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Oxidative Catalytic Cracking of Heavy Oil Residues

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Abstract

The features of oxidative cracking of vacuum distillate of Aturau and Zhetybai oil have been investigated. It was found that the yield of gasoline and light gas oil depends on the ratio of natural zeolite and clay in the composite catalysts, flow rate of air and 0.2 % catalyst suspension in the raw material and temperature of the cracking. It was shown that maximum yield of gasoline, kerosene and gas oil was achieved with the composite catalyst containing 14 % of activated zeolite. Suspension of this catalyst significantly promotes gas formation during oxidative cracking as compared to that for cracking in the inert atmosphere. This proves that catalytic destruction of high molecular hydrocarbons in the presence of trace amount of air is increased. The yield of light gas oil is increased whereas yield of gasoline and gas is decreased when flow rate of 0.2 % catalyst suspension in raw material is 1.0 hour^{-1} as compared to that for 0.1 hour^{-1} flow rate in oxidative cracking conditions. It was found (GLC method) that formation of diene and cyclodiene hydrocarbons during oxidative cracking at 0.1 hour^{-1} flow rate proceeds better than that for cracking in inert atmosphere. Oxidative cyclization into arenes proceeds when flow rate is 1.0 hour^{-1} whereas oxidative olefin dehydrogenation proceeds when flow rate is 0.1 hour^{-1}. Alpha olefins were found in gasoline, kerosene and gas oil fractions (IR-spectroscopy).

Introduction

Catalytic cracking of oil residues is an actual problem for world oil processing industry because of reduced demand for fuel oil and shortage of medium oil fractions. However, reorientation of oil industry to heavy oil processing needs more complex technologies that include purification from sulfur compounds and heavy metals. New technologies and cheap catalysts are necessary for these purposes.

Synthetic zeolites and natural clay with improved physical and chemical characteristics are widely used for cracking catalysts preparation [1]. Natural zeolites having thermal stability and mechanical durability are not well investigated. Recent years, composites (zeolites in aluminosilicate matrix with sticker) are used more and more. Synthetic amorphous aluminosilicate, natural clay and their mixtures (semi-synthetic matrix) are used as a matrix for evenly distributed zeolite. Change of catalytic activity and adsorption properties of such catalysts on mixed matrices is not monotonous depending on the composition because of formation of active sites at zeolite-matrix border due to ion exchange [2,3]. Design of new catalytic systems on the basis of the composites will let to increase economic efficiency of the technology.

Oxidative cracking is a prospective method for production of light oil from oil residues. This process excludes necessity to make special units for production of oxygen containing compounds. Besides, this gives the possibility to control octane number of the gasoline through change of the regime and oxygen concentration in the reaction mixture. There are only two papers on oxidative thermal cracking [4,5] and one paper on oxidative catalytic cracking [6]. Hereafter, the results of oxidative cracking of vacuum distillate using suspended composite catalysts on the basis of activated Chankanai zeolite and Narynkol clay are represented in this paper.

Experimental

Method for vacuum distillate production

Fraction composition of Zhetybai and Atyrau oil was determined by distillation at atmospheric pressure and in vacuum (5×10^{-2} mm.Hg). VN-4 vacuum

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*corresponding authors. E-mail: raihan@chem.iatp.kz pump and PMT-2 vacuum pressure indicator were used. Fraction in temperature interval from 110 to 220°C was isolated. This corresponds to 350-500°C temperature interval at atmospheric pressure.

Method for sulfur determination

Concentration of sulfur in the oil and vacuum distillates was determined using high temperature oxidation and subsequent determination of sulfurous acid by acid-base titration [8,9].

Method for catalyst preparation

Composite catalysts were prepared from Chankanai natural zeolite and Narynkol clay. Original clay and zeolite were grinded and screened. Fraction 63-80 μm was used in the experiments. Zeolite was promoted with lanthanum and ammonium ions through ion exchange in solution of relevant chlorides then washed to negative reaction for chloride ions and dried at 150°C. In order to obtain composite catalysts zeolite was mixed for two minutes with clay suspension in distilled water (different amount of Narynkol clay). The mixture was dewatered, dried at 150°C and calcined at 550°C for four hours. The composite catalyst was screened and fraction 63-80 μm was collected. Composites with 14, 20, 50 and 80 % of activated zeolite were used in the experiments.

