

UDC 665.64 665.35

STUDY OF THE PROCESS OF OBTAINING ALTERNATIVE MOTOR FUELS USING VEGETABLE OILS

I.A. Khalafova, N.K. Andryushenko

Azerbaijan State University of Oil and Industry
Azadliq Ave., 34, Baku, AZ1010, Azerbaijan Republic
e-mail: khalafova.irada@gmail.com

Received 06.05.2022

Accepted 10.07.2022

Abstract: The growing shortage of oil resources makes it necessary to find alternative energy sources. The leading place among them today belongs to biofuels, both due to sufficient and affordable resources, and relatively advanced technologies for their production. The requirements of modern standards for the quality of the resulting gasolines limit the content of aromatic hydrocarbons in them to no more than 42% by mass. (Euro-3), and 35% of the mass. (Euro-4 and Euro-5). Therefore, studies on the involvement of vegetable raw materials in the processes of obtaining gasoline fractions are aimed either at obtaining highly aromatic gasoline with its subsequent compounding, or at searching for catalytic systems that make it possible, if any, to reduce the content of aromatic hydrocarbons in the composition of the resulting gasolines during joint cracking of the mixture of oil and vegetable raw materials. In this work, using the model oleic acid as an example, the mechanism of the conversion of fatty acids of vegetable oils during their catalytic conversion into hydrocarbons of the gasoline series was studied. The process was studied using a mixture of vacuum gas oil with vegetable oils as cracking catalysts, industrial cracking catalysts Omnikat-210P and Tseokar-600 in pure form and in their mixture with natural halloysite nanotubes. Halloysites belong to the family of kaolinite clay minerals with a high Al/Si ratio as compared to other aluminosilicates and have a predominantly hollow tubular structure and consist of layers of aluminum and silicon oxides that are rolled into tubes. The process of catalytic cracking of vacuum gas oil with the involvement of vegetable oils (waste vegetable oils taken from the Chudo-Pechka chain of stores) in the amount of 5 wt % was studied.

Keywords: oleic acid, vegetable oils, catalytic cracking, halloysites, reaction mechanism, catalyst, Omnikat-210P, Tseokar-600

DOI: 10.32737/2221-8688-2022-3-229-241

Introduction

The ever-growing shortage of oil resources makes it necessary to search for alternative energy sources, among which today the leading place belongs to biofuels, both due to sufficient and affordable resources, and relatively advanced technologies for their production.

The leading trend in obtaining second-generation biofuels is the creation of a technology for the large-scale production of high-quality motor fuels from oxygen-containing raw materials of plant origin, using the existing fuel transport system and the infrastructure of oil refineries. The basis of these processes is both the hydro-treatment of

mixed feedstock (vegetable oils and fats and diesel oil fraction at hydro-treatment and hydro-cracking units ("Green Diesel"), and the joint cracking of a mixture of gas oil fractions with vegetable feedstock in order to obtain a gasoline fraction and/or olefins ("Green Gasoline", "Green Olefin") [1-5].

The analysis of literary sources made it possible to single out the main class of catalysts used in the production of gasoline during catalytic cracking of a mixture of petroleum fractions and vegetable raw materials. Basically, these are synthetic zeolite-containing catalysts with strong acid centers and various porosities. The most widely studied in the processes of

joint processing of vegetable oils, as well as their mixtures with petroleum fractions, is the catalyst HZSM-5, HZSM-10, HZSM-12 (the so-called 5–12-ring zeolites) [6, 7].

However, it should be noted that gasolines obtained during the process of catalytic cracking of vegetable oils have a high content of aromatic hydrocarbons. This can be explained as being due to the high content of unsaturated fatty acids with one, two or three double bonds in the triglyceride molecule of vegetable oils which, under the effect of high temperatures, are converted into olefin fragments and subsequently lead to the formation of aromatic hydrocarbons.

The requirements of modern standards for the quality of the resulting gasolines limit the content of aromatic hydrocarbons in them to no more than 42% by mass. (Euro-3), and 35% of the mass. (Euro-4 and Euro-5). Therefore, studies on the involvement of vegetable raw materials in the processes of obtaining gasoline

fractions are aimed either at obtaining highly aromatic gasoline with its subsequent compounding, or at searching for catalytic systems that make it possible, if any, to reduce the content of aromatic hydrocarbons in the composition of the resulting gasolines during joint cracking of the mixture of oil and vegetable raw materials.

The purpose of this work is to study the possibility of involving vegetable oils obtained from oil-containing crops growing on the territory of Azerbaijan in the process of obtaining gasoline fractions by processing a mixture of various petroleum fractions with these vegetable oils. In the work, a mixture of waste vegetable oils taken from the Miracle Pechka chain of stores was used as oil. At the moment, the process of recycling waste vegetable oils has not been established. Exploring the possibility of using used oils in the production of motor fuels, we can talk about improving the environment.

Experimental part

In this work, industrial cracking catalysts Omnikat-210P and Tseokar-600 in pure form and in a mixture of natural halloysite nanotubes

were studied as catalysts for cracking a mixture of vacuum gas oil with vegetable oils (Table 1-2).

