecules

Resins and asphaltenes isolated from vacuum residue and cracking products were explored by structural-group analysis (SGA) using the procedure based on the combined use of determination results for the elemental composition, molecular weights, and ¹H NMR data [21].

Elemental analysis of resins and asphaltenes was determined using Vario EL Cube CHNS ana-

lyser. Molecular mass were measured by cryoscopy in naphthalene using the Krion device (IPC SB RAS, Tomsk, Russia). The ¹H NMR spectra were recorded on the Avance-AV-300 Fourier spectrometer with 1 % concentration of resins and asphaltenes using CDCl₃ as a solvent and hexamethyldisiloxane as an internal standard.

RESULTS AND DISCUSSION

Vacuum residue cracking

Tables 1 and 2 present the data on the functional composition and material balance of the composition for liquid products of cracking in the presence of nanoscale powder and without them. Cracking for 10 min leads to the decomposition of 11.9 mass % of resins to form an additional amount of oils (4.2 mass %). Condensation reactions proceed slowly. The amount of the resulting asphaltenes and compaction products is low that is 1.2 and 2.8 mass %, respectively. An increase in the content of light fractions in the liquid product is 13.8 mass %. Increasing the cracking time till 20 min accelerates condensation reactions; asphaltene and coke contents increase by 1.8 and 6.6 mass %, respectively, compared to the initial vacuum residue, while those of oils decrease by 0.8 mass %, in comparison with source raw materials and by 4.0 mass % against cracking for 10 min. The yield of gasoline and diesel fractions increased giving 7.2 and 15.8 mass %, respectively.

When the cracking time is 30 min, condensation reactions along the route, such as oils → resins → asphaltenes → coke, prevail over decompo-

TABLE 1

Fractional composition of the initial vacuum residue, and also its thermal and catalytic cracking products at 500 °C

Cracking time, min	IBP, °C	Fractional composition, mass %		
		IBP, °C		
		200	200–360	>360
0	343	0	1.4	98.6
Cracking without NSP*				
10	154	2.9	12.3	78.3
20	133	7.2	15.8	62.8
30	110	9.3	18.1	53.9
Cracking in the presence of 0.1 mass % of NSP*				
10	112	5.5	17.9	75.0
20	94	15.5	19.2	58.6
30	42	34.6	33.2	19.3

Note. NSP is nanoscale powder.

TABLE 2

Material balance of the initial vacuum residue, and also its thermal and catalytic cracking products at 500 °C

Cracking time, min	Content, mass %				
	Oils	Resins	Asphaltenes	Coke	Gas
0	60.7	33.6	5.7	0.0	0.0
Cracking without NSP*					
10	64.9	21.7	6.9	2.8	3.7
20	59.9	18.4	7.5	6.6	7.6
30	54.7	16.1	10.5	10.4	8.3
Cracking in the presence of 0.1 mass % NSP*					
10	65.2	27.3	5.9	0.2	1.4
20	68.2	17.7	7.4	1.6	5.1
30	76.8	8.1	2.2	6.2	6.7

Note. NSP is nanoscale powder.

sition reactions (asphaltenes → resins → oils → gas). This is indicated by a significant increase in the yields of asphaltenes and coke (by 3.0 and 3.8 mass %, respectively) compared to initial raw materials. Herewith, the content of resins in liquid cracking products is 16.1 mass %, which is by 2.3 and 5.6 mass % lower than those when vacuum residue cracking for 20 and 10 min, respectively. The amount of oils decreased by 6.0 and 5.2 mass % compared to the initial vacuum residue and its cracking products with a duration of 20 min, partly due to gas formation reactions (8.3 mass %) and partially due to the enlargement of molecules and the formation of resinous components from oils. At the same time, the yield of light fractions (IBP – 360 °C) in liquid cracking products is maximum and equals to 27.4 mass %.

The cracking of vacuum residue in the presence of nanoscale powder for 10 min is accompanied by the slowing down of condensation and decomposition reactions compared to the process without the addition of nanoscale powder. There are generated 0.2 mass % of coke and 1.4 mass % of gaseous products, which is by 2.6 and 2.5 mass % lower than those during thermal cracking.

