Chemistry for Sustainable Development **28** (2020) 425–434

YOUNG SCIENTIST' PAGES

UDC 665.66, 665.652.86

DOI: 10.15372/CSD2020249

The Effect of Nanosized Molybdenum Additive on the Composition of the Cracking Products of Oxidized Vacuum Gasoil

YU. A. IOVIK[1], E. B. KRIVTSOV[1,2]

[1]Institute of Petroleum Chemistry, Siberian Branch of the Russian Academy of Sciences,
Tomsk, Russia

E-mail: jiosephe@gmail.com

[2]Tomsk State University,
Tomsk, Russia

(Received January 31, 2020; revised March 31, 2020)

Abstract

The high cost of hydrocatalytic processes is the reason of the attention of researchers to the search for alternative ways to process high-sulphur vacuum distillates. Pre-oxidation followed by cracking is considered as a promising method for refining petroleum products. This approach enables efficient destruction of polyaromatic sulphur-containing compounds in heavy hydrocarbon raw materials yielding additional amounts of distillate fractions. The effect of nano-sized molybdenum powder on the composition and quality of the products of cracking of vacuum gasoil oxidized preliminarily with a mixture of hydrogen peroxide with formic acid was investigated. It was demonstrated that the use of an optimal amount of nanosized molybdenum powder as the additive allows a substantial decrease in gas generation due to a decrease in the rates of aromatization and dealkylation of the oxidized high-molecular compounds including sulphur-containing ones. The effect of the amount of Mo additive on the transformation patterns of such sulphur-containing compounds as thiophene, benzo- and dibenzothiophene during the combined process was revealed. The changes in the structural-group parameters of resins and asphaltenes in the products of cracking of oxidized vacuum gasoil in the presence of the additive in different amounts were investigated. The data obtained allow us to extend our understanding of thermal transformations of the oxidized components of vacuum gasoil, which is an important step in the development of a technological scheme for processing high-sulphur gasoils relying on the combination of preliminary oxidation and cracking.

Keywords: sulphur-containing compounds, oxidative desulphurization, cracking, hydrogen peroxide

INTRODUCTION

Worsening of the quality of raw material entering oil refinery leads to a regular increase in the fraction of vacuum distillates obtained as a result of distillation. Further processing of these fractions is complicated by the high content of resinous-asphaltenous substances (RAS), as well as metals and heteroatomic (S, O, N) compounds [1]. Sulphur-containing compounds that are most widespread in petroleum products cause poisoning of hydrogenation catalysts and corrosion of the equipment [2]. At present, the processes of practical interest are those used in addition to widely used catalytic cracking. These additional processes allow one to prepare the raw material so that the content of heteroelements, metal and coke-generating components would decrease. These additional processes include hydrotreating, deasphaltation and demetallization [3–5]. In a number of works, separate completely hydrogen-free processes are considered: extraction-based [6, 7] and adsorption-based [8, 9] desulfurization, biodesulphurization [10].

One of the methods to process heavy hydrocarbon raw materials with efficient removal of polyaromatic compounds to obtain additional amounts of distillate fractions is a combination of oxidation and subsequent cracking. This method is practically significant because the reactivity of polyaromatic compounds in oxidation processes is higher than that of thiophene and benzothiophene [11, 12]. In addition, during the oxidation of sulphur atoms, the C–S bond becomes weaker and is easier destroyed during cracking [13, 14]. One of the substantial advantages of preliminary oxidative treatment is process conduction at room temperature and atmospheric pressure. Widely used oxidizers include hydrogen peroxide [15–17], atmospheric oxygen [18], organic peroxides [19] and some other compounds [20, 21].

However, it was demonstrated in [22] that preliminary oxidation of vacuum gasoil (VG) is not a selective process: not only sulphur-containing compounds but also aromatic hydrocarbons participate in the reactions. As a result of polarity change, the products of oxidation of the indicated types of compounds are detected in the composition of resins, the fraction of which decreases substantially. In the works carried out at the Institute of Petroleum Chemistry SB RAS (IPC SB RAS), the efficiency of the addition of nanosized powder (NSP) of molybdenum with the average particle size of 500 nm in the cracking of fractions boiling out within the range of 360–500 °C was stated. The authors of [23] showed that thermolysis of bitumen with the optimal amount of the additive allows obtaining additional amounts of distillate fractions, with the same level of gas and coke formation, due to enhancement of the depth of destruction of high-molecular components of oils, as well as RAS. The use of this additive for cracking of oxidized vacuum gasoil (OVG) will presumably allow one to enhance the depth of destruction of oxidized high-molecular components avoiding substantial losses due to gas formation.

The goal of the present work was to study the effect of the addition of molybdenum NSP on the composition and quality of the products of thermal treatment of OVG.

EXPERIMENTAL

Object of study

The VG from the Novokuybyshevsk refinery was investigated. Its physicochemical characteristics are represented in Table 1. The chosen gasoil belongs to high-sulphur species (sulphur content 2.02 mass %). The initial boiling point (IBP) of gasoil is 201 °C, about 20 mass % of distillate fractions are evaporated at a temperature up to 360 °C.

Oxidative treatment

Oxidation of VG with a mixture of hydrogen peroxide (H_2O_2) and formic acid (HCOOH) was carried out at room temperature in a reactor equipped with a mixer (mixing rate: 2500 r.p.m.).

