Study of the Structure of Asphaltenes and Coke Isolated from the Products of Cracking of a Mixture of Oil Residues and Sunflower oil by X-Ray Structural Analysis

Stanislav V. Boyar* and Mikhail A. Kopytov
Institute of Petroleum Chemistry of SB RAS
Tomsk, Russian Federation

Abstract. The aim of the work is to evaluate the effect of sunflower oil additives in oil residues on the structure of the formed asphaltenes and coke in the cracking process. Cracking of oil residues and their mixtures with sunflower oil in various ratios is carried out. Comparison of the data of X-ray structural analysis of asphaltenes and coke isolated from products of cracking is performed. The analysis showed that the addition of sunflower oil to oil residues leads to changes in the parameters of the macrostructure of asphaltenes and coke obtained in products of cracking. In coke isolated from products of cracking obtained in the presence of sunflower oil, the height of the stack of aromatic sheets (Lc) increases, while the distance between the aromatic layers (dm) does not change significantly. In asphaltenes isolated from products of cracking, the average diameter of the aromatic sheets (La) and the distance between saturated structures (dr) vary significantly. The role of sunflower oil is explained by the participation of triglyceride degradation products (mainly fatty acids and olefins) in condensation processes, which makes it possible to reduce the yield in coke and asphaltenes.

Keywords: Oil residue; Asphaltenes; Coke; Sunflower oil; Cracking; X-ray structural analysis.

*   Corresponding author E-mail address: bsv@ipc.tsc.ru

Изучение структуры асфальтенов и кокса, выделенных из продуктов крекинга смеси нефтяных остатков и подсолнечного масла методом рентгеноструктурного анализа

С. В. Бояр, М. А. Копытов

Институт химии нефти СО РАН
Российская Федерация, Томск

Аннотация. Целью работы являлось оценить влияние добавок подсолнечного масла в нефтяные остатки на структуру образующихся асфальтенов и кокса в процессе крекинга. Был проведен крекинг нефтяных остатков и их смесей с подсолнечным маслом в различных соотношениях. Выполнено сравнение данных рентгеноструктурного анализа асфальтенов и кокса, выделенных из продуктов крекинга. Анализ показал, что добавление в нефтяные остатки подсолнечного масла, приводит к изменению параметров макроструктуры асфальтенов и кокса, полученных в продуктах крекинга. В коксе, выделенном из продуктов крекинга, полученных в присутствии подсолнечного масла, увеличивается высота стопки ароматических слоёв (Lc), расстояние между ароматическими слоями (dm) существенно не меняется. В асфальтенах, выделенных из продуктов крекинга, существенно варьируется средний диаметр ароматического листа (La) и расстояние между насыщенными структурами (dr). Роль подсолнечного масла объясняется участием продуктов деструкции триглицеридов (главным образом это жирные кислоты и олефины) в процессах конденсации, что позволяет снизить выход кокса и асфальтенов.

Ключевые слова: нефтяной остаток, асфальтены, кокс, подсолнечное масло, крекинг, рентгеноструктурный анализ.

Introduction

Oil residues have a high content of resin-asphaltene components, which can quickly poison and coke catalysts [1]. This complicates the use of conventional catalytic systems for processing heavy hydrocarbon feedstocks. Therefore, at the moment more than 70 % of the volumes of heavy hydrocarbon feedstocks worldwide are treated by thermal methods [1].

To increase the depth of processing of oil residues, various additives are used in thermal processes: brown coal, oil shale, polymer-containing waste, sawdust, microspheres, and other 'cracking additives'.

The use of waste from the production of vegetable oils or used vegetable oils as a cracking additive is promising. It is known that the chemical composition of such oils does not change significantly [2],

but they can be contaminated with mechanical impurities. Therefore, in our work, in order to simplify the process of cleaning vegetable oil, we used raw unrefined sunflower oils.