Table 1. Quality indicators of the cracking catalyst Omnikat-210P with a promoter for afterburning CO into CO₂ by «Grace»

Name of indicators	average	minimal	maximum
Microactivity, min. (ASTM (DEVISON) after heat treatment at 760 °C, 5 h, 1.35 bar 100% steam	75	73	
Physical properties after calcination at 540°C, 3 h			
– surface area, m ² /g	200	180	220
– pore volume, mm ³ /g	0.4	0.35	0.43
– bulk density, g/ml	0.65	0.61	–
– wear resistance (Davison index)	5	–	8
particle size distribution, % wt.			
0-20 microns	1	–	2
0-40 microns	15	10	20
0-80 microns	60	90	70
0-149 microns	92	90	100
average particle size, microns	70	65	78
Chemical composition, % wt.			
– Al oxide (Al ₂ O ₃), % wt.	44.0	41.0	47.0
– oxide Na (Na ₂ O), % wt.	0.25	–	0.35
– oxides of rare earth elements (Re ₂ O ₃), % wt.	1.9	1.6	2.2

– platinum content in the catalyst	not lower than 2 ppm
------------------------------------	----------------------

The catalyst Tseokar-600 was produced by LLC Company KATAKHIM, Russia.

Table 2. Qualitative indicators of the catalyst Tseokar-600

Name of indicator	Normalized values
Bulk density under test conditions, kg/m ³ , within	680-780
Mass fraction of target fraction 3.0-6.0 mm, %, not less than	92
Mass fraction of whole and mechanically strong balls of fraction 2.5-5.0 mm, %, not less	86
Stable activity in terms of gasoline yield, %, not less than	52
Selectivity, %, not less	75
Mass fraction of moisture removed at 800 °C, %, no more	2.5
Mass fraction of rare earth elements in terms of their oxides, %, not less than	1.8
Mass fraction of components, %, not more than:	
sodium oxide	0.55
iron oxide	0.3
Characteristics of platinum content - volumetric ratio of carbon monoxide (IV) to carbon monoxide (II) (CO ₂ /CO), not less than	1.5
Catalyst strength under shock-abrasive action 300 s, %, not less	50

Halloysite belongs to the family of kaolinite clay minerals with a high Al/Si ratio as compared to other aluminosilicates and have a predominantly hollow tubular structure. Content of various elements in samples of halloysites are presented in Table 3.

Table 3. Content of various elements in samples of halloysites

Content of elements, mg/kg	Halloysite samples		
	USA (1)	USA (2)	New Zealand
1	2	3	4
S	38720	-	-
K	16985	-	-
Ca	20111	2406	-
Ti	1150	487	653
Cr	-	50	59
Mn	562	79	43
Fe	16416	5893	3319
Co	-	-	-
Ni	-	315	-
Cu	-	-	-
Zn	412	138	-
As	111	-	-
Rb	-	21	-
Sr	3084	240	19

Zr	60	63	183
Mo	-	63	-
Pt	-	-	463
Ba	410	132	-
Pb	107	-	84

Halloysites consist of layers of aluminum and silicon oxydes, which are twisted into tubes. The silica layer is on the outer surface of the tube, while the alumina layer refers to the inner surface of the lumen (hole) [8-10]. The outer diameters of the tubes vary from 40 to 100 nm with an average value of 70 nm [9, 11]. The diameters of the inner lumen (hole) range from 10 to 50 nm and average 20 nm [13]. The tube lengths range from 0.5 to 2.0 μm [8].

The different chemical structure of the outer and inner sides of the halloysite layer adds unique properties to halloysite nanotubes that do not exist in other nanotubes. One of the features of halloysite is the different surface and chemical properties on the inner and outer sides of the tubes [12]. Aluminum and silicon oxides

have different dielectric and ionization properties. These tubes can be selectively modified on the outside or inside, which can be useful in hydrocarbon cracking.

Halloysite nanotubes have a high specific surface area ranging from 80 to 150 m^2/g due to which these minerals have a very high cation exchange capacity from 0.02 to 0.68 mol/kg [9]. Hydrated halloysite nanotubes can adsorb low molecular weight substances into the interlayer space [9, 13, 14]. The absorption of macromolecular substances with a molecular weight above 300 g/mol mainly takes place through loading into the inner lumen of tubes, which is of particular interest in the processing of heavy hydrocarbons [8, 15–16].