Methods for catalyst analysis

Chemical composition of activated zeolite and clay and composite catalysts was determined by X-ray fluorescent method [10]. The analysis is based on X-ray fluorescention of the elements in the sample initiated by primary X-ray irradiation from X-ray tube with silver anode. Change of energy of fluorescent K_α lines was measured with ARF-6 analyzer. Lanthanum concentration in the catalysts was determined with DFS-13 spectrograph using calibrating curves made for standard samples [11]. Method detection limit for lanthanum in this method was 10^{-3}–10^{-2} %

Phase composition was determined with DRON-3M X-ray diffractometer (CuK_α – irradiation). Relative error was 10 %.

Catalytic cracking with suspended catalysts

On Fig. 1 flow unit for oxidative catalytic cracking is represented. Before the experiments the reactor (2) was washed with inert gas and heated to the necessary temperature. Then suspension of the catalyst in oil fraction was put through the reactor 2 from calibrated and heated to 95°C vessel 1 in order to reduce temperature difference between the raw material and the reactor. In order to prevent sedimentation of the powder, the mixture was stirred with argon flow. Flow rate of the suspension was controlled with tap valve 3. Flow rate of the air was checked with flow meter 4. The reactor was heated with electric winding controlled by autotransformer. The inside temperature was checked with a thermocouple 5. Gases from the reactor are condensed in cooling tube 6. Liquid products were collected in vessel 7 (cooled with ice), gas products, in gas meter 8. Gas flow from the reactor to the gas meter was measured with flow meter 9.

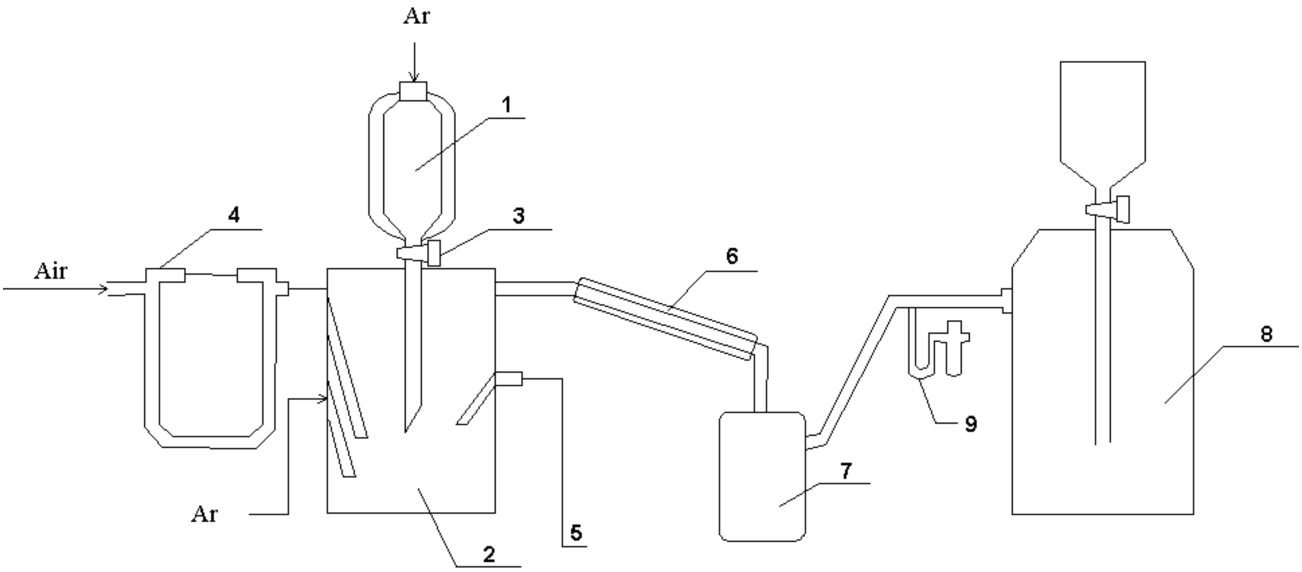


Fig. 1. Unit for catalytic cracking.

After each experiment liquid, gas and solid fractions (coke) yield were measured and calculated in %. The weight of gas product was determined from its density and volume; the weight of liquid products was determined with analytical balance. Light fraction was distilled to determine amount of gasoline and light gas oil. Amount of coke was determined by weighting the reactor before and after the experiment. Relative error of the experiments was no more than 2 %.