The publications [3, 4] provide data on the co-processing of vegetable oils and oil residues in thermal and thermocatalytic processes. Triglycerides of fatty acids, which enter into the composition of vegetable oils, can affect the direction of transformation of resins and asphaltenes in thermal and thermocatalytic processes [5].

The role of vegetable oils in the process of cracking of heavy hydrocarbon feedstock is explained by the fact that triglycerides in their composition can initiate the destruction of resin-asphaltene components. Also, the presence of a long hydrocarbon chain and a polar group allows fatty acids and triglycerides of fatty acids to exhibit surface-active properties, which can affect the aggregate stability of asphaltenes and, subsequently, the formation of coke. It is believed that the intense formation of coke in thermal processes begins with the precipitation of the solid phase of asphaltenes.

In our previous publications, we have shown that the use of sunflower oil (SFO) in the cracking process allowed not only to reduce the yield in asphaltenes and coke, but also to increase the yield in gasoline fractions [5]. In addition to a noticeable change in the component composition of products of cracking, qualitative changes in the macrostructure of asphaltenes and coke should occur. But at the moment there are few publications on the effect of vegetable oils on the coke formation process during the cracking of oil residues.

Therefore, the aim of the work was to evaluate the effect of sunflower oil additives in oil residues on the macrostructure of the asphaltenes and coke formed during cracking. The parameters of the macrostructure of the formed asphaltenes and coke were estimated based on XRD (X-ray diffraction) analysis data.

Materials and methods

The objects of study were residues of the oil from the Usinskoye oilfield (Russia) and the Zuunbayan oilfield (Mongolia) with a boiling point above 350 °C.

These oil residue (OR) differ significantly in their physical and chemical properties. The residue of the Usinsk oil (UOR) is characterized by a high coking value, a high content of resins (37.0 wt%) and asphaltenes (8.5 wt%), while it has a low content of n-alkanes [6]. On the contrary, the residue of the oil from the Zuunbayan field (ZOR) is characterized by a high content of n-alkanes and, as a consequence, a low content of asphaltenes (0.4 wt%) [6]. More detailed characteristics of oil residues are presented in our works [6].

SFO was used as an additive in an amount of up to 8.0 wt%. The oil chosen contains up to 61.5 wt% of linoleic acid, up to 12.3 wt% of oleic acid and less than 6.0 wt% of palmitic and stearic acid. More detailed characteristics of SFO are presented in our works [5, 7].

The cracking of oil residues was carried out in a batch reactor with a volume of 12 cm^3 at a temperature of 435 °C and a duration of 60 min. The description of the experiment and the choice of cracking conditions are given in our previous publications [5, 7]. The comparison was made of the products of cracking obtained without the addition of SFO and those obtained in the presence of 4.0 and 8.0 wt% of SFO, since at this ratio a decrease in the yield on coke and an increase in the yield in distillate fractions were observed, as was shown earlier [7].

To isolate asphaltenes, the cracking products were collected in a vessel and diluted with a 40-fold excess of n-hexane. The resulted solution was allowed to stand 24 hours in the dark, and then it was filtered to separate the maltenes from the precipitate, which contained asphaltenes and coke (here and hereinafter in the text, the term 'coke' means 'components insoluble in chloroform'). Thus, the n-hexane-insoluble products were collected on a filter. The resulted precipitate was washed with n-hexane in a Soxhlet apparatus to remove maltenes. Then, asphaltenes were extracted from it with chloroform. After removal of the solvents, the content of asphaltenes and coke was quantified. Coke and solid asphaltenes dried at 90 °C for 6 h were used for analysis.

The elemental composition of asphaltenes and solid products was determined using a Vario EL Cube CHNS analyzer by direct combustion at 1200 °C followed by separation of gases and combustion products in three adsorption columns and identification using a thermal conductivity detector. Elemental detection limit was not less than 0.01 wt%.