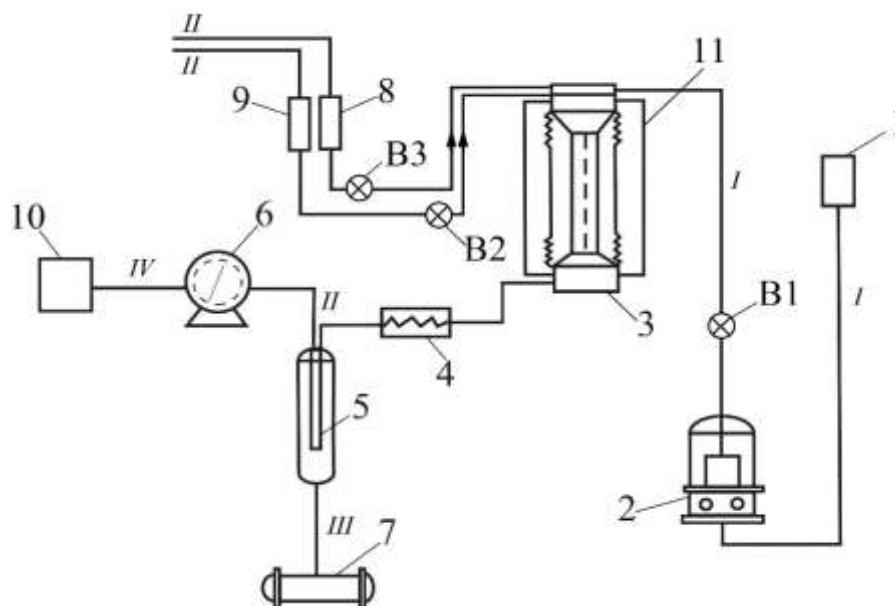


Fig. 1. Technological scheme of a flow unit for carrying out the process of catalytic cracking of linoleic acid. Lines: I - raw material supply line; II - gas supply line (nitrogen, air); III - collection line for liquid products; IV - collection line for gaseous products. 1 - container for raw materials; 2 - pump; 3 - reactor; 4 - condenser-refrigerator; 5 - degasser; 6 - gas clock; 7 - receiver of liquid products; 8, 9 - dehumidifier of incoming gases; B1, B2, B3 - throttle valves, 10 - gas meter, 11 - heating furnace

The presence of acidic segments in halloysite nanoparticles due to the high content of aluminum oxide leads to the cracking of hydrocarbons. These acidic sites catalyze the heterolytic cleavage of chemical bonds which leads to the formation of unstable carbocations which undergo chain rearrangements and cleavage of C-C bonds through β -elimination or hydride ion transfer. All these processes contribute to the formation of highly reactive radicals and ions which further accelerate the cracking process [17].

The study of the mechanism of the conversion of fatty acids of vegetable oils during their catalytic conversion into hydrocarbons of the gasoline series was carried out using the example of model oleic acid. The

process of catalytic cracking of oleic acid was carried out on a flow-through laboratory unit at temperatures of 490-510 °C, WHSV 1-20 h⁻¹ (Fig. 1).

The study of the composition of products from the process of catalytic cracking of oleic acid on the Omnikat-210P catalyst showed that as the contact time of the feedstock with the catalyst increases, the products of oleic acid conversion mainly containing aromatic compounds with no n-paraffin compounds, the content of olefinic and naphthenic hydrocarbons makes up 0.71 and 0.62% mass. respectively. As WHSV increases to 10 h⁻¹, n-paraffins appear in the composition of the catalyzate, and the content of olefinic and naphthenic hydrocarbons increases as well (Table 4).

Table 4. Hydrocarbon Composition of Oleic Acid Cracking Products Using Omnikat-210P, Tseokar-600 Catalysts and Their Mixtures with Halloysites

Hydrocarbon composition of products, % wt.	Catalysts			
	Omnikat-210P	Omnikat-210P + halloysite	Zeokar-600	Zeokar-600 + halloysite
	WHSV = 1 h ⁻¹			
paraffins	0	0	0	0
olefins	0.71	2.12	0	0.12
cycloparaffin	0.62	0.85	0	0.15
aromatic, incl.	94.37	90.71	94.68	93.68
benzene	4.15	3.90	10.95	8.65
alkylbenzenes	25.95	32.33	19.35	27.11
Bicyclic (naphthalene and its derivatives)	36.8	31.20	35.63	32.10
Tricyclic (phenanthrenes, anthracenes)	13.46	11.82	14.75	12.82
Tetracyclic (pyrene chrysene and their derivatives)	14.01	11.46	14.0	13.0
	WHSV = 10 h ⁻¹			
paraffins	1.65	1.95	1.38	1.52
olefins	2.14	2.46	3.12	3.68
Cycloparaffins (ethyl-cyclohexane)	1.35	1.94	0.34	0.95
aromatic, incl.	91.54	88.33	89.84	88.53
benzene	3.18	2.75	7.65	5.98
alkyl benzenes	30.24	34.65	26.26	30.14
Bicyclic (naphthalene and its derivatives)	31.12	30.80	34.12	31.20
Tricyclic (phenanthrenes, anthracenes)	12.00	10.46	12.45	10.34
Tetracyclic (pyrene, chrysene and their derivatives)	13.00	9.67	12.36	10.87

	WHSV = 20 h ⁻¹			
paraffins	14.60	12.2	11.5	10.2
olefins	22.10	24.3	20.34	22.6
cycloparaffins	6.40	8.3	4.6	5.3
aromatic, incl.	56.57	55.0	62.86	61.15
benzene	2.85	1.85	3.83	3.00
alkyl benzenes	42.30	45.95	34.43	39.55
polycyclic aromatics	11.42	7.2	24.6	18.6
Benzoic acid	0.18	0.12	0.43	0.35
Linoleic acid	0.05	0.06	0.07	0.02

A decrease in the contact time of the raw material with the catalyst also affects the composition of the resulting aromatic compounds. The content of benzene decreases to 3.18% mass, while the total content of various benzene derivatives slightly increases – 30.24% mass. An increase in WHSV also leads to a decrease in polynuclear aromatic compounds.