Determination of composition of gasoline, kerosene and gas oil fractions after cracking

Determination of composition of the gasoline fractions was made with TSVET-530 GLC instrument using 50 m stainless steel capillary column of 0.2 mm diameter filled with 7 % squalane. Argon with flow rate 1.0-1.3 ml/min was used as carrier gas. Flow rate division was 1/20. Temperature program was from 40 to 110°C (2°C per min). Special software was used for treatment of the results using database of 370 Covach indices for hydrocarbons. Qualitative composition of gasoline, kerosene and gas oil fraction was determined using IR-75 spectrometer.

Results and discussion

Fraction composition and sulfur concentration data for Atyrau and Zhetybai oil are listed in Table 1.

It is seen from the table that both Aturau and Zhetybai oil have almost equal concentration of sulfur, but sulfur concentration in vacuum gas oil fraction for Zetybai oil is higher than that for Atyrau oil whereas sulfur concentration in light gas oil fraction for Zetybai oil is less than that for Atyrau oil.

Yield of products after Zetybai vacuum distillate cracking in inert atmosphere and in air presence depending on zeolite concentration in the composite catalyst is shown in Table 2.

Table 1

Sulfur concentration depending on fraction composition of the raw materials

Fractions	Atyrau oil, Weight %		Zhetybai oil, Weight %	
	Hydrocarbons	Sulfur	Hydrocarbons	Sulfur
Original oil	100.0	0.9	100.0	1.0
Gasoline	0.6	-	3.5	-
Light gas oil	56.5	0.5	34.4	0.2
Vacuum gas oil	17.5	1.1	21.3	1.5
Heavy residue	25.4	-	40.8	-

Table 2

Cracking of vacuum distillate of Zhetybai oil with 0.2 % suspended catalyst at 0.1 hour^{-1} flow rate

Conditions	Percentage of zeolite in the catalyst	Yield of products, %					Losses	Total
		Gasoline	Light as oil	Liquid raction	Gas	Coke		
Inert atmosphere	0 no $LaCl_3$	11.2	15.6	73.8	22.8	1.0	2.4	100.0
	0 with $LaCl_3$	13.3	16.5	71.5	27.6	0.7	0.2	100.0
	14	10.6	16.1	80.1	19.3	0.6	-	100.0
	20	7.8	15.8	72.6	27.0	0.4	-	100.0
	50	6.3	16.4	83.9	15.6	0.5	-	100.0
Air flow 0.05 hour^{-1}	0	11.3	14.5	81.1	17.1	1.8	-	100.0
	14	18.0	23.9	56.5	41.2	1.8	0.5	100.0
	50	15.0	18.0	64.6	31.8	2.2	1.4	100.0
	80	13.0	16.9	68.2	29.8	2.1	-	100.0
	100	8.9	12.9	76.6	22.0	1.4	-	100.0

Yield of light products does not depend on the catalyst composition. In air presence maximum yield of gasoline kerosene and gas oil was achieved on the catalyst with 14 % of zeolite. Yield of gas products is also higher than that for inert atmosphere. These data show that small air concentrations promote catalytic destruction of high molecular hydrocarbons.

Natural zeolite has lower activity in cracking than synthetic zeolite and clay. However, composite catalyst with 14 % zeolite shows synergistic effect. To reveal the reason of this phenomenon we determined chemical composition of the catalysts (Table 3).

As one can see from Table 3, the results for the samples are similar regarding to main minerals of the natural components and composite catalysts. The ratio SiO_2/Al_2O_3 in Chankanai zeolite is ≈5, whereas in 14 and 20 % composites, ≈ 4. Calcite takes great share in Narynkol clay and the composite catalysts (Table 3). The more calcite concentration the more weight losses after calcination. Perhaps, it is related to destruction of $CaCO_3$. In 14 % composite catalyst concentration of lanthanum is maximum whereas concentration of sodium oxide is minimum. This perhaps may explain maximum activity of this catalyst in cracking.

This catalyst was used for investigation of airflow rate on cracking of vacuum distillate of Atyrau oil (Table 4).

