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## Thermal and Catalytic Cracking of Asphaltenes / Maltenes Mixtures

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**Abstract.** The composition of the products of thermal and catalytic cracking of mixtures of deasphalted crude oil (DAO) or maltenes with 0, 8, 12, 16 % of asphaltenes was studied. Cracking was carried out in a batch reactor at a temperature of 450 °C for 2 hours. Microsized NiCrWC powder as an additive for catalytic cracking was used. Data on the composition of products of cracking were obtained. It was found out that in the course of thermal and catalytic cracking of DAO mixtures with different content of asphaltenes the yield in gaseous and solid by-products increased with increase in their content. At the same time, the yield of distillate fractions ibp-360 °C also increased, while the content of secondary resins and asphaltenes decreased. The structure of the initial asphaltenes undergone significant changes in the course of thermal and catalytic cracking. Hence, they decreased in size, became more aromatic and had a much lower number of alkyl substituents. It was noted that the addition of NiCrWC in the cracking of DAO mixtures with different asphaltene content did not significantly affect the destruction of asphaltenes and did not contribute to an increase in the yield of the ibp – 360 °C fraction.

**Keywords:** asphaltenes, maltenes, cracking, NiCrWC additive, structure, composition.

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## Термический и каталитический крекинг смесей асфальтены / мальтены

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**Аннотация.** В работе изучен состав продуктов термического и каталитического крекинга смесей деасфальтизированной нефти (DAO) с 0, 8, 12, 16 % асфальтенов. Крекинг проводился в реакторах (автоклавах) при температуре 450 °С в течение 2 часов. При каталитическом крекинге в качестве добавки использовался NiCrWC в виде порошка микронного размера. Получены данные по составу продуктов крекинга. Установлено, что в процессе термического и каталитического крекинга смесей DAO с различным содержанием асфальтенов по мере увеличения их содержания увеличивается выход побочных – газообразных и твердых продуктов; при этом также увеличивается выход дистиллятных фракций НК-360 °С, снижается содержание вторичных смол и асфальтенов. Структура исходных асфальтенов претерпевает значительные изменения в процессе термо- и каткрекинга – они уменьшаются в размерах, становятся более ароматичными с гораздо меньшим количеством алкильных заместителей. Отмечено, что добавка NiCrWC при крекинге смесей DAO с различным содержанием асфальтенов не оказывает значимого влияния на деструкцию асфальтенов и не способствует увеличению выхода фракции НК-360 °С.

**Ключевые слова:** асфальтены, мальтены, крекинг, добавка NiCrWC, структура, состав.

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Авторы заявляют, что у них нет конфликта интересов, требующего раскрытия в данной статье.

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### Introduction

The use of hydrocarbon resources of heavy oils and oil residues presents many difficulties due to a high content of high-molecular resin-asphaltene components in them. The main trend in the development of the oil refining industry is the conversion of heavy crude oils for the purpose of increasing the yield of light distillate fuels [1–2]. The advantages of thermal over catalytic methods are the following: a lower

production costs due to the technological design simplicity, the use of inexpensive catalysts, and the absence of any restrictions on the feedstock quality [3–4]. One way of optimizing the thermal processes of heavy oil processing is the use of various activating dispersed additives, which lead to a decrease in the yield of gaseous products and coke [5–7].

Asphaltenes are potential sources of light hydrocarbons and coke precursors formed during cracking [8–12]. During processing, asphaltenes undergo many reactions, including cracking, dehydrogenation, dealkylation, and condensation, which lead to changes in their structure [13–16]. The structure and content of asphaltene, and composition of dispersion medium are the main factors that determine the relative stability of crude oil [17].

The purpose of this work was to study the influence of a NiCrWC additive on increasing the intensity of asphaltene degradation using the example of model mixtures with varied contents of asphaltenes. The dispersed NiCrWC additive was a micron-sized powder, which contained W (24.1 %), C (3.1 %), Ni (51.3 %), Cr (15.9 %), Fe (3.7 %), and O (1.9 %) [18]. Being highly active in cracking reactions, this additive catalyzes the reactions of isomerization, dehydrogenation, and cleavage of C–C bonds [18–21]. Deasphalted oil (maltenes) was chosen as a dispersion medium for the preparation of model mixtures. A comparative analysis of the yields in distillate fractions and coke, as well as changes in the chemical structure of asphaltenes and the hydrocarbon composition of the products of thermal and catalytic cracking have been carried out.