An increase in WHSV to 20 h⁻¹ in the composition of the obtained catalyzate significantly increases the amount of paraffin, olefin and cycloparfin compounds. The content of aromatic compounds decreases to 56.57% mass, while with WHSV 1-10 h⁻¹ it is 94.37-91.54% mass. The composition of aromatic compounds is represented mainly by alkylbenzenes (Table 5).

Table 5. The composition of alkyl benzenes formed during the cracking of oleic acid

Composition of alkyl benzenes, % mass.	Catalyst					
	Omnikat-210P			Omnikat-210P + halloysite		
	WHSV, h ⁻¹					
	1	10	20	1	10	20
Methyl-benzene	1.8	2.01	2.55	1.3	1.50	2.81
1,2 dimethylbenzene	2.27	3.14	6.64	6.26	8.82	14.68
1,3 dimethylbenzene	1.05	1.12	2.62	1.35	1.54	3.72
1,2,3-trimethylbenzene	0.30	0.55	3.05	2.55	2.7	3.02
1,2-diethylbenzene	6.16	7.66	9.16	7.32	7.65	8.20
1-ethyl-2-methyl benzene	3.06	4.68	6.18	4.85	4.41	5.37
1-methyl-3-propyl benzene	5.95	5.83	8.30	4.65	4.95	5.47
1-methyl-2-(2-propenyl)benzene	5.36	5.25	3.8	4.05	3.08	2.68
Total:	25.95	30.24	42.3	32.33	34.65	45.95

The data obtained allow us to suggest a mechanism for the formation of aromatic compounds along two routes: the cyclization of the hydrocarbon chain, predominantly with the participation of the hydrogen atom bonded to the C atom in the α -position with respect to the carbonyl group, which usually exhibits high

activity, as well as the interaction of olefinic hydrocarbons formed when C-C bonds are cleaved predominantly in the β -position with respect to the double bond of fatty acid molecules (according to the Diels-Alder reaction) (Fig. 2-3)

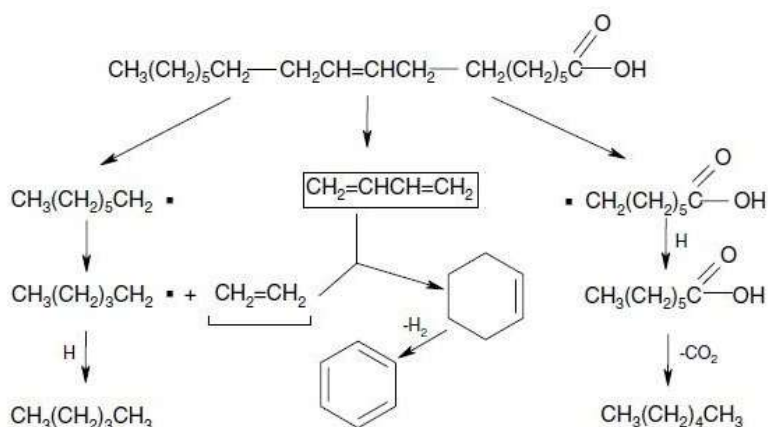


Fig. 2. Scheme of formation of aromatic compounds during the splitting of oleic acid by the Diels-Alder reaction.

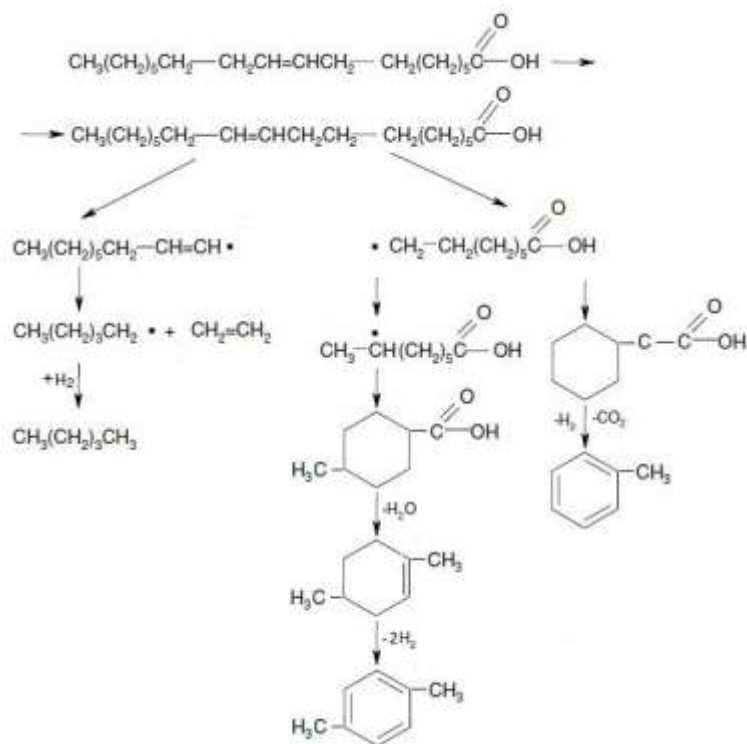


Fig. 3. Scheme of the formation of aromatic compounds during the splitting of oleic acid by the cyclization reaction

This suggests that aromatization of oxygenates can occur before deoxygenation and this is favored by the presence of a carbonyl group [18].