Diffraction patterns of coke and asphaltene powder samples were obtained using a Discover D 8 X-ray diffractometer (Bruker, Germany) using monochrome CuKα radiation, wavelength λ = 1.54184 Å. Scanning was carried out in the range of 2θ angles from 0° to 90° at a temperature of 20 °C.

The XRD patterns were processed using Origin Pro 8 and DIFFRAC EVA v1.3 (Bruker-AXS) programs. The calculation of the parameters was carried out according to the formulas reported in [8, 9]. The XRD pattern shows one reflection (γ-band) with a maximum of $2\theta_\gamma = 19\text{--}20^\circ$ suggests the presence of saturated structures and two reflections corresponding to cluster-like formations: a weak band (100) with a maximum of $2\theta_{100} = 44\text{--}45^\circ$ and a band (002) with a maximum at $2\theta_{002} = 25\text{--}26^\circ$.

Interlayer distances between the aromatic sheets (dm, Å) were calculated as follows:

$$m = \frac{\lambda}{2Sin\theta_{002}}, \text{ where } sin\theta_{002} - \text{ sine of the angle at which the band 002 was observed.}$$

The distance between saturated fragments of asphaltene molecules (dr, Å) was determined as follows:

$$dr = \frac{5\lambda}{8Sin\theta_\gamma}, \text{ where } \lambda - \text{ the x-ray wavelength, Å.}$$

Lc, Å: The average height of the stack of the aromatic sheets was calculated as follows:

$$Lc = \frac{0.92\lambda}{B_{1/2(002)}Cos\theta_{002}}, \text{ where } B_{1/2(002)} - \text{ the width at half maximum of the band 002.}$$

The average number of aromatic sheets in a stacked cluster (M) was determined as follows:

$$M = \frac{Lc}{dm} + 1$$

The average diameter of the flat aromatic fragments of molecules stacked to the cluster (La) was obtained from the following equation:

$$La = \frac{1.84\lambda}{B_{1/2(100)}Cos\theta_{100}}, \text{ where } B_{1/2(100)} - \text{ the width at half maximum of the band 100}$$

The number of aromatic rings per sheet (Na) was determined from the following equation:

$$Na = \frac{La}{2.667}$$

The aromaticity factor f_α^{XDR} or fraction of aromatic carbon was determined using the following formula:

$$f_a^{XRD} = \frac{A_{002}}{A_{002} + A_\gamma},$$ where f_α^{XDR} – the fraction of aromatic carbon; A_{002} and A_γ – the areas of the band 002 and γ, respectively.

As a rule, the parameter f_a^{XRD} determined by XRD method has a lower value compared to the corresponding value obtained using ^{13}C NMR, thus it does not represent the true aromaticity of the asphaltene molecule [9]. This is due to the fact that the calculation of f_a^{XRD} is only based on the stacked cluster of aromatic carbon but not on all the aromatic carbon in asphaltene [9].

The level of clustered organization of carbon atoms (φa), i.e. fraction of carbon atoms in clusters was calculated as follows:

$$\varphi a = f_a^{XRD} - (0.308dm - 0.970)$$

Results and Discussion

Comparison of the macrostructure of coke and asphaltenes

Fig. 1 shows the diffraction patterns of asphaltenes and coke.