### Experimental Section

The objects of study were model mixtures obtained by mixing maltenes of Usinsk oil with various amounts of asphaltenes isolated from the same oil by precipitation with n-hexane. The composition of the DAO mixtures with asphaltenes is presented in Table 1.

Deasphaltization. The crude oil sample was dissolved in a 40-fold excess of n-hexane. The hexane solution of crude oil was kept in a dark place for 24 hours. The precipitated asphaltenes were filtered off and placed into a paper cartridge. In a Soxhlet apparatus, the cartridge with asphaltenes was washed first with hot hexane to remove coprecipitated oils and resins, and then with chloroform to isolate asphaltenes. The hexane solution of maltenes obtained after deasphaltization was combined with the hexane extract after washing off the asphaltenes. The solvent was distilled off. A sample of maltenes was dried, brought to constant weight, and the yield of maltenes was determined. The solvent was removed from the chloroform solution, and the resulted asphaltenes were dried to constant weight.

Calculation of the average structural parameters was carried via the improved Brown-Ladner empirical formulas based on  $^1\text{H-NMR}$  data, data of elemental analysis, and MW values [13].  $^1\text{H NMR}$

Table 1. Composition of DAO mixtures

Content of asphaltenes in a mixture, wt%	0	8	12	16
Resins, wt%	19.6	18	17.2	16.5
Oils, wt%	80.4	73.9	70.8	67.5
Fractional composition				
lbp-360 °C, wt%	35.9	33.0	29.9	26.6
>360 °C,% wt%	64.1	67.0	70.1	73.4

spectra of asphaltenes were obtained using a Bruker AVANCE-AV-400 NMR-Fourier spectrometer at 400 MHz in CDCl<sub>3</sub> solutions with hexamethyldisiloxane as internal standard. Average molecular weights of asphaltenes were measured by cryoscopy in naphthalene. Elemental composition was determined using a Vario EL Cube CHNS analyzer by direct combustion at 1200 °C with subsequent separation of gases and combustion products in three adsorption columns (helium was a carrier gas) and identification using a thermal conductivity detector. The detection limit for each element is less than 0.01 wt%.

Distillation curves were obtained according to ASTM-D 2887.

Cracking of the samples with and without additive was carried out in a batch reactor of 12 cm<sup>3</sup> at a temperature of 450 °C and duration of 120 minutes. The weight of the feedstock loaded into the reactor was 7 g. The amount of NiCrWC additive was 0.5 wt% [21]. Argumentation in support of these conditions is described in [22]

As a catalytic additive, NiCrWC was used in the form of a micron-sized powder with a small specific surface ( $S_{sp} = 0.4014 \text{ m}^2 / \text{g}$ ), containing W (24.1 %), C (3.1 %), Ni (51.3 %), Cr (15.9 %), Fe (3.7 %) and O (1.9 %).

The procedure for preparing the NiCrWC additive and investigating its structure by X-ray diffraction analysis (Bruker D 8 X-ray powder diffractometer), electron microscopy, and electron microprobe analysis (scanning electron microscope with a Hitachi TM-1000 energy dispersive X-ray spectrometer) is described in [18]. It is shown that NiCrWC powder consists of particles of tungsten carbide and nichrome. Small amounts of nickel, chromium, iron, and oxygen are present on the surfaces of tungsten carbide particles, while those of tungsten, carbon, iron, and oxygen are observed on the surface of nichrome particles.

## Results and discussion

Table 2 presents the data on the mass balance of catalytic cracking (CC) of model mixtures. The reactions of destruction of crude oil components in the course of cracking promoted the formation of light hydrocarbons, which were included into the gas, gasoline, and diesel fractions [18]. With an increase in the asphaltene content, the yield in gases during thermal cracking (TC) increased

Table 2. Mass balance of cracking

Content of asphaltenes in a mixture, wt%	0		8		12		16	
	TC	CC	TC	CC	TC	CC	TC	CC
Coke, wt%	0.3	1.1	6.6	2.4	7.4	7.8	8.5	8.0
Gas, wt%	2.7	4.8	8.3	4.1	10.0	8.1	12.4	6.9
Liquid products including	97.0	94.1	85.1	93.5	82.6	84.1	80.8	85.9
Oils, wt%	70.9	75.6	73.0	76.2	68.8	70.6	63.0	69.6
Secondary resins, wt%	25.0	15.2	8.7	12.1	9.2	9.0	10.8	9.9
Secondary asphaltenes, wt%	1.1	3.3	3.4	5.2	4.6	4.5	7.0	6.4
Fractional composition:								
ibp-360 °C, wt%	34.6	52.7	56.4	62.9	52.5	54.9	48.2	54.6

