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BEHAVIOR OF Y TYPE ZEOLITE CATALYST UNDER AEROSOL NANOCATALYSIS CONDITIONS

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Abstract. The study of Y-zeolite catalyst in aerosol nanocatalysis conditions with vibrating bed (AnCVB) was conducted. The method of conducting the experiment of catalytic cracking of vacuum gas oil was described. The influence of the controlling parameters of AnCVB technology (frequency of vibration and temperature) on the change in the composition and yield of cracking products was shown. The selectivity of cracking for the light products (gasoline and diesel) exceeds the industrial indicators by up to 22.3 %.

Keywords: catalytic cracking, vacuum gas oil, aerosol nanocatalysis, vibrating bed, gasoline fraction, diesel fraction.

1. Introduction

Catalytic cracking is the most common process of secondary processing of crude oil. The main products of this process are gasoline and diesel fractions, and other minor products are gases and coke. In the industry, the process is conducted in a lift-reactor at 723–823 K. In the modern units of catalytic cracking only zeolite-containing aluminium-silicate catalysts with rare-earth metals are used [1].

Industrial organization of catalytic cracking has the following disadvantages [2]:

- the necessity for a catalyst regenerator which volume is twice of reactor volume (*e.g.* in order to process 2 million tons of raw material per year (unit G-43-107/M1) the volume of reactor must be 800 m^3 and the volume of regenerator must be 1600 m^3);

- the necessity for permanent supply of a catalyst, since after 1-2 seconds of work additional losses of the catalyst due to abrasion take place. (In the industry: additional supply of catalyst is 0.545 kg per ton of raw material, which is 3 tons of additional catalyst per day.

Minimum price of cracking catalysts is 25,000 $ per ton);

- the usage of high concentration of the catalyst (about 700 kg/m^3 of reactor);

- the necessity of steam injection into the reaction zone for stripping of cracking products from the catalyst surface in the amount of 0.5–0.75 GJ per ton of raw materials;

- one-time supply of the catalyst is 350 tons.

A new promising technology of aerosol nano-catalysis with vibrating bed (AnCVB) may become an alternative industrial organization of catalytic cracking.

2. Experimental

The studies were conducted at a laboratory unit shown in Fig. 1, by using Y-zeolite catalyst that was prepared from kaolin. The catalyst was provided by the Institute of Bioorganic Chemistry and Petrochemistry of National Academic of Science of Ukraine.

The pre-heated vacuum gas oil is fed into the reactor (5) by syringe-batcher (1), which is located in the thermal cabinet (2), and is heated by heater (13). Cracking reactions take place inside the reactor. The temperature in the reaction zone is measured by a thermocouple (11), and sustained by a regulator (12). In order to keep the catalyst inside the reactor a metal-cloth filter (6) is placed at the bottom of reactor. The liquid products of reactions leave the reactor and go through water-cooled condenser (7) and then gathered in a flask of the liquid fraction (8). The reaction products are two fractions – liquid and gas. The non-condensed gases of cracking go through the point of sampling (9) and enter into the gas washer (10), where they bubble through the water layer. Then the gases are directed into a gas container (15), passing through container with water (14). The reactor is moving upward and downward in a

reciprocating motion with the help of vibrating device (4). The oscillation frequency and temperature are set and controlled by a regulator (12).
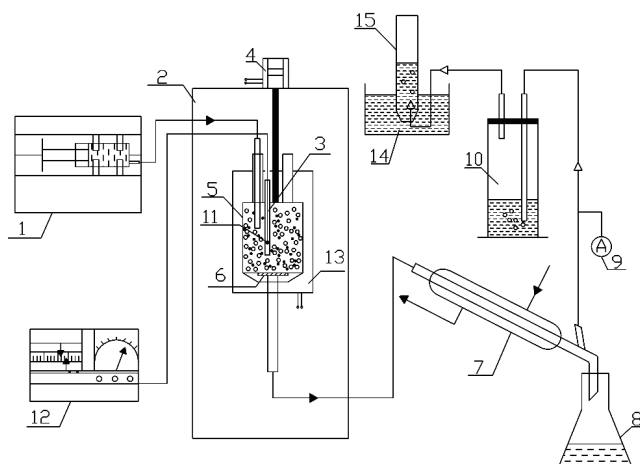

Fig. 1. Laboratory unit for the study of cracking of vacuum gas oil by aerosol nanocatalysis technology: syringe-batcher (1); thermal cabinet (2); pocket of thermocouple (3); vibrating device (4); reactor (5); metal-cloth filter (6); water condenser (7); receiver of the liquid fraction (8); the point of sampling (9); gases washer (10); thermocouple (11); regulator of vibration frequency and temperature (12); heater (13); water container (14) and gas receiver (15)

The liquid phase is subjected to fractional distillation by using an apparatus ULAB 1-42A. The content of the gaseous products of the reaction can be analytically determined by using a calibrated gaseous chromatographs, such as LHM-8, COLOR-500 (ethylene and hydrogen were determined with an accuracy not less than 0.01 vol %). Products composition and octane number of gasoline fraction (research and motor methods) were determined by chromatograph CRYSTAL-5000.2 [2].

