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RESEARCH OF CATALYTIC CRACKING OF HEAVY RESIDUE OF PETROLEUM PRODUCTS

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ABSTRACT

The article presents catalytic cracking to evaluate the characteristics of the used finely dispersed publicly available industrial catalysts in the reactor-regenerator unit of an installation for the production of gasoline that meets the requirements of the EURO 4 and EURO 5 standards.

Keywords: Catalytic, Cracking, Fuel Oil, Gasoline, Reactor, Pilot Run, And Catalysts.

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INTRODUCTION

Currently, the oil and gas industry of Kazakhstan faces the urgent task of increasing the depth of processing of hydrocarbon raw materials, in particular, the yield of light fractions. Thus, it is expected to increase the volume of commercial petroleum products produced: gasoline, kerosene, and diesel fuel.[1,2] As is known, the capacity of heavy residue catalytic cracking units at oil refineries in the countries of independent states is about 2-2.5 million tons/year and specializes in processing heavy oil and secondary residues in order to increase the range of raw materials.[3,4] The installation includes a reactor-regenerator unit, fractionation section, absorption stabilization section, flue gas energy recovery section, combustion gas desulfurization section, dry gas desulfurization section, etc. As a result, we obtain the main products: purified dry gas, liquefied petroleum gas (LPG), gasoline, light catalytic gas oils (LCG), as a component of diesel fuel, and by-products - heavy residues.[5,6] The run of a catalytic cracking unit with a capacity of 2 million tons/year was carried out for a comprehensive assessment of the characteristics of the used finely dispersed publicly available industrial catalysts in order to comprehensively assess the technological characteristics of the test catalyst in the reactor-regenerator unit installations.[7] The main technological parameters of the process when assessing the characteristics of the catalyst used are shown in Table-1.

Table-1: Product Quality Control Indicator

No.	Names	Indicators
1	Component C_3 in dry gas:	≤2%
2	Component C_5 in liquefied gas:	≤0.5%
3	Gasoline boiling point:	≤210°C
4	Distillation temperature of 95% diesel:	360°C
5	Heavy residue density:	≤1050 kg/m^3
6	Fractional column bottom temperature:	≤345°C

From Table-1 it follows that the main indicators of product quality are expressed in the temperature limits of gasoline: the boiling point of gasoline should not exceed 210°C, otherwise, a negative impact on subsequent technological processes is possible. The purpose of the pilot launch is the development of the oil refining and petrochemical industry of the republic by increasing the depth of processing of heavy oil residue - fuel oil, obtained from the processing of Kumkol and Aktobe oils in an atmospheric distillation unit using publicly available fine catalysts.[3,4]

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EXPERIMENTAL

Material and Methods

To determine the elemental composition and study the structural features of the mixture under experimental conditions, testing methods were chosen using a scanning electron microscope (SEM) brand Jeol JSM-6490l V, Incident beam monochromator D878-PC75-17.0 (London, England), IR Fourier spectrometer (Shimadzu IR Prestige-21), and other instrumental methods.

General Procedure

The processing quantity of the plant's raw materials is about 229.2~230.8 t/h, the volumetric flow rate of the raw materials is 255 m^3/h, the density of the raw materials is shown in Table-2, and the agreement value is 230.5 t/h. The procedure for collecting the necessary data for a pilot run:

by raw material: crude oil consumption is measured by a flow meter. Crude oil samples are collected daily in 2 samples and analyzed in laboratories using standard methods.

according to the resulting products: dry gas, liquefied petroleum gas, gasoline, light catalytic gas oil, and heavy residue are measured by flow meters of the subsequent installation. Monitoring of each flow meter is carried out before the run. The products of dry gas, liquefied petroleum gas, gasoline, LCG, and heavy residue are analyzed twice a day, and 2 samples of catalysts are collected separately for analysis every day. Table-2 shows the physical and chemical properties of fuel oil from the Shymken oil refinery plant.

Table-2: Analysis of Raw Materials - Atmospheric Distillation Fuel Oil

Names	Value according to tech. regulations	Stage I	Stage II
Density, kg/m^3 (20°C)	0.9039	0.899	0.905
Residual carbon (on the catalyst), %	4.41	3.85	3.98
API	25.0	25.0	24.7
Content Ca, mg/g	4	15.11	14.51
Content Mn, mg/g	<1	0.45	0.54
Content Ni, mg/g	19	16.71	16.74
Content V, mg/g	1	3.21	4.00
Content Zn, mg/g	1	0.19	0.16
Content Na, mg/g	70.2	83.74	148.90
Content Fe, mg/g	13-14	13.07	13.76
Content S, ppm	2270	3409	4120
Content C, %	86.06	-	-
Content H_2, %	13.42	-	-
Content N_2, ppm	3400	-	-