Table 3

Chemical composition of the catalysts according to X-ray fluorescent analysis

Chemical composition	Activated Narynkol clay	Composite with 14 % zeolite	Composite with 20 % zeolite	Activated Chankanai zeolite
CaO	20.45	19.79	15.14	1.94
SiO_2	37.95	39.98	47.28	68.02
Al_2O_3	8.49	9.97	11.51	14.28
MgO	6.10	6.27	4.61	1.41
Fe_2O_3	4.07	3.77	4.01	1.76
K_2O	1.91	2.29	3.16	4.47
Na_2O	1.10	<0.50	0.55	1.08
TiO_2	0.44	0.23	0.45	0.29
P_2O_5	0.11	0.13	0.11	0.03
MnO	0.09	0.15	0.11	0.06
Losses in calcinations	19.47	17.43	13.52	7.04
La	0.13	0.26	0.20	0.24
Total	100.58	100.27	100.65	100.62

Table 4

Influence of airflow rate on oxidative cracking of vacuum distillate of Atyrau oil at 500°C with raw material flow rate of 0.1 hour^{-1} with 0.2% suspension of 14% composite.

Air flow rate, hour^{-1}	Yield of products, %					Losses	Total
	Gasoline	Light gas oil	Liquid fraction	Gas	Coke		
0	14.0	22.4	76.5	22.4	0.2	0.9	100.0
0.03	14.1	23.0	71.6	28.1	0.3	-	100.0
0.05	13.8	36.3	74.1	26.7	0.2	-	101.0
0.08	14.2	27.5	80.6	19.1	0.3	-	100.0
0.10	12.0	23.0	76.9	22.6	0.2	0.3	100.0
0.15	15.2	15.1	73.8	25.1	0.5	0.6	100.0

It is seen from the table that change of airflow rate affects only yield of kerosene and gas oil fractions. Maximum yield was observed at 0,05 hour^{-1} flow rate. Comparing to the data obtained in similar conditions for vacuum gas oil of Zhetybai oil (Table 2) one can see that increased sulfur concentration in the raw material (Table 1) reduces light gas oil share in the products from 36,3 by 23,9 %. This points out on deactivation of the composite catalyst by sulfur compounds.

Despite high share of light fuel (50.0 % in total in optimum conditions) during oxidative cracking of heavy fraction of Atyrau oil, the productivity of the technology does not meet industrial requirements because of low flow rate of the suspension through the reactor. So, we investigated the possibility to increase productivity of the unit through increase of suspension flow rate up to 1 hour^{-1} (see Table 5).

Table 5

Influence of air flow rate to oxidative cracking of vacuum distillate of Atyrau oil at 500°C.
Raw material flow rate is 1.0 hour $^{-1}$ in 0.2 % suspension of 14 % zeolite catalyst.

Air flow rate, hour^{-1}	Yield of products, %					Total
	Gasoline	Light gas oil	Liquid fraction	Gas	Coke	
0.05	2.8	46.3	96.1	3.9	-	100.0
0.10	1.8	47.5	96.4	2.8	0.8	100.0
0.15	2.7	53.2	94.4	4.7	0.9	100.0
0.20	2.2	39.4	91.2	7.6	1.2	100.0

One can see that at 1 hour^{-1} raw material flow rate yield of light gas oil is increased whereas yield of gasoline is declined by 5-6 times. Maximum share of kerosene and gas oil fractions was found at airflow rate of 0,15 hour^{-1}.

To determine optimum conditions of oxidative cracking at 1 hour^{-1} raw material flow rate we investigated influence of the temperature (Table 6).

Table 6

Oxidative cracking of vacuum distillate of Atyrau oil in the presence of 0,2 % suspension of 14 % zeolite catalyst
at raw material flow rate of 1,0 hour^{-1} and airflow rate of 0,15 hour^{-1} depending on the temperature.

Temperature °C	Yield of products, %					Total
	Gasoline	Light gas oil	Liquid fraction	Gas	Coke	
400	0.4	43.7	100.6	4.0	-	104.6
450	0.4	44.3	99.4	5.3	0.3	105.0
500	2.7	53.2	94.4	4.7	0.9	100.0
550	1.5	40.1	89.4	11.1	0.4	100.9

It was found that in 400-500°C temperature interval the product contains little amount of gasoline, increased by 9 % amount of kerosene and gas oil and same amount of gas. At 550°C concentration of light hydrocarbons in liquid phase is declined and gas amount is growing. This is related to heavier destruction of hydrocarbons at increased temperatures. Therefore, optimum temperature for oxidative catalytic cracking is 500°C.