3. Results and Discussion

Results of experimental studies are presented in Table 1. It was noted that the ignition temperature of the given catalyst in the conditions of AnCVB was 723 K. Conversion of raw materials does not exceed 59.6 % at a single pass (column 8, row 4), and the selectivity of the process was rather high – about 89.1 %. The experimental results showed that this indicator (column 9) is higher than that in the industry by 6.2–22.3 mas %. More detailed increase by 6–12 % is given by rows 16, 20, 31; increase by 12–15 % is given by rows 4, 11, 28, 30; and increase by 15–22.3 % is given by rows 2, 6, 10, 14, 15, 18, 19, 22, 26, 27.

It is established that the highest indicators of the process selectivity were observed at the temperatures of 723 and 773 K. This can be explained by the fact that the formation of gas fraction under these conditions is insignificant in the range of 0–2 mas %. However, it should be noted that the contribution to the quantitative characteristics of the products belongs to the frequency of vibration. At 6.5 Hz and at the temperatures of 423 and 473 K, a significant evolution of the gas fraction in the amount of 11.9 and 21.0 mas % at the general conversion of 47.1 and 47.6 %, respectively (column 5, rows 23 and 24), was noted. In the rest of experiments at 773–823 K indicators for gas fraction varied from 0 to 6.2 mas % at the corresponding conversions (columns 5 and 8, rows 3, 4, 7, 8, 11, 12, 15, 16, 19, 20, 23, 24, 27, 28, 31, 32).

A controlled effect of the frequency of vibration on the output of the reaction products was noted. It was shown that at the frequency of 7 Hz and the temperature of 773 K, the products of the gas fraction and diesel fraction were completely absent, and the yield of gasoline fraction was 14.7 mas % (column 6, row 27), the conversion and selectivity were 15.7 and 93.7 %, respectively. As a result, the process of cracking that uses Y-zeolite catalyst in AnCVB can be controlled with the aim of producing the necessary products with high selectivity. To achieve this, optimal conditions for the process need to be chosen. Due to the achieved selectivity of the light oil products it is possible to significantly reduce the costs of the separation stages of oil products. The rate of cracking per weight of the catalyst exceeds the industrial indicators (column 12) by 10^4–10^5 times, which allows to reduce the capital investments and the consumption of the catalyst.

These data show that the use of Y-zeolite catalyst under AnCVB conditions is promising from an economic point of view.

In Figs. 2 and 3 the dependence of conversion degree of vacuum gasoil on the temperature over Y-zeolite catalyst at different frequencies of vibration is shown. It is noted that this dependence for the oscillation frequency 4 and 5.5 Hz has an oscillatory character and this allows to determine precisely the optimal regime.

At 823 K and 4 Hz (Fig. 2) the conversion degree tends to a maximum value. This indicates that Y-zeolite catalyst has a relatively high thermal stability since at relatively low frequency and high temperature the catalyst does not lose its activity.

At 823 K and 5.5 Hz (Fig. 2) the conversion degree decreases. This can be explained by the fact that the increase of temperature and the oscillation frequency of the reacted mass under these conditions do not limit the cracking process.

For the frequency of 4.5 and 5 Hz (Fig. 2) the conversion degree reaches its constant value. This indicates that under the given conditions some other parameter is limitative, neither the temperature nor the frequency.

At the frequencies of 6 and 6.5 Hz (Fig. 3) the dependence of conversion degree on the temperature in the interval of 773–823 K grows slightly. This indicates that the optimum conditions are practically achieved. At the frequency of 7.5 Hz (Fig. 3) the conversion degree at the temperature of 723–823 K is practically constant, although it has rather low values up to 3.8 mas %, which indicates that further frequency increase is not reasonable.