from 2.7 to 12.4 %, while in the presence of a NiCrWC additive it increased from 4.8 to 6.9 %. The yield of gases from cracking of a mixture containing 8 % of asphaltenes in a presence of NiCrWC is lower (4.1 %) than that from cracking of maltenes, although asphaltenes should be an additional potential source of light hydrocarbons in this case. During cracking of DAO mixtures with 8–16 % asphaltenes in the presence of NiCrWC additive, the yield in gases was 1.2–2.0 times lower than that during thermal cracking. According to the data obtained, no clear dependence of the yield of gaseous products of cracking in the presence of NiCrWC on the content of asphaltenes in the model mixtures was revealed.

In addition to gaseous products, insoluble solid products like coke are also by-products of cracking. Free radicals resulted from reactions of degradation of hydrocarbons, resins, and asphaltenes may be involved in reactions of condensation to form coke. As can be seen from Table 2, the yield of coke from cracking increases with increasing of content of asphaltenes in the mixture. Coke is also formed during the cracking of maltenes (0 % of asphaltenes), which is probably due to the condensation of resins and high molecular weight hydrocarbons. In the case of catalytic cracking of DAO with 0 % of asphaltenes, the coke yield was 1.1 %. Thermal cracking of DAO with 8 % of asphaltenes led to a sharp increase in coke yield from 0.3 to 6.6 % compared to that for DAO with 0 % asphaltenes. In the case of cracking with NiCrWC, the rate of condensation reactions of DAO with 8 % of asphaltenes was significantly lower than in the course of TC. With a further increase in the amount of asphaltenes in the mixture with DAO to 12 and 16 %, 7.4 and 8.5 % of coke were formed during thermal cracking, while during CC the yield in coke was 7.8 and 8.0 %, respectively.

In liquid products of TC and CC, the content of ibp-360 °C distillate fractions was higher than their content in the initial mixtures (Tables 1,2). Most of these fractions were formed during cracking of DAO mixtures with 8 % asphaltenes both in the presence of NiCrWC additive and without it. With an increase in the amount of asphaltenes to 12 and 16 %, the yields of these fractions decreased, but remained rather high and exceeded the content of the ibp – 360 °C fraction in the initial DAO mixtures by 1.8–2.0 times.

In addition to the fractional composition, the content of resins and asphaltenes in liquid products of cracking of model mixtures also changes (Table 2). Figure 1 shows the amount of secondary resins and asphaltenes in liquid products of cracking change curves with content of asphaltenes. In the initial DAO, the resins content was 19.6 %. The content of secondary resins in the thermal cracking products of DAO without asphaltenes reached 25.0 %. The increase in the content of resins was possibly due to the destruction of large molecules of initial resins, which resulted in the formation of a higher amount of secondary resins with a lower molecular weight and lower H/C ratio. They contained a lower number of heteroatoms and carbon atoms in the alkyl side chains, as well as a lower number of aromatic rings compared to the initial resins molecules [23]. In addition, resins could also be formed as a result of condensation reactions with the participation of hydrocarbon radicals.

In other products of TC and CC, the content of secondary resins was lower than in the initial ones. Probably, in these cases, asphaltenes determined the direction of thermal conversions of mixture components, hence condensation reactions became predominant, which led to the involvement of resins into the formation of secondary asphaltenes and then coke. In comparison with thermal cracking, the addition of NiCrWC had no significant effect on the yield of secondary resins when the content of asphaltenes in mixtures with DAO was 12 and 16 % (Fig.1a).