After ring closure, the carbonyl group can be converted at the acid sites of the catalyst during tautomerism to the enol form, which, in turn, can be dehydrated and further

dehydrogenated to form o-xylene, or after ring closure, decarboxylation and dehydrogenation can occur to form the corresponding alkylbenzenes.

Reducing the contact time of the feedstock with the catalyst leads to the decrease in the share of cleavage reactions of long-chain carbon chains and to the decrease in the share of

formed benzene and an appropriate increase in the share of alkyl-benzenes. This fact is also confirmed when a mixture of Omnikat-210P with halloysites is used as a catalyst.

Studies showed that in the case of using catalytic systems with halloysites, the mechanism of formation of aromatic compounds proceeds mainly along the first route.

Table 1 shows that the addition of halloysites to the composition of catalysts leads to an increase in the amount of olefinic hydrocarbons formed while reducing the amount of benzene formed.

The amount of o-xylene formed when using a mixture of the Omnikat-210P catalyst with halloysites is higher even at $WHSV = 1 \text{ h}^{-1}$ and amounts to 6.26 % mass, while when using the Omnikat-210P catalyst with halloysite at $WHSV = 20 \text{ h}^{-1}$ content of o-xylene increases to 14.68%.

The use of Tseocar-600 as a catalyst at low mass feed rates (1 h^{-1}) leads to almost 100% conversion of oleic acid into aromatic compounds. The composition of the catalyzate does not contain paraffin, olefin or cycloparfin compounds.

The content of the resulting alkyl benzenes is lower, and the content of polycyclic aromatic compounds is somewhat higher than when using the Omnikat-210P catalyst and its mixture with halloysites.

When halloysites are added to the

composition of the tested catalyst at $WHSV = 1 \text{ h}^{-1}$, the amount of alkyl-benzenes formed noticeably increases, while the amount of polycyclic aromatic compounds formed decreases.

The use of a mixture of Tseocar-600/halloysite leads to a decrease in the composition of the formed aromatic compounds of benzene.

When using Tseocar-600 in its pure form and with halloysite at $WHSV = 20 \text{ h}^{-1}$, the amount of n-paraffins and olefins increases, and the composition of hydrocarbon gases is mainly represented by unsaturated compounds (ethylene, propylene).

The use of catalysts Omnikat-210P and Omnikat-210P/halloysite leads to a noticeable decrease in the composition of the formed gases of ethylene cracking, with a simultaneous increase in the amount of propylene formed.

At the next stage of the research, the process of catalytic cracking of vacuum gas oil with the involvement of vegetable oils (cottonseed, sunflower, as well as a mixture of vegetable oils used in the food industry) in its composition amounting to 5% mass., was considered which was carried out on flow laboratory installation in the temperature range of 480-520 °C and $WHSV = 22.0 \text{ h}^{-1}$. V

The material balance of the process of catalytic cracking of the 5% mixture of waste vegetable oils with vacuum gas oil is given in table 6.

Table 6. Material balance of the process of catalytic cracking of a 5% mixture of used vegetable oils with vacuum gas oil at a temperature of 480-520 °C

Type of raw material	Catalyst											
	Omnikat-210P			Omnikat-210P + halloysite			Tseokar-600			Tseokar-600+ halloysite		
	Температура процесса, °C											
	480	500	520	480	500	520	480	500	520	480	500	520
Taken, % mass.:												
Vacuum gas oil	95	95	95	95	95	95	95	95	95	95	95	95
Vegetable oil	5	5	5	5	5	5	5	5	5	5	5	5
Received, % mass.:												
Gases up to C ₄	13.0	14.5	18.6	13.5	15.0	19.5	13.5	15.7	19.2	14.4	16.8	20.1
Gasoline fraction n.k.-200 °C	38.8	46.3	41.6	40.0	47.5	42.6	39.8	46.8	44.4	40.8	49.4	45.1

Light gas oil 200-350 °C	16.2	6.3	4.8	15.5	6.3	4.1	17.5	7.0	4.5	18.6	6.8	4.0
heavy gas oil	26.9	27.4	29.0	25.8	25.9	28.2	24.1	25.3	25.9	21.2	21.8	25.0
coke	2.7	2.9	3.4	2.6	2.8	3.2	2.8	3.0	3.5	2.6	2.7	3.3
Losses + water*	2.4	2.6	2.6	2.6	2.5	2.4	2.3	2.2	2.5	2.4	2.5	2.5
Conversion, % mass.	54.5	63.7	63.6	56.1	65.3	65.3	56.1	65.5	67.1	57.8	68.9	68.5
Selectivity for gasoline, %	71.2	73.0	65.4	71.3	73.0	65.2	71.0	71.5	66.2	71.0	72.0	66.0

Results and discussion

An analysis of the data obtained makes it possible to conclude that there is a tendency to raise the yield of the gasoline fraction with rise in temperature of the catalytic cracking process from 480 °C to 500 °C. Under these conditions, an increase in the yield of gas and gasoline fractions and a decrease in the content of heavy gas oil were revealed. At the same time, an increase in the yield of gasoline fraction at a temperature of 500 °C in comparison with the data obtained during the processing of pure

vacuum gas oil is 0.7–1.4%, and the largest increase is observed for catalytic systems with halloysites (Fig. 4).