TABLE 1

Characterization of vacuum gasoil from the Novokuybyshevsk refinery

Parameter	Value
Elemental composition, mass %:	
Carbon	82.62
Hydrogen	11.80
Nitrogen	0.94
Sulphur	2.02
Oxygen, *etc.*	2.62
H/C	1.71
Fraction composition, mass %:	
Initial boiling temperature, °C	201
200–360 °C	18.5
>360 °C	81.5
Material composition, mass %:	
Oils	91.3
Resins	8.6
Asphaltenes	0.1
Content of sulphurous compounds, mass %:	
Thiophene, Benzothiophene	0
Dibenzothiophene	0.012
$\sum C_1$-Dibenzothiophene	0.334
$\sum C_2$-Dibenzothiophene	1.239

We used oxidation conditions that were established previously: the molar ratio of sulphur in VG (S_o) and the used amount of hydrogen peroxide S_o/H_2O_2 = 1 : 5, process duration 90 min [24]. The molar ratio of H_2O_2/HCOOH was 3 : 4.

Thermal treatment

Cracking of initial and oxidized vacuum gasoil was carried out in autoclave reactors 12 cm^3 in volume. The mass of the sample portion was 7 g. Mass was measured using the analytical balance AND HR-200 (Japan) of the 1st class of precision with the discreetness of 0.1 mg.

The material balance was calculated as follows: reactor mass without the sample was measured, and then the mass of the reactor with the sample prepared for cracking was determined. The yield of gaseous products corresponded to the mass loss by the reactor with the sample after degassing. After the removal of liquid products, the reactor was washed with chloroform and weighted. Thus obtained difference between the mass of the reactor before the experiment and its mass after the experiment was determined as the mass of coke. The cracking temperature was 500 °C, the duration of the process was from 15 to 60 min.

Characterization of nanosized molybdenum powder

The nanosized molybdenum powder was introduced in the amount of 0.01–0.15 mass %. The specific surface area of NSP of molybdenum is 3.3 m^2/g, the average particle size is 500 nm. The choice of the additive was made on the basis of the works carried out at the IPC SB RAS previously [23]. The microstructure of molybdenum NSP before and after the process was studied with the help of the scanning electron microscope TM-3000 (Hitachi, Japan) equipped with the system of energy-dispersive X-ray (EDX) microanalysis Quantax 70 (Bruker, Germany). The recording was carried out with the accelerating voltage of 15 kV. Nanometre-sized molybdenum powder is represented by the particles of the regular spherical shape forming agglomerates (Fig. 1, *a*). According to the EDX-spectrum, molybdenum oxides are present in the powder surface (see Fig. 1, *b*).

Research procedures

The material composition of VG, OVG and the products of their cracking was determined using a standard scheme (STO 1246–2011). The content of asphaltenes was determined using the cold Golde method.

The fraction composition of the liquid products of cracking was determined by means of gas-liquid chromatography (GLC) with the help of Kristall-2000M chromatograph (Khromatek, Russia) with the flame ionization detector. Linear temperature rise from 50 to 290 °C was performed with a heating rate of 15 °C/min. The length of the capillary column was 30 m, the inner diameter 0.25 mm. The content of petrol and diesel fractions was calculated on the basis of retention times of *n*-alkanes (undecane and heneicosane).

Sulphur content was determined according to GOST R 51947–2002 by means of energy-dispersive X-ray fluorescence spectrometry using a Spektroskan SL instrument (Spektron, Russia). Analysis of sulphurous compounds was carried out by means of GLC with a Kristall-2000M chromatograph with the flame photometric detector, with linear temperature rise from 50 to 290 °C, the rate of column heating was 4 °C/min. A capillary column was used (length: 30 m, inner diameter 0.25 mm). Phase: CR-5 2.5 μm thick. The qualitative composition of sulphurous compounds was determined by comparing retention times of the analyzed components with individual sulphur-containing compounds (thiophene, benzothiophene, dibenzothiophene and their homologues).

The structural group analysis of resins and asphaltenes

The obtained resins and asphaltenes were investigated by means of the structural group analysis (SGA) according to the procedure developed at the IPC SB RAS [25]. The use of the data on the analysis of the elemental composition, average molecular mass and ^{1}H NMR spectroscopy allows us to calculate the average distribution of atoms between structural fragments of the molecules of high-molecular compounds. This distribution gives us information on the size and structure of molecules, the composition and the amount of different structural groups.