The XRD patterns of asphaltenes of the initial oil residues (AZ0 and AU0) show a pronounced γ-band, the intensity of which noticeably decreases relative to the (002) band for all asphaltene samples isolated from the products of cracking (Fig. 1 a and Fig. 1 b). This suggests a decrease in the content of saturated structures in the macromolecule of these asphaltenes.
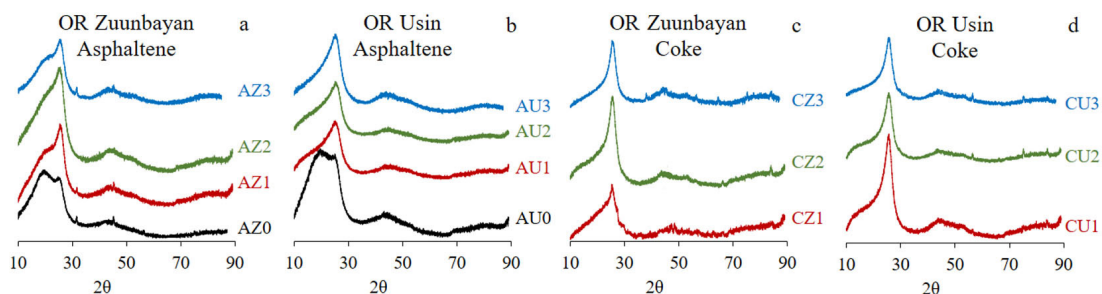
note for name of samples: A – asphaltenes, C – coke, Z – Zuunbayan oil residue, U – Usinsk oil residue, 0 – asphaltenes isolated from initial oil residue, 1 – samples isolated from products of cracking oil residue without additives, 2 – samples isolated from products of cracking oil residue with 4 wt% of sunflower oil, 3 – samples isolated from products of cracking oil residue with 8 wt% of sunflower oil. For example: AZ3 – asphaltenes of Zuunbayan oil residue isolated from products of cracking oil residue with 8 wt% of sunflower oil.

Fig. 1. X-ray diffraction patterns of samples: asphaltenes of Zuunbayan oil residue and products of its cracking (a); asphaltenes of the Usinsk oil residue and products of its cracking (b); coke of the products of cracking of the Zuunbayan oil residue (c); coke of the products of cracking of the Usinsk oil residue (d)

The parameters of macrostructure of asphaltenes and coke, calculated from XRD data, are shown in Tables 1 and 2. The Tables 1 and 2 also provide data on the yield (Y, wt%) and H/C ratios in the samples.

The main parameters of the isolated initial asphaltenes have typical values for similar products [10]. The features of this sample include a large diameter of the stack (La) and a small number of sheets in a stack (M).

Compared to asphaltenes AZ0 of the initial ZOR, the average number of sheets in a stack (M) increases from 2.77 to 7.25 in asphaltenes AZ1 isolated from the products of cracking (without SFO additives), while the number of aromatic rings in the sheet (Na) and, accordingly, the average diameter of the aromatic sheets (La) remain almost unchanged.

Asphaltenes AZ1 of the products of ZOR cracking, in comparison with AZ0, are characterized by a lower value of the level of clustered organization of carbon atoms (φa) and a lower value of the H/C ratio. The AZ1 asphaltene yield is 5.0 wt%, which is more than 12 times higher than the content of AZ0 asphaltenes in the initial OR. The increase in the content of asphaltenes AZ1 occurs mainly due to the cracking of maltenes. In the course of cracking, the polyaromatic components of maltenes and the initial asphaltenes AZ0 lose long alkyl substituents; therefore, the resulted asphaltenes AZ1 are characterized by a lower H/C value.

The average interlayer distance in a stack (dm) for asphaltenes isolated from products of cracking AZ1 – AZ3 decreases from 3.8 Å to 3.5 Å, as shown in Table 1. Naphthenic rings and alkyl chains in

Table 1. Parameters of the macrostructure of asphaltenes and coke isolated from the Zuunbayan oil residue and products of its cracking

	Sample	Y, wt%	H/C	dm, Å	dr, Å	Lc, Å	M	La, Å	Na	f_a^{XRD}	φa
asphaltenes	AZ0	0.4	1.38	3.81	5.43	6.72	2.77	22.37	8.39	0.52	0.32
	AZ1	5.0	0.95	3.50	5.63	21.91	7.25	23.06	8.65	0.39	0.28
	AZ2	4.0	0.85	3.54	5.81	20.03	6.66	25.95	9.73	0.30	0.18
	AZ3	3.6	0.91	3.51	5.58	22.52	7.42	33.26	12.47	0.28	0.17
coke	CZ1	5.6	0.77	3.52	5.33	24.36	7.93	26.00	9.75	0.41	0.29
	CZ2	3.6	0.65	3.50	5.43	28.53	9.14	27.59	10.34	0.52	0.41
	CZ3	1.8	0.63	3.49	5.22	27.58	8.91	38.66	14.49	0.40	0.30