The slowing down of cracking reactions is also indicated by decreasing resin content in the composition of liquid products only by 6.3 mass % and by an increase in the content of oils by 4.5 mass %, whereas it is 11.9 mass % during cracking without nanoscale powder. Nevertheless, herewith the yield of light fractions is 23.4 mass %, which is 8.2 mass % higher than the cracking without nanoscale powder. It is likely that their addition with a time of 10 min promotes the cracking of the heavy portion of oils and the formation of

lower molecular mass components that are part of gasoline and diesel fractions.

During cracking of vacuum residue in the presence of nanoscale powder for 20 min, decomposition (the formation of oils from resins and gas from oils) and condensation reactions (generating asphaltenes from vacuum residue and coke from asphaltenes) are accelerated. The yields of oils and gas are increased by 3.0 and 3.7 mass %, respectively, those of resins decrease by 9.6 mass % compared to cracking with nanoscale powder for 10 min. The outputs of asphaltenes and coke grow up by 1.5 and 1.4 mass %, correspondingly. Deeper decomposition of high-molecular-mass components leads to increased yields of gasoline and diesel fractions by 10.0 and 1.3 mass % compared to cracking with nanoscale powder for 10 min. As demonstrated by vacuum residue cracking results over 20 min with the addition of nanoscale powder and without it, nanoscale powder facilitates the slowing down of generating coke and asphaltenes from resins, in other words, there is an acceleration of decomposition of resins to form additional amounts of oils.

Cracking for 30 min with the addition of nanoscale powder is characterised by the maximum decomposition of vacuum residue components. Resin content is reduced by 25.5 and 8.0 mass % compared to the initial vacuum residue and cracking without the addition, respectively. The amount of oils in liquid products is increased by 18.1 and 22.1 mass % compared to the original vacuum residue and cracking without the addition, correspondingly. Asphaltene content is minimum (2.2 mass %). The yields of by-products of gas and coke are lower than those when cracking

TABLE 3

Hydrocarbon composition of oils of cracking products of the initial vacuum residue, and also its thermal and catalytic cracking products at 500 °C

Sample	Oil yield, mass %	Hydrocarbon composition of oils, mass %			
		Saturated (<i>n</i> -alkanes)	Aromatic		
			Mono-	Di-	Tri- + poly-
Initial	60.7	35.1 (11.1)	14.7	5.2	5.7
After 30 min cracking at 500 °C without NSP	54.7	23.8 (7.4)	11.3	6.7	12.9
Same, in the presence of NSP	76.8	43.0 (23.0)	9.5	2.8	20.7

without additives, by 1.6 and 4.2 mass % respectively. The content of fractions boiling out till 360 °C is maximum and equals to 67.8 mass %.

In such a way, when the nanoscale powder is added, reaction rates of condensation of resins to generate asphaltenes and coke, and also to give gaseous cracking products are slowed down. There is a deeper decomposition of resins and additional amounts of lower molecular mass components that are part of light fractions are generated.

In order to deeper explore vacuum residue cracking, group analysis of oils, and also their GC-MS examination were carried out to determine hydrocarbon composition and *n*-alkane content in oils of the initial vacuum residue and cracking products at 500 °C and 30-minutes length in the presence of nanoscale powder and without it (Table 3). In oils of the initial vacuum residue, there are prevailing saturated hydrocarbons (35.1 mass %), of which 11.1 mass % of *n*-alkanes. The contents of mono-, bi-, and a sum of tri- and polyaromatic hydrocarbons are 14.7, 5.2, and 5.7 mass %, respectively.

During vacuum residue cracking, oil content is reduced by 6.0 mass %, which is probably due to condensation of components of oils and gas formation (the content of *n*-alkanes decreased by 3.7 mass %). The contents of saturated and monoaromatic compounds are decreased by 11.3 and 3.4 mass %, respectively, apparently due to their partial condensation and the formation of more condensed components (tri- and polyaromatic ones, and also resins). This is indicated by increasing the contents of bi-, and also a sum of tri- and polyaromatic hydrocarbons by 1.5 and 7.2 mass %, correspondingly.