The elemental analysis of resins and asphaltenes under investigation was carried out with the help of a Vario EL Cube CHNS analyzer (Elementar Analysensysteme, Germany). Molecular masses were measured by means of cryoscopy in naphthalene using a Krion instrument developed at the IPC SB RAS. The NMR ^{1}H spectra

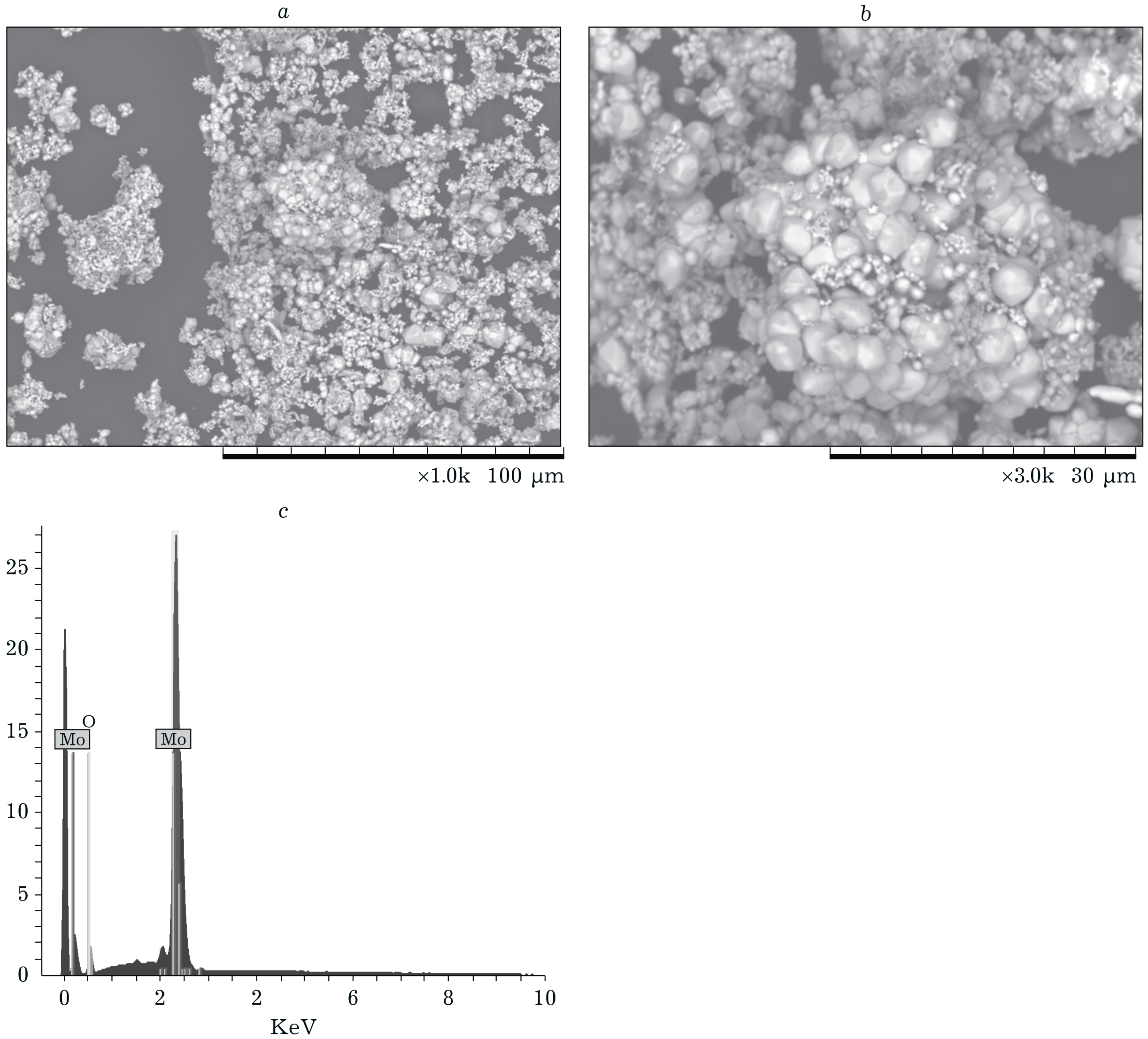

Fig. 1. Microphotographs with different magnification (*a*, *b*) and EDX spectrum (*c*) of nanosized molybdenum powder.

were recorded with AVANCE-AV-600 Fourier Transform spectrometer (Bruker, Germany), the solvent was deuterochloroform, the internal standard was hexamethyldisiloxane at 1 % concentration of resins.

RESULTS AND DISCUSSION

Experimental selection of the optimal conditions of VG oxidation and the effect of this preliminary treatment on the thermal stability of its components were described in detail in [22, 24]. It was demonstrated that cracking of VG treated preliminarily with the oxidizer in excess (with the molar ratio of $S_o/H_2O_2 = 1 : 5$) leads to the deep destruction of oil components even for process duration 30 min: the total amount of the formed distillate fractions is more than 70 mass % (Table 2). Condensation reactions are accelerated: the yield of asphaltenes and coke increases almost by a factor of 1.5 in comparison with the results of VG cracking for 60 min. The degree of desulphurization also turns out to be higher (the residual content of sulphur is 0.67 mass %). This change in the content of sulphur in the products confirms that preliminary treatment with the oxidizer in excess indeed allows one to involve high-molecular sulphur-containing components into cracking and to destroy them efficiently in the case of shorter process duration.