Table 2. Parameters of the macrostructure of asphaltenes and coke isolated from the residues of Usinsk oil and products of its cracking

	Sample	Y, wt%	H/C	dm, Å	dr, Å	Lc, Å	M	La, Å	Na	f_a^{XRD}	φa
asphaltenes	AU0	8.5	1.17	3.57	5.79	17.47	5.89	16.64	6.24	0.31	0.18
	AU1	9.9	0.74	3.57	5.95	17.94	6.03	25.11	9.41	0.48	0.35
	AU2	8.3	0.72	3.54	5.98	17.47	5.93	21.88	8.20	0.41	0.28
	AU3	8.7	0.74	3.57	6.08	16.16	5.53	15.99	5.99	0.47	0.34
coke	CU1	19.0	0.63	3.51	5.68	25.82	8.35	31.23	11.71	0.53	0.42
	CU2	19.5	0.59	3.50	5.68	26.23	8.49	43.74	16.40	0.54	0.43
	CU3	16.7	0.58	3.49	5.53	27.18	8.78	22.68	8.51	0.44	0.34

the structure of asphaltenes are nonplanar structures and cause steric repulsion [11]; therefore, after the destruction of saturated structures, the distance in the stacks (dm) decreases.

Co-cracking of ZOR and SFO results in the formation of asphaltenes AZ2 and AZ3 with an even lower value of the level of clustered organization of carbon atoms (φa) as compared with AZ1 asphaltenes. This value decreases from 0.28 to 0.17 in the series AZ1 > AZ2 > AZ3. In the same series, the average diameter of the aromatic sheets (La) increases from 23.06 to 33.26 Å and, accordingly, the number of rings in the sheet (Na) also increases from 8.65 to 12.47. The average number of sheets in a stack (M) varies from 6.66 to 7.42. Also, in comparison with asphaltenes AZ1, asphaltenes AZ2 and AZ3 obtained in the presence of SFO are characterized by a lower H/C index.

An increase in the number of aromatic rings in the sheet (Na) of asphaltenes (AZ2 and AZ3) may indicate that the products of degradation of triglycerides of unsaturated fatty acids (TGUFA) markedly affect the transformation of ZOR components. The SFO additives affect not only the structure, but also the yield of asphaltenes AZ2 and AZ3, the content of which is slightly reduced in the products of cracking in comparison with those obtained without SFO.

The SFO additives also affect the macrostructure of the formed coke and help to reduce the coke yield from 5.6 wt% up to 1.8–3.6 wt% (Table 1). The average number of sheets in a stack (M) increases from 8 to 9 due to the introduction of SFO and the average stack height of the aromatic sheets (Lc) in the macrostructure of coke aggregates increases from 24.36 to 28.53 Å.

The number of aromatic rings in the sheet (Na) in the case of coke isolated from products of cracking increases in the series CZ1 < CZ2 < CZ3 from 9.75 to 14.49, while the H/C ratio decreases from 0.77 to 0.63.

Asphaltenes AU0 of the initial UOR (Table 2) have an average stack height of the aromatic sheets (Lc) of about 17.47 Å, the average diameter of the aromatic sheets (La) about 16.64 Å, and the number of aromatic cores in the sheet (Na) equal 6.24. The average interlayer distance in the stacks (dm) is about 3.6 Å. The distance between aliphatic chains and naphthenic sheets (dr) is about 5.8 Å. Asphaltenes AU0 differ from AZ0 in the larger size of average stack height of the aromatic sheets (Lc) and a smaller number of aromatic rings in the sheet (Na).