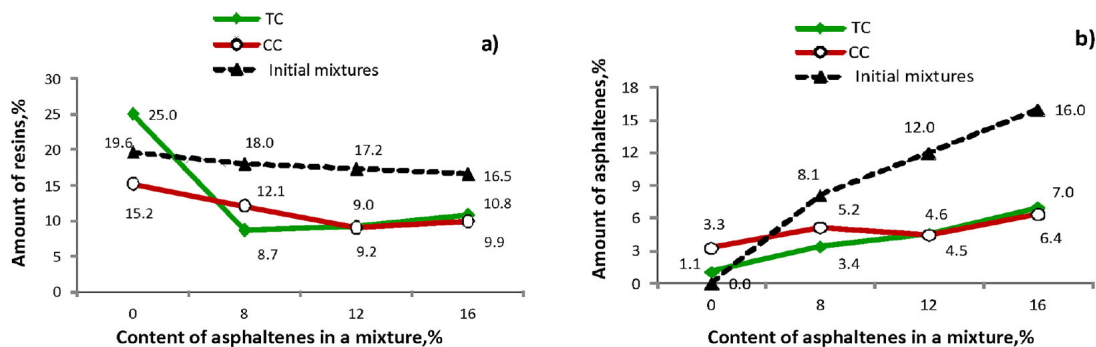


Fig. 1. Content of resins (a) and asphaltenes (b) in DAO mixtures and cracking products

The precursors of secondary asphaltenes were the initial asphaltenes decomposed in the processes of TC and CC, as well as asphaltenes formed from resins and polyarenes [24–25]. As can be seen from Table 2, secondary asphaltenes are also formed during cracking maltenes. Comparison of the yields of secondary asphaltenes with the amount of asphaltenes contained in the initial model mixtures shows that cracking in the presence of NiCrWC leads to a decrease in the amount of asphaltenes by a factor of 1.5–2.7. Differences in the yield of secondary asphaltenes during TC and CC were observed only for DAO mixtures with 0 and 8 %. With an increase in the amount of asphaltenes in the mixture to 12 and 16 %, the presence of the additive had no effect on the yield of secondary asphaltenes (Fig. 1b).

#### *Structural group characteristics of asphaltenes*

The structure of the initial asphaltenes changed during cracking due to the reactions of destruction, dehydrogenation, dealkylation, aromatization, and condensation [12, 26]. Table 3 presents the structural parameters of the initial asphaltenes and secondary asphaltenes formed during cracking.

Thermal cracking of DAO with 0 % asphaltenes led to the formation of asphaltenes, whose MW and the H/C ratio were similar to those of the initial asphaltenes. Asphaltenes formed during cracking of DAO with 0 % asphaltenes in the presence of NiCrWC additive were hydrogen-depleted (H/C = 0.80) and smaller in size than asphaltenes formed during thermal cracking. This was due to the effect of NiCrWC additive on the direction of thermal conversions of crude oil components and, as a consequence, the formation of asphaltenes, which differed in structure from the asphaltenes formed during thermal cracking.

The molecules of secondary asphaltenes of the products of TC and CC of DAO mixtures with an asphaltene content of 8, 12, and 16 % were smaller than the molecules of the initial asphaltenes and asphaltenes formed during the TC and CC of DAO with 0 % asphaltenes (Table 3). It should be noted that in all cases the effect of the additive on the size of asphaltene molecules was observed. Hence, the molecular weights of secondary asphaltenes molecules formed during catalytic cracking were higher than those of molecules formed during thermal cracking. The H/C ratios of secondary asphaltenes formed during TC and CC were similar. In comparison with the initial asphaltenes, an increase in nitrogen content and a decrease in total sulfur were observed in secondary asphaltenes.

The asphaltenes formed during the cracking of DAO with 0 % asphaltenes were structurally similar to the initial asphaltenes, as evidenced by the close values of the length of alkyl substituents

Table 3. Structural parameters of initial asphaltenes and secondary asphaltenes of the products of cracking

Content of asphaltenes in a mixture, wt%	0 %		8 %		12 %		16 %		
	Initial asphaltenes	Secondary asphaltenes							
Analysis items		TC	CC	TC	CC	TC	CC	TC	CC
Molecular weight, MW	1400	1253	930	738	832	528	569	603	637
Carbon, wt%	78.9	82.9	84.7	84.2	83.5	79.8	83.3	82.0	84.0
Hydrogen, wt%	7.8	7.8	5.6	5.3	5.4	5.5	5.4	5.6	5.6
H/C, mol/mol	1.19	1.13	0.80	0.76	0.77	0.82	0.79	0.82	0.80
Sulfur, wt%	3.9	4.0	2.3	3.5	3.6	3.2	3.6	3.3	3.6
Nitrogen, wt%	1.1	1.3	1.8	1.9	1.9	1.9	1.8	1.9	1.9
H <sub>AU</sub> /C <sub>A</sub>	0.60	0.53	0.49	0.45	0.44	0.52	0.48	0.51	0.48
Length of alkyl substituents, n	3.69	3.78	2.33	2.57	2.66	2.42	2.51	2.48	2.55
Total rings, R <sub>T</sub>	16.1	16.8	16.9	14.1	15.7	9.1	10.6	10.6	11.8
Aromatic rings, R <sub>A</sub>	9.6	11.1	12.9	11.5	12.7	7.0	8.4	8.2	9.3
Naphthenicrings, R <sub>N</sub>	6.5	5.7	4.0	2.6	3.0	2.4	2.2	2.4	2.5
Total carbon numbers, C <sub>T</sub>	92.1	86.6	65.6	51.8	57.9	35.1	39.5	41.2	44.6
Aromatic carbon numbers, C <sub>A</sub>	44.3	41.4	47.0	38.3	41.9	28.9	28.8	34.0	32.0
Aromaticity factor, (f <sub>a</sub> )	0.48	0.50	0.72	0.74	0.72	0.72	0.73	0.71	0.72
σ	0.48	0.49	0.35	0.30	0.32	0.31	0.30	0.32	0.32