After OVG cracking for 60 min, the highest degree of desulphurization is achieved (0.62 mass %). However, under these conditions, we observe substantial losses of the sample due to gas formation (up to 20 mass %). It is assumed that the use of molybdenum NSP will allow us to enhance the

TABLE 2

Material balance of oxidized vacuum gasoil cracking (cracking temperature 500 °C)

Characteristics	Content, mass %							
	G	L / S_o	C	O	R	A	Fraction	
							IBP–200 °C	200–360 °C
Before cracking, sample:								
VG	–	100.0 / 2.02	–	91.3	8.6	0.1	0.0	18.5
OVG	–	100.0 / 2.02	–	74.3	25.2	0.5	0.0	17.8
VG cracking, 60 min	8.9	90.8 / 1.89	0.3	81.3	8.8	0.7	34.2	40.0
OVG cracking, min:								
15	4.5	95.1 / 1.20	0.4	78.1	15.8	1.1	21.2	45.7
30	9.4	90.1 / 0.67	0.5	80.8	8.0	1.3	33.3	39.4
45	9.7	89.1 / 0.66	1.2	80.4	7.9	0.8	35.4	37.8
60	19.4	79.4 / 0.62	1.2	70.6	7.1	1.7	24.4	29.1
OVG cracking, 60 min, amounts of Mo NSP, mass %:								
0.01	14.0	83.5 / 0.87	2.5	79.3	3.1	1.1	20.6	32.8
0.05	13.8	85.1 / 0.96	1.1	75.0	8.7	1.4	25.2	30.9
0.10	14.3	82.9 / 0.87	2.8	74.3	7.4	1.2	24.9	29.9
0.15	24.5	72.2 / 0.94	3.3	67.0	4.6	0.6	32.0	25.5

Note. G – gaseous products, L – liquid products, S_o – total sulphur content, C – coke, O – oils, R – resins, A – asphaltenes, VG – vacuum gasoil, OVG– oxidized vacuum gasoil.

degree of destruction of the products of oxidation of the high-molecular VG components avoiding the indicated negative effects [23].

The results of the thermal treatment of OVG in the presence of molybdenum NSP for 60 min are presented in Table 2. The use of the additive in the amount of only 0.01 mass % allows a decrease in the yield of gaseous products by a factor of 1.5 (in comparison with OVG cracking without the additive). The total amount of the obtained distillate fractions is conserved, however, their mass ratio changes. The yield of the fraction 200–360 °C turns out to be higher by 3 mass % in comparison with the fraction IBP–200 °C, which also confirms that cracking reactions slow down. Due to resin condensation according to the route resins → asphaltenes → coke, the yield of densification products increases by a factor of 2. A decrease in resin content in the liquid products occurs also due to resin destruction with the formation of low-molecular components. Presumably, this result is due to the fact that after the introduction of a small amount of molybdenum NSP into the system, less stable products of the oxidation of high-molecular compounds of VG are the first to get adsorbed on the surface of the additive. Adsorption of these components prevents their deep destruction, thus decreasing active gas formation which is observed during OVG cracking.

An increase in the amount of molybdenum NSP from 0.01 to 0.05 mass % causes a decrease in the total yield of side products (gas and coke) by 1.6 mass % more. The content of distillate fractions increases by almost 3 mass %, mainly due to the formation of the components of lower-boiling fraction IBP–200 °C. Simultaneously with the deceleration of gas formation, the content of fractions boiling above 360 °C increases in the liquid products of cracking. The use of this amount of the additive is likely to decelerate dealkylation reactions that cause the formation of the components of gaseous products through the detachment of alkyl substituents (C_1–C_4 hydrocarbons). Since a decrease in the yield of gas and coke with the additive introduced in the amount of 0.05 mass % turns out to be maximal, this amount of the additive was chosen to be optimal.

Further increase in the amount of added molybdenum NSP to 0.15 mass % causes a substantial acceleration of cracking of all OVG components. Deep destruction of oil components with boiling points above 360 °C proceeds. The additional formation of gas accounts for 75 rel. % in comparison with the material balance of the process with the optimal amount of the additive (0.05 mass %) and for 25 rel. % in comparison with simple thermal cracking. The percentage of the fraction IBP–200 °C in cracking products increases correspond-

TABLE 3

Effect of molybdenum NSP additive on the content of different types of sulphurous compounds in the products of cracking of oxidized vacuum gasoil

Compound	Content, mass %				
	1	2	3	4	5
Thiophene	0.013	0.018	0.081	0.029	0.026
$\sum C_1$-thiophene	0.410	0.469	0.873	0.812	0.830
$\sum C_2$-thiophene	0.227	0.399	0.567	0.560	0.466
$\sum C_3$-thiophene	0.098	0.201	0.303	0.197	0.102
$\sum C_4$-thiophene	0.035	0.066	0.066	0.066	0.035
$\sum C_5$-thiophene	0.010	0.024	0.019	0.005	0.010
$\sum$ of thiophene homologues	0.793	1.177	1.909	1.669	1.469
Benzothiophene	0.013	0.021	0.025	0.017	0.080
$\sum C_1$-benzothiophene	0.093	0.259	0.204	0.148	0.449
$\sum C_2$-benzothiophene	0.147	0.532	0.339	0.238	0.527
$\sum C_3$-benzothiophene	0.061	0.242	0.105	0.077	0.072
$\sum C_4$-benzothiophene	0.053	0.137	0.077	0.059	0.024
$\sum$ of benzothiophene homologues	0.366	1.190	0.750	0.539	1.150
Dibenzothiophene	0.023	0.040	0.035	0.029	0.069
$\sum C_1$-dibenzothiophene	0.080	0.198	0.130	0.105	0.217
$\sum C_2$-dibenzothiophene	0.119	0.345	0.179	0.093	0.166
$\sum$ of dibenzothiophene homologues	0.223	0.583	0.343	0.227	0.451