In comparison with AZ0 asphaltenes, the smaller interlayer distance in stacks (dm) and the larger distance between the saturated fragments (dr) in AU0 asphaltenes indicate that there are less saturated structures in AU0 asphaltenes. This assumption is confirmed by the lower H/C ratio for AU0 compared to the H/C ratio for AZ0, which are equal to 1.17 and 1.38, respectively.

In asphaltenes isolated from products of cracking (AU1, AU2, AU3), in comparison with asphaltenes of the initial residue (AU0), the distance between aromatic sheets (dm) does not change significantly. In the series AU1 > AU2 > AU3 a decrease in the average stack height of the aromatic sheets (Lc), the average diameter of the aromatic sheets (La), and the number of aromatic rings in the sheet (Na) is observed.

The introduction of SFO affects the yield of asphaltenes, the content of which decreases from 9.9 wt% up to 8.3–8.7 wt%. Hence, AU1 were resulted from cracking without SFO, while AU2 and AU3 were obtained by cracking in the presence of SFO.

The coke yield in the products of UOR cracking was high (19.0 wt%). The introduction of SFO in the amount of 4 wt% did not significantly affect the coke yield, while the addition of SFO in an amount

of 8 wt% led to a decrease in the coke yield to 16.7 wt%. Perhaps, to reduce the yield of coke in the UOR cracking process, it is advisable to decrease the temperature or duration of cracking.

In comparison with coke without SFO (CU1), a significant decrease in the average diameter of the aromatic sheets (La) from 31.23 to 22.68 Å and the fraction of carbon atoms concentrated in the clusters (φa) from 0.42 to 0.34 is observed for coke (CU3) obtained by cracking of UOR in the presence of 8 wt% of SFO.

In the series CU1 < CU2 < CU3, the H/C ratio decreases from 0.63 to 0.58. These values are lower than those for coke obtained by cracking of ZOR.

The common patterns are observed for different samples of coke and asphaltenes obtained in the course of cracking in the presence of SFO. In the coke isolated from the products of cracking of UOR and ZOR obtained in the presence of SFO, the average stack height of the aromatic sheets (Lc) increases.

A decrease in the H/C ratio in coke samples isolated from products of cracking obtained in the presence of SFO, in comparison with samples obtained in the course of cracking without SFO additives (Tables 1 and 2) may be associated with an increase in the H/C ratio in maltenes. Refining of oil residues is mainly achieved in two ways: by thermal cracking or hydrocracking, which are based on the methods of carbon redistribution or hydrogen addition, respectively [12, 13].

Contribution of oils to the process of cracking of oil residues

Earlier, we have shown in our work [5] that the co-cracking of the oil residue and SFO allows not only to reduce the yield of coke and asphaltenes, but also to increase the yield of distillate fractions, i.e. products with a high H/C ratio. To establish the role of SFO in the transformation of the components of oil residues in the cracking process, we have studied the transformation of the initial vegetable oils at temperatures from 400 to 500 °C.

Figure 2 shows the scheme of thermal destruction of vegetable oils to fatty acids at temperatures from 390 to 480 °C [14].