In order to reveal the mechanism of the reactions during catalytic cracking we determined hydrocarbon composition of gasoline fraction using GLC method (Table 7).

It is seen from Table 8 that in case of low flow rate

Table 7

Composition (%) of gasoline fraction at 500°C obtained from vacuum distillate of Atyrau oil during cracking of 0,2 % suspension of 14 % composite.

Hydrocarbons	Raw material flow rate 0.1 hour^{-1}, inert atmosphere	Raw material flow rate 0.1 hour^{-1}, Airflow rate 0.05 hour^{-1}	Raw material flow rate 1.0 hour^{-1}, Airflow rate 0.15 hour^{-1}
Normal hydrocabons	4.5	3.2	4.2
Isoparaffins	28.6	27.1	29.7
Naphthenes	12.8	10.0	9.2
Olefins	20.2	18.0	8.6
Cycloolefins	1.6	1.3	4.3
Arenes	28.6	26.8	41.3
Diene hydrocarbons	1.3	10.3	1.6
Cyclodienes	0.2	0.7	0.1
Non-identified	6.5	0.1	-
Octane number	91.2	88.3	89.6

of the raw material suspension the yield of diene and cyclodiene hydrocarbons in cracking products in air presence is more than that for inert atmosphere. This data coincide with the literature [12] data that in air presence share of reactions of oxidative dehydrogenation of olefins is more. Increase of raw material flow rate up to 1 hour^{-1} changes the direction of oxidative cracking. Concentration of olefin and diene hydrocarbons in gasoline fraction after cracking is declined, whereas concentration of aromatic hydrocarbons is increased. So, in this condition oxidative dehydrogenation is suppressed and cyclization to arenes proceeds. Increase of cyclo-olefin concentration also proves this. The change of the reaction route may be explained as follows. At low flow rate the vacuum gas oil quickly acquires temperature of the rector and runs out of it because of evaporation. High temperature and short reaction time (in the reactor) provide prevailing of oxidative dehydrogenation of hydrocarbons. Increase of raw material flow rate increases time of contact of vacuum gas oil and the catalyst because the raw material is accumulated in the reactor as a liquid phase. There is enough time for oxidative dehydrogenation of cycloparaffins and condensation of olefins into aromatic hydrocarbons on the catalyst surface.

As it was shown in [6], octane number of gasoline after oxidative cracking is higher due to formation of oxygen containing hydrocarbons. IR-spectra of gasoline (Table 8) showed that reaction of partial oxidation during oxidative cracking does not proceed (there is no or very little absorption bands at 1700-1728 cm^{-1}). However, formation of sulfoxides during oxidation of sulfur containing hydrocarbons is possible. Absorption bands at 740-750 cm^{-1} indicate their presence. Both in gasoline (Table 8), kerosene and gas oil fractions (Table 9) we found out alpha-olefins.

Table 8

Absorption bands (cm^{-1}) in IR-spectra of gasoline fraction after cracking of vacuum distillate of Atyrau oil at 500°C with 0.2 % suspension of 14 % composite catalyst.

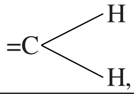
Raw material flow rate 0.1 hour^{-1}, Inert atmosphere	Raw material flow rate 0.1 hour^{-1}, Airflow rate 0.05 hour^{-1}	Raw material flow rate 1.0 hour^{-1}, Airflow rate 0.05 hour^{-1}	Raw material flow rate 1.0 hour^{-1}, Airflow rate 0.15 hour^{-1}	Classification of the bands
3040	-	3040	-	Valence vibration band for C–H in terminal double bonds  α-olefins