Note. The amount of molybdenum NSP additive, mass %: absent (1); 0.01 (2); 0.05 (3); 0.10 (4); 0.15 (5).

ingly. It is possible that the introduction of the additive in the amount more than 0.05 mass %, which is accompanied by an increase in surface area, leads to an increase in the probability of adsorption of other components (the products of oxidation of aromatic compounds that did not enter the reactions of hydrocarbon oxidation). As a result, the products of oxidation of high-molecular compounds remain in the volume, which leads to their deep destruction accompanied by the acceleration of gas formation reactions. It should be noted that RAS involved in condensation reactions are almost completely transformed into densification products with an increase in the amount of the introduced additive, following the route resins → asphaltenes → coke (residual content of asphaltenes is only 0.6 mass %).

The regularities of the transformation of sulphur-containing compounds (homologues of thiophene, benzothiophene and dibenzothiophene) in the liquid products of gasoil cracking (Table 3) are in good agreement with the assumptions formulated above. A decrease in the degree of desulphurization in the liquid products of cracking with molybdenum additive confirms the deceleration of reactions involved in the destruction of high-molecular sulphur-containing compounds. The efficiency of desulphurization decreases by 40–55 rel. %.

It is established that the largest amount of thiophene and its homologues in the liquid products of cracking may be obtained if the amount of the introduced molybdenum NSP is 0.05 mass %. Presumably, these compounds are the major products of slowed destruction of the unstable oxidized framing of high-molecular sulphur-containing components adsorbed on the surface of molybdenum NSP (for example, polyaromatic sulphurous compounds). Obtaining the product containing mainly low-molecular aromatic sulphurous compounds serves as a positive result of the combined process because these components may be readily removed during subsequent hydrocatalytic treatment.

The total content of the homologues of benzo- and dibenzothiophenes in the liquid products of cracking turns out to be higher than after simple thermal treatment of OVG. However, their yields decrease with an increase in the amount of the used molybdenum NSP from 0.01 to 0.1 mass %. The introduction of the additive in the amount of 0.15 mass % leads to an increase in the content of these compounds in cracking products by a factor of 2. The yield of substituted derivatives (C_3- and C_4-benzothiophenes and C_2-dibenzothiophene) turns out to be higher after the addition of 0.01 mass % molybdenum NSP. With an increase in the amount of molybdenum NSP to 0.15 mass %, we observe the accumulation of unsubstituted benzo- and dibenzothiophenes and their derivatives having two methyl substituents or one ethyl substituent (C_1–C_2) in the liquid products of cracking. The obtained distribution of the homologues of benzo- and dibenzothiophenes confirms that the introduction of the additive into the system in the amount exceeding the optimal one causes a substantial acceleration of the reactions involved in cracking of all OVG components, first of all, dealkylation reactions.

The addition of molybdenum NSP also affects the structure of RAS in the liquid products of cracking. According to the calculation of the structural group parameters, the averaged molecule of resins in VG has the molecular mass lower than the value reported in the literature (500–1000 Da) – only 358 Da (Table 4). The molecule has one structural unit containing up to two condensed aromatic rings and not more than three naphthene rings.

TABLE 4

Structural group parameters of the resins of vacuum gasoil and the products of its cracking

Parameter	1	2	3	4	5	6
Molecular mass, Da	358	359	349	313	547	486
Number of atoms in average molecule:						
C	24.3	22.5	25.0	21.7	38.6	34.8
H	33.9	33.6	24.2	22.7	29.7	27.7
N	0.4	0.1	0.3	0.2	0.3	0.2
S	0.5	0.8	0.2	0.1	0.1	0.1
O	0.7	1.8	0.9	1.5	2.9	2.1
Number of blocks in molecule, m_a	1.2	1.1	1.5	1.3	1.9	1.8
Ring composition:						
K_o	4.4	3.5	6.2	6.2	11.3	10.2
K_a	1.7	1.2	3.2	2.0	5.7	4.5
K_{sat}	2.7	2.2	2.9	4.2	5.6	5.2
Aromaticity factor, f_a	31.9	24.1	59.5	44.0	64.9	64.0
Number of carbon atoms of different types in the average molecule:						
C_a	7.8	5.4	14.9	9.5	25.1	22.3
C_n	11.0	9.0	9.3	11.0	13.2	12.2
C_p	5.5	8.1	0.8	1.2	0.3	0.4
C_α	4.2	3.3	5.0	4.5	6.5	5.5
Degree of substitution in aromatic cores, σ_a	0.6	0.6	0.4	0.5	0.4	0.3
H/C	1.4	1.5	1.0	1.0	0.8	0.8

Note. 1 – resins in VG; 2 – resins in OVG; 3 – resins in liquid products of OVG cracking; 4 – resins of the liquid products of OVG in the presence of 0.05 mass % molybdenum NSP; 5 – asphaltenes of the liquid products of OVG cracking; 6 – asphaltenes of the liquid products of OVG cracking in the presence of 0.05 mass % molybdenum NSP; the fraction of carbon atoms: C_a – carbon in aromatic cycles; C_n – carbon in naphthene rings; C_p – carbon in aliphatic fragments; C_α – number of carbon atoms in the α-position to the aromatic ring; number of rings: K_o – total, K_a – aromatic; K_{sat} – saturated.