From Table-2 it can be seen that in comparison with the crude oil index according to the technological regulations, fuel oil from mixed paraffinic raw materials from the Kumkol (70%) and (Aktobe - 30%) fields have low density and moderate coking properties, API tends to decrease, this is explained by the fact that the feedstock becomes heavy and the content of heavy metals is relatively high, especially Ca, Ni, Fe, Na and V. The Ni content basically complies with the regulations, the Ca content has increased more than 3 times, the content V has increased 4-5 times and Fe content in crude oil has not been analyzed but is currently relatively high, ranging from 12.19-16.70 ppm. The sulfur content also increased, usually an increase in sulfur content indirectly indicates that the raw material has become heavy, and also an increase in sulfur content can lead to the formation of sulfur oxides in flue gases, and their effect is interpreted by the authors differently: it is assumed that sulfur, reacting with the metal surface, acts as a corrosion inhibitor and can help prevent corrosion of the internal surface of the device. The raw material is preheated flows down the elevator reactor and comes into contact with the micro spherical catalyst for 2-4 seconds. Steam is used for lifting. Next, a cracking reaction occurs, splitting heavy hydrocarbons, and then the gas-product mixture passes into the separation zone of the reactor, where cyclones are installed to capture the catalyst (Fig.-1).

From the top of the reactor, the catalysts enter the further separation of the resulting products. The coked catalyst, which has lost its activity and selectivity, flows by gravity into the regenerator for regeneration,

where the air supply is taken into account; at a temperature of 700-750ºC, the surface of the catalyst is burned out with coke deposition. After this, the catalyst restores its original properties, i.e. activity and selectivity are restored and fed back into the elevator reactor via the transport line by gravity. The flue gases pass through cyclones, where the catalysts are captured and sent for further heat recovery.

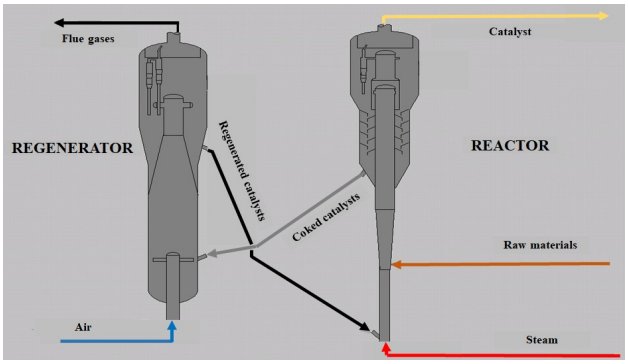

Fig.-1: Operating Principle of the Reactor and Regenerator

RESULTS AND DISCUSSION

The work also analyzed the qualitative characteristics of products and a comparative analysis of the distribution of products before and after calcium contamination (Table-3).

Table-3: Product Characteristics

Names	Mileage results		
	Stage I	Stage II	In 2 stages
Processing volume, t/h	229.2/229.5	230.8/229.8	229.8
Gasoline yield (no more than 210°C), wt.	49.91	50.21	50.06
Dry gas yield, wt.%	4.88	4.92	4.90
Petrol	91.8/91.7	91.6/91.5	-
The flash point of heavy residue, ^{0}C	85/64	92/85	-
Liquefied gas output, wt.%	13.12	12.03	12.58
Total liquid yield, wt.%	82.93	83.10	83.01

Table-3 it shows that at stages I and II, the yield of gasoline exceeds 49.9%, and the yield of dry gas ranges from 4.88 to 4.92%, this is due to an increase in the content of heavy metals and is accompanied by dehydrogenation, leading to an increase in the thermal reaction cracking by a chain mechanism, the octane number of gasoline according to the research method is from 91.5 to 91.8, the yield of liquefied gas is stable from 12.03 to 13.12%, and the yield of light gas oil is 82.93 ~ 83.10 % respectively. To study the elemental and mineralogical composition of the catalyst, microscopic analysis was carried out using an SEM JSM-6490l V (Jeol, Japan). The elemental chemical composition of the catalyst was determined by the energy-dispersive method. The results are shown in Fig.-2 and Table-4.