Table 8

Continued

Raw material flow rate 0.1 hour^{-1}, Inert atmosphere	Raw material flow rate 0.1 hour^{-1}, Airflow rate 0.05 hour^{-1}	Raw material flow rate 1.0 hour^{-1}, Airflow rate 0.05 hour^{-1}	Raw material flow rate 1.0 hour^{-1}, Airflow rate 0.15 hour^{-1}	Classification of the bands
2970	2980	2973	2967	Valence vibration band for C–H in CH_3
2939	2953	2947	2927	
2877	2874	2940	2860	
2867	2892	2873	-	
-	1700	1728	-	Valence vibration band for carbonyl oxygen
1660	1667	1656	-	Vibrations of terminal methylene group
1486	1519	1486		Deformation vibrations of C–H in CH_2 and CH_3
1480	1486	1480		
1470	1469	1464	1467	
1464	1466	1453	1460	
1393	1393	1393	1387	Deformation flat vibrations of terminal methylene group
927	933	931	-	Asymmetric valence vibrations in terminal epoxy groups or valence vibration of S–O and S=O groups in sulfoxides
751	755	747	740	Valence vibration of C–S, or S–O and S=O groups in sulfoxides

Table 9

Absorption bands (cm^{-1}), in IR-spectra of kerosene and gas oil fractions after cracking of vacuum distillate of Atyrau oil at 500°C in 0.2% suspension of 14% composite.

Raw material flow rate 0.1 hour^{-1}, Inert atmosphere	Raw material flow rate 0.1 hour^{-1}, Airflow rate0.05 hour^{-1}	Raw material flow rate 1.0 hour^{-1}, Airflow rate 0.05 hour^{-1}	Raw material flow rate 1.0 hour^{-1}, Airflow rate 0.15 hour^{-1}	Classification of the bands
-	-	3020	-	Valence vibration of C–H band in terminal $=CH_2$
2965	2971	2968		Valence vibration of C–H in CH_3
2940	2940	2940	2933	
2869	2872	2873	2860	
1527	1664	1647	-	Valence vibration of terminal methylene group $R_2C=CH_2$
		1681		
1480	1482	1480	1460	Deformation vibrations of C–H in CH_2 and CH_3
1473	1477		-	Asymmetric deformation vibration of C–H in CH_3
1467	1467	1472	-	

Table 9

Continued

Raw material flow rate 0.1 hour^{-1}, Inert atmosphere	Raw material flow rate 0.1 hour^{-1}, Airflow rate0.05 hour^{-1}	Raw material flow rate 1.0 hour^{-1}, Airflow rate 0.05 hour^{-1}	Raw material flow rate 1.0 hour^{-1}, Airflow rate 0.15 hour^{-1}	Classification of the bands
1386		1393	1387	Deformation vibrations of terminal methylene group =CH_2
-	931	-	-	Nonflat formation vibrations of C–H bond in terminal epoxy groups or valence vibration of S–O and S=O groups in sulfoxides

In general, IR-spectra indicate presence of the same functional group of hydrocarbons both in light gas oil and cracking gasoline.

Influence of catalytic cracking conditions of vacuum gas oil on the degree of destruction of high molecular hydrocarbons was determined with GLC method both for the raw material (Table 10), and for kerosene and gas oil fractions of the product (Table 11-13). As one can see from Table 10 the main part in the original gas oil take hydrocarbons with 14-22 carbon atoms. Share of high molecular hydrocarbons (over C_{24}) is 10 % (Table 10).

In light gas oil C_{10}-C_{17} hydrocarbons take great share after cracking of this raw material with low flow rate in inert atmosphere (Table 11) and in air presence (Table 12). No high molecular hydrocarbons were found.

Table 10

Hydrocarbon composition of vacuum distillate of Atyrau oil

Hydrocarbons	Hydrocarbon concentration, %		
	Linear structure	Other with same number of carbon atoms	Total
below C_{10}	-	1.8	1.8
C_{10}	-	0.9	2.7
C_{11}	0.6	1.6	4.9
C_{12}	0.5	2.5	7.9
C_{13}	0.3	4.1	12.3
C_{14}	0.6	5.9	18.8
C_{15}	1.0	3.2	23.0
C_{16}	1.1	8.0	32.1
C_{17}	3.0	18.8	53.9
C_{18}	3.5	13.5	70.9
C_{19}	1.1	6.6	78.6
C_{20}	1.1	5.5	85.2
C_{21}	0.5	3.3	89.0
C_{22}	0.3	1.4	90.7
C_{23}	0.2	1.2	91.1
C_{24}	0.3	-	91.4