The formation of fatty acids and olefins during the cracking of vegetable oils without catalysts at temperatures from 400 to 500 °C has been previously reported in the literature [15]. At the initial stage of SFO transformation, triglycerides are thermally cracked with the formation of various oxygen-containing compounds, the main part of which is fatty acids. Then the cleavage of C-O and C–C bonds occurs with the formation of CO_2, CO, paraffins, olefins and other products [15, 16]. Presumably, it is the presence of olefins and UFA (Unsaturated fatty acids) that affects the transformation of the components of oil residues in secondary reactions.
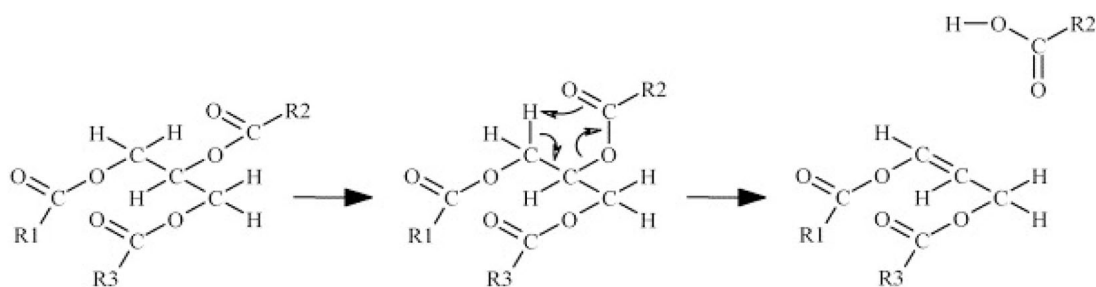

Fig. 2. Scheme of thermal destruction of triglycerides [14]

Based on the theory of free radical reactions [17], the cracking mechanism can be represented on the basis of two processes, namely, dealkylation and condensation [17, 18].

The formation of asphaltenes and coke during cracking is possible due to two types of condensation reactions [18]. The first type of condensation proceeds through the formation of naphthene-aromatic hydrocarbons by the Diels-Alder reaction, then naphthene-aromatic hydrocarbons are dehydrogenated and converted into polycyclic aromatic hydrocarbons [18]. This type of condensation reaction explains the formation of predominantly asphaltenes with a continental structure [11]. The second type of condensation reaction proceeds due to the recombination of radicals and the formation of larger molecules.

An increase in the content of olefins in the reaction medium, due to the destruction of SFO, can hinder recombination reactions and facilitate condensation (Diels-Alder reaction). Also, TGUFA, UFA and other oxygen-containing hydrocarbons obtained in the course of SFO cracking can act as surfactants, thereby slowing down the aggregation of coke precursors and the formation of coke itself. It is known from the literature that the use of surfactants in the cracking of oil residues allows an increase in the yield of maltenes and a decrease in the yield of coke and gas.

Conclusions

It is shown that the addition of sunflower oil to oil residues during thermal cracking leads to changes in the parameters of macrostructure of the resulted asphaltenes and coke.

In the coke separated from the products of cracking of oil residues obtained in the presence of sunflower oil, the average diameter of the aggregate (Lc) increases, while the distance between the aromatic layers (dm) does not change significantly. In asphaltenes isolated from products of cracking, the diameter of the aromatic core (La) and the distance between the saturated structures (dr) vary significantly.

The role of sunflower oil can be explained by the participation of triglyceride degradation products (mainly fatty acids and olefins) in condensation processes. Olefins and unsaturated fatty acids can inhibit radical recombination, which can affect the formation of coke and asphaltenes. Also, triglycerides and unsaturated fatty acids formed from sunflower oil during cracking can act as surfactants, thereby slowing down the aggregation of coke precursors and the formation of coke itself.

References

[1]   Castañeda L. C., Muñoz J. A. D., Ancheyta J. Current situation of emerging technologies for upgrading of heavy oils. *Catalysis Today 2014*. 220–222, 248–273.

[2]   Головников А. В., Филиппова О. П., Яманина Н. С., Копылов А. Б. Исследование структуры, свойств и физико-химических характеристик отработанных масел. *Известия ТулГУ. Технические науки 2012*. 1, 120–126. [Golovnikov A. V., Filippova O. P., Yamanina N. S., Kopylov A. B. Research of structure, properties and physical and chemical characteristics of the fulfilled oils. *News of Tula state university. Technical sciences 2012*. 1, 120–126. (In Russ.)]