Table 1

Cracking of vacuum gas oil by the yield of light oil products

(the reactor volume is 38 cm^3, the oscillation amplitude is 10 mm, the amount of dispersing material is 20 cm^3, the catalyst concentration is 3 g/m^3, the flow rate of vacuum gasoil is 1.1 ml/min)

No.	Temperature, K	Frequency, Hz	Composition of cracking products, mas %				Conversation, mas %	Selectivity, mas %	Yield, mas %.	Cracking rate	
			coke	gas	gasoline fraction	diesel fraction				kg/m^3·h	kg/kg$_{cat}$·h
1	2	3	4	5	6	7	8	9	10	11	12
1	400	4	0	0	0	0	0	0	0	0	0
2	450		1.4	0	7.2	28.2	36.8	**96.2**	35.4	**541.6**	180533
3	500		1.7	2	2.6	7.9	14.4	72.5	10.5	160.1	53360
4	550		2	4	10.7	42.4	59.6	**89.1**	53.1	**812.1**	270703
5	400	4.5	0	0	0	0	0	0	0	0	0
6	450		1.3	0	0	14.1	15.4	**91.5**	14.1	**215.0**	71653
7	500		1.4	2.3	0	9.7	13.4	72.6	9.7	148.5	49503
8	550		1.5	4.8	0	8.4	14.7	57.2	8.4	128.9	42959
9	400	5	0	0	0	0	0	0	0	0	0
10	450		1.3	0.3	3.7	21.4	26.6	**94.0**	25	**382.5**	127500
11	500		1.4	1.7	6.5	17.7	27.2	**88.6**	24.1	**369.1**	123033
12	550		1.8	5.4	6.7	13.7	27.5	73.9	20.4	**311.4**	103800
13	400	5.5	0	0	0	0	0	0	0	0	0
14	450		1.2	0	0	19.1	20.3	**94.1**	19.1	**291.9**	97290
15	500		1.2	0	4.7	37.2	43.0	**97.2**	41.3	**639.5**	213152
16	550		1.5	1.1	7.1	9.4	19.1	**86.3**	16.5	**252.2**	84057
17	400	6	0	0	0	0	0	0	0	0	0
18	450		0.9	0	5.4	15.6	21.9	**95.9**	21.0	**320.6**	106865
19	500		1.2	0	6.5	20.8	28.5	**95.8**	27.3	**417.2**	139056
20	550		1.5	6.2	8.7	24.3	40.8	**81.1**	33.0	**505.1**	168355
21	400	6.5	0	0	0	0	0	0	0	0	0
22	450		0.8	0	0	14.9	15.7	**94.9**	14.9	**227.4**	75808
23	500		1.7	11.9	14.4	19.1	47.1	71.1	33.5	**511.8**	170591
24	550		3.0	21.0	9.4	14.3	47.6	49.7	23.7	**361.7**	120568
25	400	7	0	0	0	0	0	0	0	0	0
26	450		0.8	0	0	14.2	15.0	**94.6**	14.2	**217.1**	72368
27	500		1.0	0	14.7	0	15.7	**93.7**	14.7	**224.5**	74838
28	550		1.2	4.5	12.9	37.8	56.4	**89.8**	50.7	**774.7**	258225
29	400	7.5	0	0	0	0	0	0	0	0	0
30	450		0.5	0	0	3.5	4.0	**87.7**	3.5	54.2	18063
31	500		0.7	0	0	3.8	4.5	**84.4**	3.8	58.0	19327
32	550		1.0	2.8	2.5	0	6.4	39.7	2.5	38.6	12858
The industrial data for Nexus-345p as a catalyst (unit G-143/M1) [2]											
33	525	-	5-5.5	17.8	50.2	15.5	86	74.9	65.7	205.3	0.444

Per the reactor volume, the reaction rate is higher than that in the industry (column 11) by the following values:

Table row	2	4	6	10	11	12	14	15	16
Δ, %	264	396	105	186	180	152	142	312	123
Table row	18	19	20	22	23	24	26	27	28
Δ, %	156	203	246	111	249	176	106	109	377
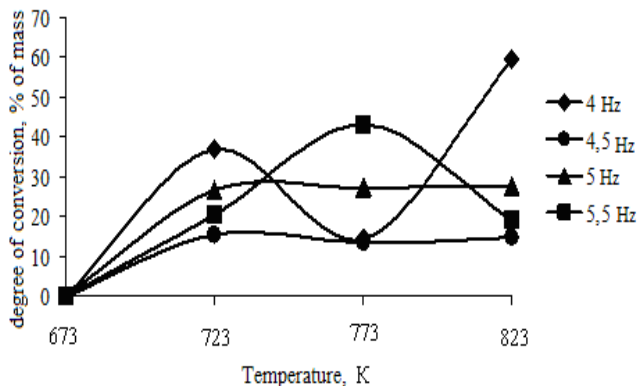
Fig. 2. The dependence of conversion degree on temperature at the oscillation frequency of 4–5.5 Hz (the reactor volume is 38 cm^3, the oscillation amplitude is 10 mm, the volume of dispersing material is 20 cm^3)
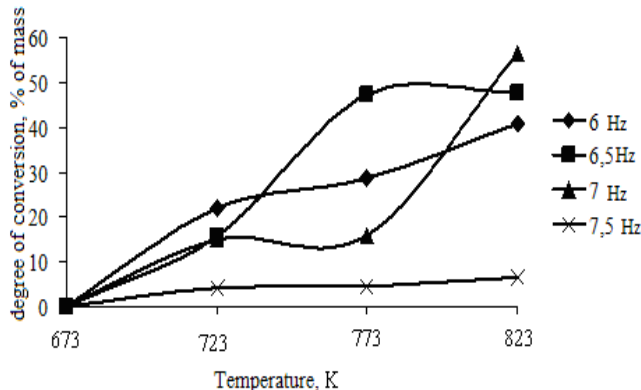