According to the ring composition, the average molecule has not very high aromaticity factor (f_a) – about 30 %. On average, there are three or four substituents (aliphatic fragments or naphthene rings) per one aromatic ring, which is indicated by the calculated degree of substitution – 0.6. The total number of carbon atoms in alkyl substituents is five-six.

Oxidation does not have a substantial effect on the structure of resin molecules in VG. The molecular mass of an average molecule of resins in OVG, in which the oxidized sulphur-containing and aromatic compounds are concentrated, remains practically unchanged in comparison with the average molecule of resins in VG. The number of structural blocks is conserved. The distribution of heteroatoms changes: in the resins of VG, one oxygen atom is present in two out of three molecules on average, while in the resins of OVG there are two such atoms per one molecule. A decrease in the value of f_a by 8 %, together with an increase in the number of sulphur and carbon atoms of aliphatic fragments, provides evidence that the compounds subjected to oxidation are substituted derivatives of aromatic hydrocarbons and such sulphur-containing compounds as, for example, dibenzo- and benzonaphthothiophenes. Their polarity changes so that these compounds are extracted within the resins during the determination of the material composition.

After OVG cracking, oxygen content in the structure of resin molecules decreases by a factor of 2, that is, ethoxidized fragments of high-molecular hybrid hydrocarbons and polyaromatic sulphur-containing compounds are indeed removed as a result of partial destruction or condensation with the formation of asphaltenes. Every second averaged molecule becomes two-

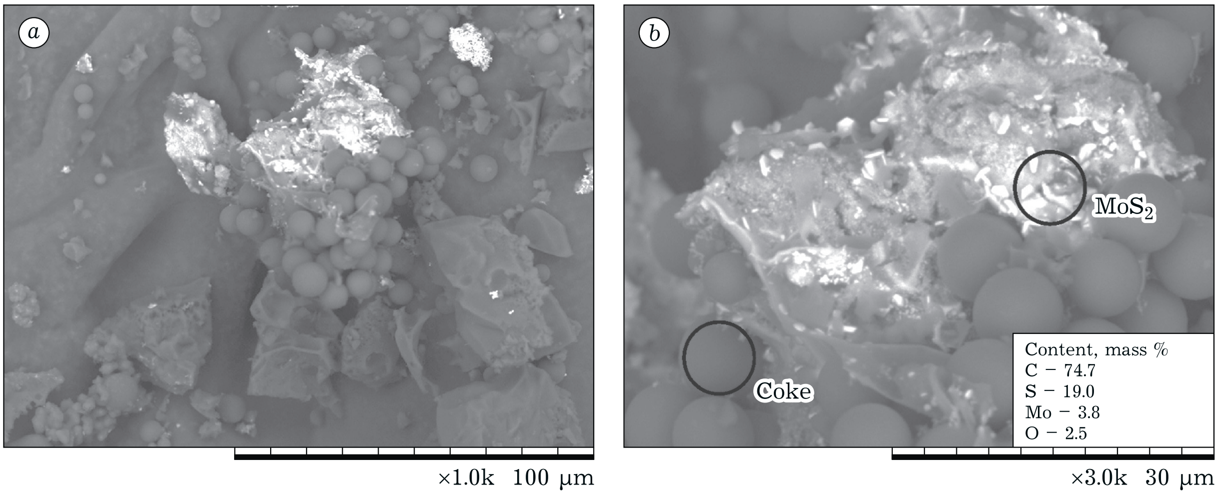

Fig. 2. Microphotographs of molybdenum nanosized powder (NSP) after cracking, with different magnification (*a*, *b*). Insert (*b*) shows elemental analysis of the surface of molybdenum NSP.

block molecule. Cyclization and aromatization of saturated fragments during thermal treatment lead naturally to an increase in the number of aromatic rings in the averaged resin molecule from one to three and to an increase in f_a from 24 to ~60 %, respectively. A decrease in the parameters C_p (the number of carbon atoms in aliphatic fragments) and σ_a (the degree of substitution in aromatic cores) is due to the dealkylation of aromatic fragments in addition to cyclization.

A part of resins is transformed into asphaltenes during the thermal treatment of OVG. The averaged asphaltene molecule in the products of OVG thermolysis has the molecular mass 547 Da and is composed of two structural blocks containing five-six saturated and aromatic rings. High oxygen content (there are up to three oxygen atoms per one molecule) provides evidence that some oxidized fragments of resins do not undergo destruction but are condensed to form asphaltenes. Sulphur atoms are practically absent in the averaged molecule. The low value of C_p parameter (0.3) points to the absence of aliphatic fragments. It is probable that there is not more than one alkyl substituent containing not more than one carbon atom per every third asphaltene molecule. The atomic ratio of H/C for asphaltenes is smaller than for resins, due to dehydration, aromatization and condensation during cracking, which results in the condensation of resins into asphaltenes which are absent from VG.