The smallest rise in the gasoline fraction is observed when using a mixture of used vegetable oils (having a heavier composition) for Omnikat-210P and Tseokar-600 catalysts (0.7-0.8% mass.). However, the addition of halloysites to the composition of the catalyst makes it possible to slightly increase the yield of gasoline (up to 1% mass.).

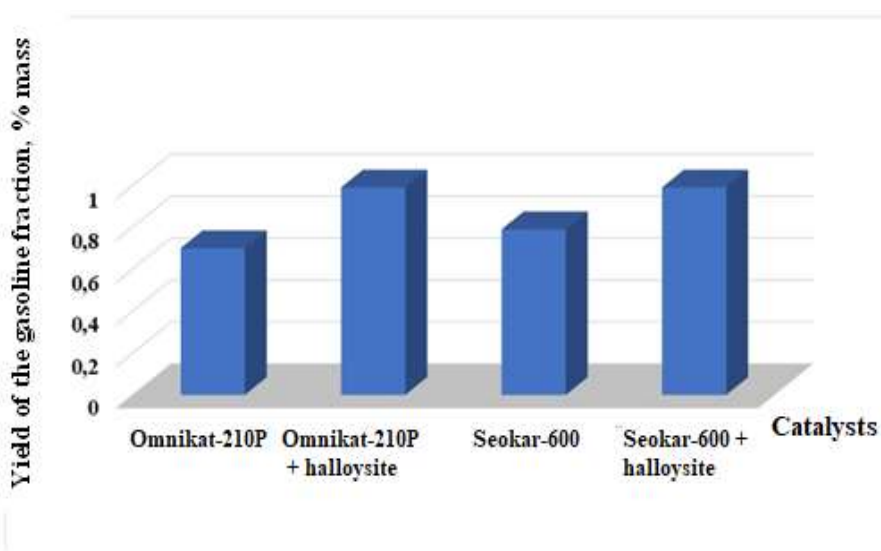


Fig. 4. Increase in the yield of gasoline fraction for a 5% mixture of vegetable oils with vacuum gas oil in comparison with the processing of pure v/gas oil at 500 °C

Table 7 provides the quality indicators of gasoline fractions obtained in the process of catalytic cracking of a mixture of vacuum gas oil with used vegetable oils at 500 °C in

comparison with traditional catalytic cracking gasolines, received on H. Aliyev Oil Refinery [19].

Table 7. Physical and chemical properties of gasolines from the process of catalytic cracking of vacuum gas oil with waste vegetable oils using catalysts Omnikat-210P (I), Tseokar-600 (II) and their mixtures with halloysites (IA, IIA)

Indicators	Catalytic cracking gasoline (H.Aliyev Oil Refinery)	Catalyst			
		(I)	(IA)	(II)	(II A)
		Vacuum gas oil + 5% mixture of used vegetable oils			
1	2	3	4	5	6
Density at 20 °C, kg/m ³	726.2-738.9	739.0	738.2	737.0	736.4
Fractional composition, °C:					
start of boiling	35-38	37.0	37.0	37.0	35.0
10% is distilled at the same rate	50-70	68.0	60.0	55.0	50.0
50 % ----	104-115	115.0	112.0	106.0	105.0
90 % ----	185-190	190.0	190.0	185.0	183.0
End of boiling	195-205	205.0	202.0	200.0	200.0
Iodine number I ₂ /g	30-50	40.2	44.0	45.1	49.0
Acidity mg KOH/ 100 cm ³	0.30-1.50	0.99	0.93	0.95	1.07
Saturated vapor pressure, kPa	38.6-54.2	43.1	45.0	46.1	47.4
Concentration of actual resins, mg/100 cm ³	0.95-2.1	1.60	1.52	1.54	1.47
Sulfur content, % mass.	0.012-0.016	0.011	0.011	0.011	0.011
Copper plate test	+	+	+	+	+
Hydrocarbon composition, % mass.:					
n-paraffins	15.0-30.0	21.45	18.93	17.34	14.4
iso-paraffins	20.0-30.0	24.30	25.40	24.7	27.6
naphthenes	7.0-16.0	6.30	7.65	7.12	7.65
Olefins	15.0-18.0	17.90	19.42	19.54	20.85
aromatics, incl.	23.0-30.0	30.05	28.60	31.30	29.50
benzene	1.8-3.2	1.85	1.34	2.05	1.65
Octane number	90-91	91	91	91.5	91.5

Gasoline fractions obtained in the process of catalytic cracking of mixtures of vacuum gas oil with waste vegetable oils were studied in the laboratory of H.Aliyev Oil Refinery (Table 7). The group hydrocarbon composition of gasoline fractions was analyzed chromatographically on a Perkin Elmer Auto System XL chromatograph (column length 100 m, diameter 250 µm, filler dimethylsiloxane).