Table 11

Hydrocarbon composition of kerosene gas oil fractions after cracking of vacuum gas oil of Atyrau oil at 500°C in inert atmosphere with 0,1 hour^{-1} flow rate of 0,2 % suspension of 14 % composite catalyst

Hydrocarbons	Hydrocarbon concentration, %		
	Linear structure	Other with same number of carbon atoms	Total
below C_{10}	-	4.1	4.1
C_{10}	-	2.4	6.5
C_{11}	0.4	5.8	12.7
C_{12}	0.5	8.1	21.3
C_{13}	1.6	6.2	29.1
C_{14}	0.6	7.1	36.8
C_{15}	1.0	10.8	48.6
C_{16}	1.1	9.3	59.0
C_{17}	1.2	9.8	70.0
C_{18}	0.7	10.2	80.9
C_{19}	0.4	7.3	88.6
C_{20}	0.3	1.2	90.1
C_{21}	0.2	3.2	93.5
C_{22}	0.3	3.3	97.1
C_{23}	0.1	2.6	99.8

Table 12

Hydrocarbon composition of kerosene gas oil fractions after cracking of vacuum gas oil of Atyrau oil at 500°C with 0,1 hour^{-1} flow rate of 0,2 % suspension of 14 % composite catalyst. Airflow rate is 0.05 hour^{-1}

Hydrocarbons	Hydrocarbon concentration, %		
	Linear structure	Other with same number of carbon atoms	Total
below C_{10}	-	2.5	2.5
C_{10}	-	3.6	6.1
C_{11}	0.4	5.8	12.3
C_{12}	0.5	6.7	19.5
C_{13}	0.4	7.2	27.1
C_{14}	1.0	10.1	38.2
C_{15}	0.7	12.4	51.3
C_{16}	0.9	13.5	65.7
C_{17}	0.5	10.7	76.9
C_{18}	0.3	6.3	83.5
C_{19}	0.2	3.8	87.5
C_{20}	0.3	2.9	90.7
C_{21}	0.2	1.4	92.3
C_{22}	0.1	-	92.4

Table 13

Hydrocarbon composition of kerosene gas oil fractions after cracking of vacuum gas oil of Atyrau oil at 500°C with 1.0 hour^{-1} flow rate of 0,2 % suspension of 14 % composite catalyst. Airflow rate is 0.15 hour^{-1}

Hydrocarbons	Hydrocarbon concentration, %		
	Linear structure	Other with same number of carbon atoms	Total
below C_{10}	-	3.9	3.9
C_{10}	-	1.5	5.4
C_{11}	0.1	1.8	7.3
C_{12}	0.3	2.0	9.6
C_{13}	0.2	2.6	12.4
C_{14}	0.6	4.4	17.4
C_{15}	0.7	10.2	28.3
C_{16}	0.9	14.5	43.7
C_{17}	1.3	16.2	61.2
C_{18}	0.9	11.4	73.5
C_{19}	0.7	9.3	83.5
C_{20}	0.5	5.1	89.1
C_{21}	0.4	4.2	93.7
C_{22}	0.2	3.2	97.1
C_{23}	0.1	1.7	98.9
C_{24}	0.1	0.7	99.7

If raw material flow rate is 1,0 hour^{-1} kerosene and gas oil fraction of the product contains high molecular hydrocarbons C_{13}-C_{19} (Table 13). Yield of gas and gasoline is declining. Kerosene and gas oil fraction is prevailed (compare with Tables 4 and 5). The obtained data show that decomposition of high molecular hydrocarbons is symmetric during oxidative cracking of vacuum gas oil at 1.0 hour^{-1} flow rate.

Conclusions

Optimum conditions for cracking of vacuum distillate using low percent suspension of natural composites to produce light hydrocarbons with high yield were determined.

It is shown that activity of the composite catalysts depends on the ratio of activated zeolite and natural clay. Suspension of 0.2 % composite with 14 % zeolite in heavy oil is the best for production of light motor fuel.

During oxidative cracking of vacuum gas oil olefin dehydrogenation is increased at low flow rate of the raw material. Formation of aromatic hydrocarbons of gasoline fraction is growing together with raw material flow rate growth.

Formation of kerosene and gas oil fractions mainly and reduction of gas and gasoline yield during cracking when raw material flow rate is 1.0 hour^{-1} proves that destruction of high molecular hydrocarbons proceeds symmetrically.

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