The calculation of the structural group parameters of resins and asphaltenes of OVG after cracking in the presence of molybdenum NSP not only confirms the formulated assumptions that this additive promotes deceleration of dealkylation reactions but also provides evidence that aromatization processes are slowed down. The use of the additive allows obtaining resins in which the averaged molecule contains a lower amount of heteroelements (sulphur and nitrogen). Oxygen brought into the system during preliminary oxidation is removed not so easily: during OVG cracking, one oxygen atom is removed from each resin molecule, while during thermal treatment with molybdenum NSP one such atom is removed only from every second molecule. The number of blocks in an average structure decreases: only every fourth resin molecule is two-block. The deceleration of aromatization processes is also evidenced by the change of the ring composition. After thermal treatment in the absence of the additive, three rings of both types are determined in the averaged structure of the resins. The total number of rings is conserved during cracking with molybdenum NSP, however, now each resin molecule has two aromatic and four saturated rings. Correspondingly, f_a value of the resulting resins decreases by 16 %. An increase in parameters C_p and σ_a also confirms the deceleration of alkylation reactions: each molecule has an alkyl substituent not longer than two atoms.

Sulphur-containing fragments of polyaromatic compounds are not involved in condensation reactions: the content of this heteroelement in asphaltene structure is only 0.1.

Microphotographs of the surface of molybdenum NSP show (Fig. 2, *a*) that cracking under optimal conditions (additive in the amount of 0.05 mass %) causes the destruction of its agglomerates. Partial coking of powder surface is observed. The particles of the formed coke are spherical. According to the literature data [26], this kind of densification product is formed from the residues of raw drops decomposed within the reactor volume. The resin-asphaltene substances in such a drop are condensed with the formation of spatially cross-linked carbon polymer which is transformed into spherical coke particles 50–100 μm in size during heating to 500 °C. There are also hexagonal inclusions on molybdenum surface (see Fig. 2, *b*). Elemental analysis (see Fig. 2, *b*, insert) shows that they are likely to be composed of the molybdenum disulphide. Taking into account the mass of the additive, which is only 0.01–0.15 mass % of the raw material mass, and the amount and distribution of molybdenum disulphide particles over NSP particles after cracking, we may assume that the amount of MoS_2 is insufficient to change the direction of the thermal transformations of gasoil components.

CONCLUSION

It is established that the use of the optimal amount of molybdenum NSP (0.05 mass %) for OVG cracking allows us to reduce the losses due to gas and coke formation by a factor of 1.5. The content of distillate fractions in the resulting liquid products increases due to the formation of the components of lower boiling fraction IBP–200 °C. The application of this amount of the additive is likely to slow down the destruction of oxidized high-boiling VG components, specifically dealkylation and aromatization. In addition, under these conditions, the product containing mainly low-molecular sulphur-containing aromatic compounds (thiophene and its homologues) may be obtained; further processing of these products is not a difficult task.

Deceleration of aromatization and dealkylation in the case of the use of 0.05 mass % molybdenum NSP affected the averaged structure of the molecules of resins and asphaltenes. The number of blocks in molecules decreases in comparison with the structure of RAS in the products of OVG cracking, aromaticity factor decreases, the content of saturated cycles and the H/C atomic ratio increase.

Since deceleration of gas formation leads to a decrease in the efficiency of desulphurization of liquid products, the results obtained herein point to the fact that the major route of the removal of sulphur-containing fragments in the process under consideration is not condensation with the formation of the products of densification but their destruction with the formation of hydrogen sulphide and sulphur dioxide. This problem may be solved by enhancing the selectivity of the oxidation of sulphur-containing compounds.

Acknowledgements

The work was carried out within the State Assignment to the IPC SB RAS (project V.46.2.2) financed by the Ministry of Science and Higher Education of the Russian Federation.

REFERENCES

1 Al-Attas T., Ali S., Zahir M. H., Xiong Q., Al-Bogami S. A., Malaibari Z. O., Razzak Sh. A.Recent advances in heavy oil upgrading using dispersed catalysts, *Energy Fuels*, 2019, Vol. 33, No. 9, P. 7917–7949.

2 Mahe L., Dutriez T., Courtiade M., Thiebaut D., Dulot H., Bertoncini F. Global approach for the selection of high temperature comprehensive two-demensional gas chromatography experimental conditions and quantitative analysis in regards to sulfur-containing compounds in heavy petroleum cuts, *J. Chromatogr. A*, 2011, Vol. 1218, P. 534–544.

3 Dik P. P., Klimov O. V., Koryakina G. I., Leonova K. A., Pereyma V. Yu., Budukva S. V., Gerasimov E. Yu., Noskov A. S. Composition of stacked bed for VGO hydrocracking with maximum diesel yield, *Catal. Today*, 2014, Vol. 220–222, P. 124–132.

4 Pimerzin A. A., Tomina N. N., Nikulshin P. A., Maksimov N. M., Mozhaev A. V., Ishutenko D. I., Vishnevskaya E. E. Catalysts of petroleum fraction purification based on Mo and W heteropolycompounds [in Russian], *Kataliz v Prom-sti*, 2014, No. 5, P. 49–55.

5 Magomedov R. N., Popova A. Z., Maryutina T. A., Kadiev Kh. M., Khadzhiev S. N. State and outlooks for demetallization of heavy petroleum raw material (a review) [in Russian], *Neftekhimiya*, 2015, Vol. 55, No. 4, P. 267–290.