As can be seen from Table 7, the quality indicators of gasoline fractions obtained in the process of catalytic cracking of a mixture of vacuum gas oil with waste vegetable oils are almost identical to the quality indicators of traditional catalytic cracking gasolines.

However, they have a slightly heavier fractional and more flavored hydrocarbon composition.

Thus, in the course of the current study, the possibility of involving vegetable oils in the process of catalytic cracking was revealed. It found that by adding 5% vegetable oils to the composition of vacuum gas oil, the yield of gasoline fraction rises with a simultaneous improvement in the quality of the resulting gasoline, both operational and environmental. At the same time, the addition of halloysites to the composition of industrial catalytic cracking catalysts makes it possible to reduce the content of aromatic hydrocarbons in the composition of the gasoline fraction by 1.4–1.8 mass%.

References

1. Donnis B., Egeberg R., Blom P. et al. Hydroprocessing of Bio-Oils and Oxygenates to Hydrocarbons. Understanding the Reaction Routes. *Topics in Catalysis*. 2009, vol. 52, no. 3. p. 229
2. Furimsky E. Catalytic hydrodeoxygenation. *Applied Catalysis A: General*, 2000, vol. 199 (2), pp. 147-190.
3. Senol O.I., Viljava T.R., Krause A.O.I. Hydrodeoxygenation of aliphatic esters on sulphided NiMo/ γ -Al₂O₃ and CoMo/ γ -Al₂O₃ catalyst: The effect of water. *Catalysis Today*. 2005, vol. 106. pp. 186-189.
4. Abbasov V.M., Rustamov M.I., Mammadova T.A., Andryushchenko N.K., Askerova E.N., Veliev H.R. Obtaining a new generation of diesel fuels hydrotreating mixture of oil and vegetable raw materials. *Chemistry and Technology of Fuels and Oils*. 2010, no. 3, pp. 8-11.
5. Mammadova T.A., Andryushchenko N.K., Alieva S.Z., Askerova E.N., Alieva Z.M. Research of process of reception of non-polluting diesel fuels by joint processing of oil and vegetative raw materials. *Azerbaijan chemical journal*, 2010, no.1, pp. 184-187.
6. Chow P.W. Production of synthetic crude petroleum. US Patent 5233109 (1993)
7. Park K.C., Ihm S.K. Comparison of Pt/Zeolite Catalysts for n-Hexadecane Hydroisomerization. *Appl. Catal., A: General*. 2000, vol. 203, pp. 201-209.
8. Price R., Gaber B., Lvov Y. In-vitro release characteristics of tetracycline, khellin and nicotinamide adenine dinucleotide from halloysite; a cylindrical mineral for delivery of biologically active agents. *Journal of Microencapsulation*. 2001, vol. 18, pp. 713-723.
9. Joussein E., Petit S., Churchman J., et al. Halloysite clay minerals – a review. *Clay Minerals*. 2005, vol. 40, pp. 383-426.
10. Tari G., Bobos I.C., Gomes S.F. et al. Modification of surface charge properties during kaolinite to halloysite-7Å transformation. *J. Colloid and Interface Sci.* 1999, vol. 210, pp. 360-366.
11. Bates T., Hildebrand F., Swineford A. Morphology and Structure of Endelite and Halloysite. *American Mineralogist*. 1950, vol. 35, pp. 463-484.
12. Yuan P., Southon P.D., Liu Z., et al. Functionalization of halloysite clay nanotubes by grafting with γ -aminopropyltriethoxysilane. *J. Phys. Chem. C*. 2008, vol. 112, pp. 15742-15751.
13. Carr R.M., Chaikum N., Patterson N. Intercalation of Salts in Halloysite. *Clays & Clay Miner.* 1978, vol. 26, no. 2, pp. 144-152.
14. Hiller S., Ryan P.C. Identification of halloysite (7 angstrom) by ethylene glycol solvation: the «MacEwan effect». *Clay Minerals*. 2002, vol. 37, no. 3, pp. 487-496.
15. Levis S.R., Deasy P.B. Characterisation of halloysite for use as a microtubular drug delivery system. *International Journal of Pharmaceutics*. 2002, vol. 243, pp. 125-134.
16. Kelly H.M., Deasy P.B., Zaika E., et al. Formulation and preliminary in vivo dog studies of a novel drug delivery system for the treatment of periodontitis. *International Journal of Pharmaceutics*. 2004, vol. 274, pp. 167-183.
17. Levis S.R., Deasy P.B. Use of coated microtubular halloysite for the sustained release of diltiazem hydrochloride and propranolol hydrochloride. *International Journal of Pharmaceutics*. 2003, vol. 253, pp. 145-157.
18. Mammadova T.A., Andryushchenko N.K., Lyatifova T.S., Askerova E.N., Teyubov H.S., Kesemenli H.G. Production of catalytic cracking gasoline by processing a mixture of petroleum and vegetable raw materials. *Oil Processing and Petrochemistry*. 2012, no. 11, pp. 15-18.
19. Mamedova T.A., Andryushchenko N.K., Lyatifova T.S., Askerova E.N., Abdulova Sh.N., Ibrahimov Kh.D. Investigation of process of the catalytic cracking of the mixture of vacuum gasoil and cotton oil over zeolite containing catalyst. *Processes of Petrochemistry and Oil Refining*. 2012, vol.13, no. 2 (50), pp. 148-155.