Fig. 3. The dependence of the conversion degree on temperature and oscillation frequency of 6–7.5 Hz (the reactor volume is 38 cm^3, the oscillation amplitude is 10 mm, the amount of dispersing material is 20 cm^3)
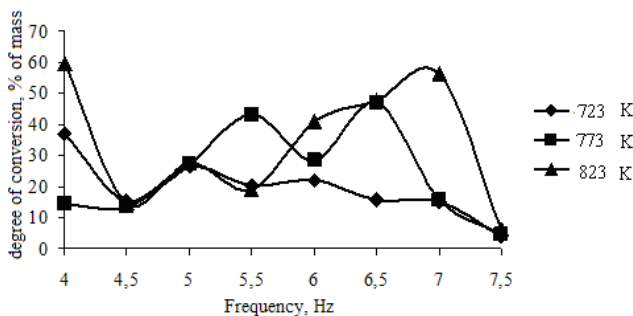

Fig. 4. The dependence of the degree of conversion on the frequency of oscillation at the temperature of 723–773 K (the reactor volume is 38 cm^3, the oscillation amplitude is 10 mm, the volume of dispersing material is 20 cm^3)

Table 2

Values of octane number of gasoline fraction depending on the experimental conditions for Y-zeolite catalyst

Frequency, Hz	Temperature, K	Yield of fraction 308–453 K, mas %	Octane number research method
4	450	7.2	85.87
	500	2.6	91.28
	550	10.7	90.31
5	450	3.7	87.66
	500	6.5	89.79
	550	6.7	91.66
5.5	500	4.7	90.94
	550	7.1	91.90
6	450	5.4	92.70
	500	6.5	89.85
	550	8.7	92.09
6.5	500	14.4	94.30
	550	9.4	96.36
7	500	14.7	92.31
	550	12.9	92.71
7.5	550	2.5	92.19

Fig. 4 shows the change of conversion degree of vacuum gasoil depending on the frequency of vibration over Y-zeolite catalyst at different temperatures. The oscillation frequency is taken in the range from 4 to 7.5 Hz, because under these conditions a stable regime of the process was noted. Dependences have an oscillatory character, which is in agreement with the theoretical positions of oscillation processes and studies on AnCVB [3-6].

Table 2 represents values of octane number of gasoline fraction.

All values of the octane number are at the level of 90 points by the research method calculated using the chromatograph Crystal 5000.2 This indicates that the quality of the gasoline fraction obtained using AnCVB technology complies with the standard of gasoline fraction of catalytic cracking [1].

4. Conclusions

The organization of the catalytic cracking on Y-zeolite catalyst by AnCVB technology is promising in the viewpoint of energy and resource conservation. The amount of the catalyst is reduced almost by 10^6 times in comparison with the industrial organization of the process. Selectivity of the process for light oil products exceeds the industrial values maximally by 22.3 mas %, which allows to significantly reduce the cost of the separation stages. Low one-pass conversion for this type of catalyst (Y-zeolite) requires consideration of the scheme with recycle. However, another type of catalyst (Si-Zr) under aerosol conditions allows to use a scheme without recycle.

The process can be recommended for implementation both in parallel with the operating units as well as independently at small refineries, which cannot afford the full cycle of the existing processes of catalytic cracking.

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ПОВЕДІНКА ЦЕОЛІТВМІСНОГО КАТАЛІЗАТОРА ТИПУ У В УМОВАХ АЕРОЗОЛЬНОГО НАНОКАТАЛІЗУ

Анотація. Наведено результати цеолітвмісного каталізатору типу Y в умовах аерозольного нанокаталізу у віброрідженому шарі (AnCVB). Розглянуто методику проведення експерименту для процесу каталітичного крекінгу вакуумного газойлю. Показано, що внаслідок зміни специфічних для технології AnCVB параметрів (частота вібрації каталітичної системи) можна змінити склад продуктів крекінгу та вихід бензину і дизельного палива. Селективність процесу крекінгу в умовах AnCVB за світлими нафтопродуктами перевищує дані промисловості на 22,3 %.

Ключові слова: каталітичний крекінг, вакуумний газойль, аерозольний нанокаталіз, віброрідженний шар, бензинова фракція, дизельна фракція.