6 AL Otaibi R. L., Liu D., Hou X., Song L., Li Q., Li M., Almigrin H. O., Yan Z. Desulfurization of Saudi Arabian crudes by oxidation–extraction method, *Appl. Petrochem.* Res., 2015, No. 5, P. 355–362.

7 Ibrahim M. H., Hayyan M., Hashim M. A., Hayyan A. The role of ionic liquids in desulfurization of fuels: A review, *Renew. Sust. Energ. Rev.*, 2017, Vol. 76, P. 1534–1549.

8 Sarda K. K., Bhamdari A., Pant K. K., Jain S. Deep desulfurization of diesel fuel by selective adsorption over Ni/Al_2O_3 and Ni/ZSM-5 extrudates, *Fuel*, 2012, Vol. 93, P. 86–91.

9 Lee K. X., Valla J. A. Adsorptive desulfurization of liquid hydrocarbons using zeolite-based sorbents: a comprehensive review, *React. Chem. Eng.* 2019, No. 8, P. 1357–1386.

10 El-Gendy N. Sh., Nassar H. N. Biodesulfurization in Petroleum Refining, Wiley-Scrivenen, 2018. 1200 p.

11 Hossain M. N., Park H. Ch., Choi H. S. A comprehensive review on catalytic oxidative desulfurization of liquid fuel oil, *J. Catal.*, 2019, Vol. 229, No. 9, P. 229–241.

12 Li J., Yang Zh., Li S., Jin Q., Zhao J. Review on oxidative desulfurization of fuel by supported heteropolyacid catalysts, *J. Ind. Eng. Chem.*, 2020, Vol. 82, P. 1–16.

13 Weh R., Klerk A. Thermochemistry of sulfones relevant to oxidative desulfurization, *Energy Fuel*, 2017, Vol. 31, No. 6, P. 6607–6614.

14 Javadli R., Klerk A. Desulfurization of heavy oil, *Appl. Petrochem. Res.*, 2012, No. 1, P. 3–19.

15 Palomeque-Santiago J. F., Lopez-Medina R., Oviedo-Roa R., Navarrete-Bolanos J., Mora-Vallejo R., Montoya-de la Fuente J. A., Martinez-Magadan J. M. Deep oxidative desulfurization with simultaneous oxidative denitrogenation of diesel fuel and straight run gas oil, *Appl. Catal. B: Environ.*, 2018, Vol. 236, P. 326–337.

16 Kairbekov Zh. K., Myltykbaeva Zh. K., Muktaly D., Nysanova B., Anisimov A. V., Akopyan A. V. Peroxide oxidative desulfurization of a diesel fuel, *Theor. Found. Chem. Eng.*, 2018, Vol. 52, No. 4, P. 667–680.

17 Abdullah G. H., Xing Y. Oxidation of dibenzothiophene in diesel with *in situ* produced hydrogen peroxide, *Energy Fuels*, 2018, Vol. 32, No. 8, P. 8254–8258.

18 Shvets V. F., Sapunov V. N., Kozlovskiy R. A., Luganskiy A. I., Gorbunov A. V., Sovetin F. S., Gartman T. N. Cracking of heavy oil residues in a continuous flow reactor initiated by atmospheric oxygen, *Chem. Eng. J.*, 2017, Vol. 329, No. 1, P. 275–282.

19 Wang D., Qian E. W., Amano H., Okata K., Ishihara A., Kabe T. Oxidative desulfurization of fuel oil: Part I. Oxidation of dibenzothiophenes using *tert*-butyl hydroperoxide, *Appl. Catal. A: Gen.*, 2003, Vol. 253, No. 1, P. 91–99.

20 Krivtsov E. B., Golovko A. K. Kinetics of the oxidation of sulphurous compounds of the diesel fraction of petroleum by the ozone-oxygen mixture [in Russian], *Izv. TPU. Inzhiniring Georesursov*, 2012, Vol. 321, No. 3, P. 157–161.

21 Akopyan A. V., Fedorov R. A., Tarakanova A. V., Andreev B. V., Anisimov A. V., Karakhanov E. A. Oxidative desulphurization of hydrocarbon raw materials (a review) [in Russian], *Zhurn. Priklad. Khimii*, 2018, Vol. 91, P. 457–471.

22 Iovik Y. A., Krivtsov E. B. Chemical transformations of sulfur-containing components of vacuum distillate in the course of combined thermo-oxidative treatment, *AIP Conf. Proc.*, 2018, Vol. 2051, P. 020107.

23 Sviridenko N. N., Krivtsov E. B., Golovko A. K., Krivtsova N. I. Cracking of natural bitumen in the presence of nanosized powders Mo and CuO, *Pet. Coal*, 2016, Vol. 58, No. 7, P. 732–735.

24 Iovik Yu. A., Krivtsov E. B., Golovko A. K. Features of oxidative desulphurization of vacuum gasoil [in Russian], *Izvestiya TPU. Inzhiniring Georesursov*, 2018, Vol. 329, No. 11, P. 52–60.

25 Patrakov Yu. F., Kamyanov V. F., Fedyaeva O. N. A structural model of the organic matter of Barzas liptobiolith coal, *Fuel*, 2005, Vol. 84, P. 189–199.

26 Gyulmisaryan T. G., Gilyazetdinov L. P. Raw Material for the Production of Furnace Carbon Black, Moscow: Khimiya, 1975. 160 p. (in Russ.).