BİTKİ YAĞLARINDAN İSTİFADƏ EDİLƏN ALTERNATİV MÜHƏRRİK YANACAQLARININ ALINMASI PROSESİNİN ARAŞDIRILMASI

İ.A. Xələfova, N.K. Andryuşenko

*Azərbaycan Dövlət Neft və Sənaye Universiteti
Azadlıq pr., 34, Bakı, AZ1010, Azərbaycan Respublikası
e-mail: khalafova.irada@gmail.com*

Xülasə: Neft ehtiyatlarının artan çatışmazlığı alternativ enerji mənbələrinin tapılmasının təcili ehtiyacını diktə edir. Bu gün onların arasında aparıcı yer həm kifayət qədər və əlverişli resurslara, həm də onların istehsalı üçün nisbətən qabaqcıl texnologiyalara görə bioyanacaqlara məxsusdur. Benzinlərin keyfiyyətinə dair müasir standartların tələbləri onların tərkibindəki aromatik karbohidrogenlərin kütləsini 42%-dən (Avro-3) və 35%-dən (Avro-4 və Avro-5) çox olmamaqla məhdudlaşdırır. Buna görə də, bitki xammalının benzin fraksiyalarının alınması proseslərinə cəlb edilməsinə dair tədqiqatlar ya sonrakı birləşmə ilə yüksək aromatik benzin əldə etməyə, ya da mümkünə aromatik tərkibini azaltmağa imkan verən katalitik sistemlərin axtarışına yönəldilmişdir. Bu işdə olein turşusu modelindən nümunə kimi istifadə edilməklə, bitki yağlarının yağ turşularının benzin sırasının karbohidrogenlərinə katalitik çevrilməsi zamanı onların çevrilmə mexanizmi tədqiq edilmişdir. Sənaye krekinq katalizatorlarından Omnikat-210P və Tseokar-600-dən təmiz formada və onların təbii halloysit nanoboruqları ilə qarışığından istifadə etməklə vakuum qazoylunun bitki yağları ilə qarışığının krekinq prosesi tədqiq edilmişdir. Bitki mənşəli yağların (Çudo-Peçka mağazalar şəbəkəsindən götürülmüş tullantı bitki yağları) 5 küt. % həcmində cəlb edilməsi ilə vakuum qazoylunun katalitik krekinq prosesi tədqiq edilmişdir.

Açar sözlər: olein turşusu, bitki yağları, katalitik krekinq, halloysitlər, reaksiya mexanizmi, katalizator, Omnikat-210P, Tseokar-600

ИССЛЕДОВАНИЕ ПРОЦЕССА ПОЛУЧЕНИЯ АЛЬТЕРНАТИВНЫХ МОТОРНЫХ ТОПЛИВ С ИСПОЛЬЗОВАНИЕМ РАСТИТЕЛЬНЫХ МАСЕЛ

И.А. Халафова, Н.К. Андрюшенко

*Азербайджанский Государственный Университет Нефти и Промышленности
Пр. Азадлыг 34, Баку, AZ 1010, Республика Азербайджан
эл. адрес: khalafova.irada@gmail.com*

Аннотация: Возрастающий дефицит нефтяных ресурсов диктует настоятельную необходимость поиска альтернативных энергоисточников. Ведущее место среди них на сегодняшний день принадлежит биотопливам, благодаря достаточным и доступным ресурсам и относительно развитым технологиям их получения. Требования современных стандартов к качеству получаемых бензинов ограничивают содержание ароматических углеводородов в них не более 42 % масс. (Евро-3), и 35 % масс. (Евро-4 и Евро-5). Поэтому исследования по вовлечению растительных видов сырья в процессы получения бензиновых фракций направлены либо на получение высокоароматизированного бензина с последующим его компаундированием, либо на поиск каталитических систем, позволяющих, по возможности, снизить содержание ароматических углеводородов в составе получаемых бензинов при совместном крекинге смеси нефтяного и растительного сырья. В данной работе на примере олеиновой кислоты изучен механизм превращения жирных кислот растительных масел при каталитическом превращении их в углеводороды бензинового ряда. Процесс исследован при использовании в качестве катализаторов крекинга смеси вакуумного газойля

с растительными маслами промышленных катализаторов крекинга Омникат-210П и Цеокар-600 в чистом виде и в смеси их с природными нанотрубками галлуазитов. Галлуазиты принадлежат к семье каолининовых глинистых минералов с высоким соотношением Al/Si по сравнению с другими алюмосиликатами и имеют преимущественно полую трубчатую структуру и состоят из слоёв оксидов алюминия и кремния, которые скручены в трубки. Исследован процесс каталитического крекинга вакуумного газойля с вовлечением в его состав растительных масел (отработанных растительных масел, взятых из сети магазинов «Чудо-печка») в количестве 5 % масс.

Ключевые слова: олеиновая кислота, растительные масла, каталитический крекинг, галлуазиты, механизм реакции, катализатор, Омникат-210П, Цеокар-600