The addition of nanoscale powder results in an increase of the yield of oils by 16.1 mass % (see Table 2) due to a significant increase in saturated series and a sum of tri- and polyaromatic moieties of hydrocarbons (7.9 and 15.0 mass %, correspondingly). The content of *n*-alkanes in saturated hydrocarbons

is increased from 11.1 to 23.0 mass % due to the deep decomposition of resin-asphaltene components, the molecular structure of which contains *n*-alkane moieties. It is likely that they are detached during cracking with nanoscale powder and pass to the composition of saturated hydrocarbons. The contents of mono- and diaromatic hydrocarbons are reduced by 5.2 and 2.4 mass % probably due to condensation reactions to form tri- and polyaromatic hydrocarbons.

Structural-group analysis of resins and asphaltenes

In order to determine the main directions for the decomposition of high-molecular-mass components, structural-group analysis of resins and asphaltenes isolated from the initial vacuum residue and cracking products was carried out (Table 4). It was found that average species of initial resins of vacuum residue were averagely comprised of one or two components ($m_a = 1.5$); the average structural component contained 6.4 rings including 3.1 aromatic and 3.3 naphthenic ones. Asphaltene molecules are comprised of two components ($m_a = 2.0$); the average structural component consists of 13.4 rings including 5.6 aromatic and 7.8 naphthenic ones. The H/C atomic ratio in resins and asphaltenes is low – 1.42 and 1.03, respectively. Aromaticity index of resin molecules is significantly lower than that of asphaltenes, which attests to a significantly greater fraction of aromatic carbon atoms in average asphaltene species. The degree of substitution of aromatic rings in resins is higher than that in asphaltenes. Resins have significant numbers of carbon atoms in aliphatic moieties – 14.5, whereas asphaltenes – just 1.9 atom.

During bitumen cracking for 30 min, the average structure of asphaltene molecules is changed. The molecular mass (MM) of asphaltenes is decreased from 718 to 702 amu; the total number of rings – from 13.4 to 12.6 (resulting from reducing

TABLE 4

Structural-group parameters of resin and asphaltene molecules in the initial vacuum residue, and also its thermal and catalytic cracking products at 500 °C

Parameter	Asphaltenes			Resins		
	1	2	3	1	2	3
Average molecular mass	718	702	411	600	472	329
Elemental composition, mass %:						
C	82.91	82.00	83.24	81.66	78.46	81.12
H	7.14	5.75	4.56	9.64	8.18	6.63
N	1.74	1.57	1.21	1.29	1.48	2.31
S	4.93	4.57	2.97	4.07	3.75	3.42
O	3.28	11.86	8.02	3.34	8.31	6.5
H/C atomic ratio	1.03	0.84	0.66	1.42	1.25	0.98
Number of rings						
K_t	13.4	12.6	11.4	6.4	4.2	6.7
K_a	5.6	7.4	3.7	3.1	3.7	2.5
K_{sat}	7.8	5.2	7.7	3.3	0.5	4.2
m_a	2.0	2.2	1.6	1.5	1.6	1.3
σ_a	0.48	0.39	0.54	0.55	0.43	0.23
Carbon atoms distribution, %						
γ_a	46.4	62.0	57.7	31.9	50.8	49.0
γ_n	49.8	35.9	40.6	32.6	6.3	48.0
γ_p	3.8	2.1	1.7	35.5	42.9	3.0
Number of carbon atoms of different type in average species:						
C_a	23.0	29.7	16.4	13.0	15.7	10.9
C_n	24.7	17.2	11.6	13.3	1.9	10.7
C_{aliph}	1.9	1.0	0.5	14.5	13.2	0.7
C_α	7.9	7.9	6.7	5.6	5.0	2.0
C_γ	1.9	1.0	0.4	3.6	1.7	0.6

Note. 1 – initial vacuum residue; 2 and 3 – products of the thermal cracking of vacuum residue (2 – for 30 min, 3 – in the presence of nanoscale powder for 30 min). The number of carbon atoms in average species: C_a – in aromatic and C_n – in naphthenic rings, C_{aliph} – in aliphatic fragments, C_α – in α -position to the aromatic ring, C_γ – in β -positions and further from the aromatic ring. The number of rings: K_t – total, K_a – aromatic, and K_{sat} – saturated. The fraction of carbon atoms: γ_a , γ_n , and γ_p – in aromatic, naphthenic and paraffinic fragments, respectively; σ_a is the degree of substitution of aromatic rings; m_a is the number of molecular components.

the content of aromatic cycles from 5.6 to 7.4 and naphthenic ones from 7.8 to 5.2). The number of carbon atoms in aliphatic moieties (C_{aliph}) is decreased from 2 to 1. These changes in average asphaltene species indicate that molecules during vacuum residue cracking become more condensed, with a lower number of aliphatic moieties.