[3]   Doronin V. P., Potapenko O. V., Lipin P. V., Sorokina T. P. Conversion of vegetable oils under conditions of catalytic cracking. *Catalysis in Industry 2013*. 6(1), 53–59.

[4]   Doronin V. P., Lipin P. V., Potapenko O. V., Arbuzov A. B., Sorokina T. P. Features of combined conversion of naphthenic hydrocarbons and fatty acids under catalytic cracking conditions. *Petroleum chemistry 2016*. 56(8), 745–752.

[5]   Kopytov M. A., Boyar S. V., Golovko A. K. Thermal conversion of petroleum residue in the presence of vegetable oil. *AIP Conference Proceedings 2018*. 2051, 020131.

[6]   Kopytov M. A., Golovko A. K. Changes in structural-group characteristics of resins and asphaltenes of heavy oils in the primary distillation process. *Petroleum chemistry 2017*. 57(1), 39–47.

[7]   Kopytov M. A., Boyar S. V., Mozhaiskaya M. V. Thermal Transformations of Petroleum Residue Components in the Presence of Power-Plant Flyash Ferrospheres and Sunflower Oil. *Petroleum Chemistry 2020*. 60(3), 348–357.

[8]   Yen T. F., Erdman J. G., Pollack S. S. Investigation of the Structure of Petroleum Asphaltenes by X-Ray Diffraction. *Analytical Chemistry 1961*. 33(11), 1587–1594.

[9]   Alhumaidan F. S., Hauser A., Rana M. S., Lababidi M. S., Behbehani M. Changes in asphaltene structure during thermal cracking of residual oils: XRD study. *Fuel 2015*. 150, 558–564.

[10]   Akimov A. S., Sviridenko N. N., Morozov M. A., Panin S. V., Aleksenko V. O., Vlasov V. A., Vosmerikov A. V. Structural changes and chemistry of petroleum macromolecular components during thermocatalytic processing. *AIP Conference Proceedings 2019*. 2167, 020007.

[11]   Sheng Q., Wang G., Jin N., Husein M. M., Gao J. Three-level structure change of asphaltenes undergoing conversion in a hydrogen donor solvent. *Fuel 2019*. 255, 115736.

[12]   Samano V., Guerrero F., Ancheyta J., Trejo F., Diaz J. A. I. A batch reactor study of the effect of deasphalting on hydrotreating of heavy oil. *Catalysis Today 2010*. 150(3–4), 264–271.

[13]   Carlson C. S., Langer A. W., Stewart J., Hill R. M. Thermal Hydrogenation. Transfer of Hydrogen from Tetralin to Cracked Residua. *Industrial & Engineering Chemistry 1958*. 50(7), 1067–1070.

[14]   Dupain X., Costa D. J., Schaverien C. J., Makkee M., Moulijn J. A. Cracking of a rapeseed vegetable oil under realistic FCC conditions. *Applied Catalysis B: Environmental 2007*. 72(1–2), 44–61.

[15]   Idem R. O., Katikaneni S. P. R., Bakhshi N. N. Catalytic conversion of canola oil to fuels and chemicals: Roles of catalyst acidity, basicity and shape selectivity on product distribution. *Fuel Processing Technology 1997*. 51(1–2), 101–125.

[16]   Doronin V. P., Potapenko O. V., Lipin P. V., Sorokina T. P. Catalytic cracking of vegetable oils and vacuum gas oil. *Fuel 2013*. 106, 757–765.

[17]   Greensfelder B. S., Voge H. H., Good G. M. Catalytic and Thermal Cracking of Pure Hydrocarbons: Mechanisms of Reaction. *Industrial and Engineering Chemistry 1949*. 41(11), 2573–2584.

[18]   Sun X., Li X., Tan X., Zheng W., Zhu G., Cai J., Zhang Y. Pyrolysis of heavy oil in supercritical multi-thermal fluid: An effective recovery agent for heavy oils. *Journal of Petroleum Science and Engineering 2021*. 196, 107784.