(n), the total number of rings (R<sub>T</sub>), the aromatic factor (f<sub>a</sub>), and the degree of hydrogen substitution in aromatic systems (σ). The cracking of DAO with NiCrWC resulted in the formation of asphaltenes, whose structure was more aromatic and poor in side aliphatic chains as compared to the initial analogs.

Secondary asphaltenes formed during thermal cracking of a mixture of DAO with 8 % of asphaltenes were smaller in size than the initial asphaltenes and consisted of 14.1 rings, 80 % of which were aromatic, while the structure of the initial asphaltene molecules contained 16.1 rings, where only 60 % were aromatic rings. In addition, they contained 1.4 times less of alkyl substituents than the molecules of the initial asphaltenes. Molecules of secondary asphaltenes formed during thermal cracking of a mixture of DAO with 12 % and 16 % of asphaltenes had 9.1 and 10.6 cycles in their structure, respectively, where on average 78 % were aromatic cycles. The number of alkyl side chains was practically the same as in the molecules of secondary asphaltenes during the cracking of a mixture of DAO with 8 % asphaltenes.

A similar tendency was observed in the catalytic cracking of a DAO mixture with an asphaltene content of 8 %, 12 %, and 16 % in the presence of NiCrWC. Hence, the structure of the molecule was 2 cycles larger, and the degree of aromaticity was similar to that of secondary asphaltenes during TC. The number of alkyl substituents slightly exceeded that in the molecule of secondary asphaltenes during thermal cracking of the same mixtures. Apparently, the condensation reactions leading to the formation of coke were slightly inhibited due to the use of NiCrWC additive.

It should be noted that the difference between the average structures of asphaltenes obtained after TC and CC decreased in the following series of asphaltene content: 0 → 8 → 12 → 16 %. This fact can be explained by the more active destruction of asphaltenes on the catalyst surface, which, accordingly,

leads to the active deposition of condensation products. Thus, the faster the catalyst cokes, the smaller the difference between the structural changes of asphaltene molecules.

Secondary asphaltenes become more aromatic and their solubility decreases. Changes in the chemical structure of asphaltenes promote their aggregation and deposition on the surface of catalytic particles, which contributes to the formation of coke.

### Conclusion

Comparative analysis of the data on the mass balance of the products of thermal and catalytic cracking of DAO mixtures with different content of asphaltenes revealed that with an increase in the amount of asphaltenes in the mixture, the yield of gaseous and solid by-products increased, but at the same time the yield in distillate ibp-200 °C and 200–360 °C fractions also increased, while the content of secondary resins and asphaltenes decreased. The positive effect of use the NiCrWC additive was a decrease in the yield of gaseous products and a significantly higher increase in the yield of the 200–360 °C fraction as compared to thermal cracking. The formation of coke during thermal and catalytic cracking also occurred in the absence of asphaltenes, which was probably due to the condensation reactions of the resulting radicals of resin components and high molecular weight hydrocarbons.

The structure of the initial asphaltenes undergone significant changes in the course of thermal and catalytic cracking. Hence, the molecular weight and the H/C ratio decreased, while the degree of aromaticity increased. The H/C ratio of secondary asphaltenes formed during thermal and catalytic cracking are similar.

The investigation has shown that the use of NiCrWC additive for the cracking of DAO mixtures with different content of asphaltenes did not have a significant effect on the destruction of asphaltenes and did not contribute to an increase in the yield of the ibp – 200 °C fraction.

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