Resin content during vacuum residue cracking for 30 min is reduced more than twice (Table 2). The molecular mass in average oil species of cracking products is decreased from 600 to 472 amu and the total number of rings – from 6.4 to 4.2 (due to naphthenic cycles from 3.2 to 0.5 and a slight increase in aromatic ones from 3.1 to 4.7).

The number of carbon atoms in aliphatic moieties (C_{aliph}) is reduced by just one due to the

detachment of aliphatic substituents to form gaseous products, which is also indicated by a decrease in the H/C ratio from 1.42 to 1.25. The degree of substitution is decreased by 12 % due to partial detachment of substituents.

When 0.1 mass % of nanoscale powder was added, the trend of flowing cracking reactions, and also structural characteristics of average species of resins and asphaltenes were significantly changed. There was a decrease in MM of asphaltenes by 307 amu and 291 amu compared to that of the initial vacuum residue and cracking without nanoscale powder, respectively. The total number of rings and components reduced by 2.0 and 0.4, correspondingly, compared to initial asphaltenes. Herewith, the number of aromatic cy-

cles in asphaltene molecules decreased by 1.9 and 3.7 compared to initial asphaltenes and ones after cracking without nanoscale powder. The atomic H/C ratio became lower by 0.37; the number of carbon atoms in aliphatic moieties (C_{aliph}) decreased by 1.4. In such a manner, the slowing down of formation reaction of asphaltenes during cracking vacuum residue with nanoscale powder promoted the fact that average asphaltene species became more condensed and coke-like ones.

The average molecular mass of vacuum residue crating products in the presence of nanoscale powder is reduced almost twice compared to the initial vacuum residue – from 600 to 329 amu, which is due to C–C bond breaking between cycles and aliphatic moieties. This is indicated by a decrease in C_{aliph} from 14.5 to 0.7. The number of rings in average species is insignificantly increased – from 6.4 to 6.7; herewith, K_a is decreased from 3.1 to 2.5, while K_{sat} grows up from 3.3 to 4.2. Greater condensability of molecules is also indicated by the fact that when the number of rings is increased, the quantity of carbon atoms in naphthenic cycles (C_n) is decreased from 13.3 to 10.7. The atomic H/C ratio is insignificantly decreased – from 1.42 to 0.98 due to the almost complete detachment of the alkyl framework. At the same time, the degree of substitution (σ_a) of aromatic rings is decreased by 22 %.

CONCLUSION

The research paper presents the results of the investigation on the effect of process time of the thermal cracking of vacuum residue from the Novokuibyshevsk refinery on the yield and the fractional composition of the products formed. The addition of nanoscale WC/Ni-Cr powder has been explored during cracking of vacuum residue from the Novokuibyshevsk refinery. Furthermore, it has been demonstrated that in its presence the yield of light fractions (IBP – 360 °C) increases from 1.4 to 66.4 mass % during vacuum residue cracking.

It has been determined that the cracking of vacuum residue with the addition of WC/Ni-Cr powder at 500 °C for 30 min is accompanied by the decomposition of mono- and diaromatic hydrocarbons. The content of oil components is enhanced by 16.1 mass % due to saturated, and also tri- and polyaromatic hydrocarbons because of decomposition of resin-asphaltene components. The

content of *n*-alkanes in the composition of oils is increased by more than twice compared to that of the initial bitumen (from 11.1 to 23.0 mass %) resulting from the decomposition of high-molecular-mass *n*-alkanes and the detachment of aliphatic moieties of resin molecules (carbon content is decreased from 14.5 to 0.7 atoms).

It has been demonstrated that the addition of nanoscale WC/Ni-Cr powder during vacuum residue cracking facilitates substantial decomposition of resin-asphaltene components. It has been revealed that average structures of high-molecular-mass components are decreased in size due to the detachment of the aliphatic framework. In addition, the number of components that mainly consist of aromatic rings is decreased in the composition of average species of resins and asphaltenes due to C–C bond breaking between components. Presumably, the contents of saturated, and also tri- and polyaromatic hydrocarbons is increased in the composition of oils due to the detachment of components and alkyl chains from resin and asphaltene molecules.

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