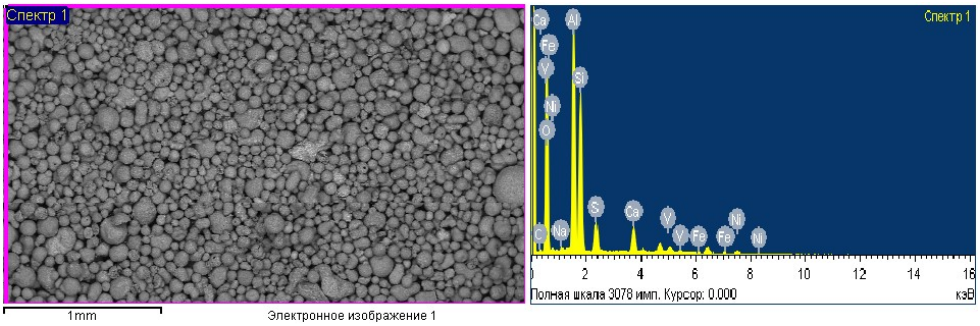

Fig.-2: Microstructure of Catalyst

From Fig.-2 it can be seen that the results of microscopic studies of catalysts carried out using a scanning SEM using the energy-dispersive method are shown in the form of yellow spectra. Based on these data, the elemental composition of the test sample is determined and converted to the oxide form.

Table-4: Elemental Composition of Catalyst

Element	Weight,%	Oxides	Interms of oxides, %	Element	Weight,%	Oxides	Interms of oxides, %
C	4.42	-	-	Ca	4.30	CaO	6.02
O	47.31	-	-	V	0.61	V_2O_5	1.76
S	2.93	-	-	Na	0.53	Na_2O	0.71
Al	19.18	Al_2O_3	36.2	Fe	2.04	Fe_2O_3	2.70
Si	17.51	SiO_2	39.9	Ni	1.18	NiO_4	2.15

From Table-4 it follows that the catalyst contains useful components such as carbon (C), aluminum (Al), silicon (Si), nickel (Ni), etc. The presence of such components allows it to be used as a catalyst to increase the rate of chemical reactions in the installation.[8,9.] The infrared spectral analysis of the catalyst (Fig.3) was carried out using an IR Fourier spectrometer, Shimadzu IR Prestige-21, Kyoto, Japan).

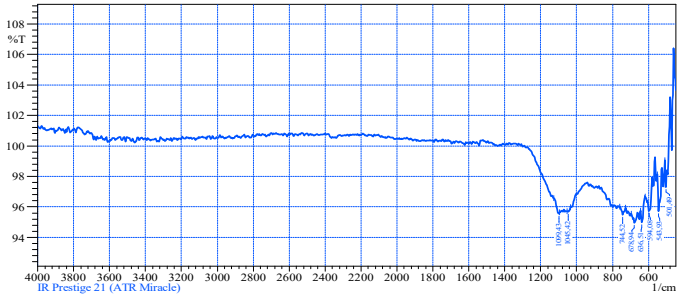

Fig.-3: IR-spectrum of Catalyst

Figure-3 shows the IR spectrum of the catalyst, from which it follows:

- spectra 1099.44-1045.42cm^{-1}in herent in the presence of silicate substances fit Si-O-Si and Si-O-C chemical bonds in catalyst;
- spectra 744.52 which are inherent in the silicon-containing compounds by the C-S group;
- spectra in the interval of 678.94–501.49 cm^{-1} are inherent in the compounds Al^{3+}, Fe^{3+}, Ca^{2+} and etc. in the valence state Si-O-Al, Si-O-Fe, and Si-O-Ca.

To determine the phase composition of the copper phytocompound, X-ray phase analysis was carried out using an Incident beam monochromator D878-PC75-17.0 (London, England). The research results are presented in Fig.-4.

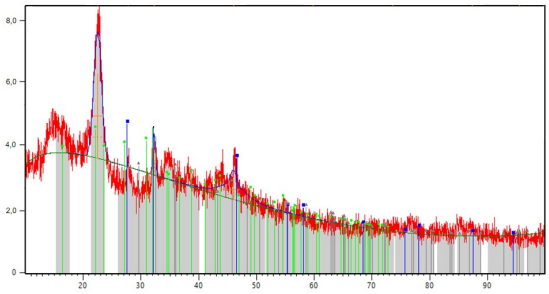

Fig.-4**:** X-ray Phase of Catalyst

From Fig.-4 it follows that the analysis of the image confirms that the structure of the sample is amorphous and crystalline. Peaks with values of interplanar distances A^0 = 4.24-3.84-2.45-2.28-1.81-1.53 indicate the presence of quartzite in the crystal structure of the sample - SiO_2, which is the main component. The composition of the sample under study contains in significant quantities: iron oxide - Fe_2O_3, with diffraction maxima A^0 = 2.77-2.56-2.21-2.08-1.66-1.48 and aluminum oxide -Al_2O_3, for which diffraction maxima A^0 = 7.14-3.34-3.02. Typical values are -2.70-2.12-1.66. The presence of nickel impurities is evidenced by low-intensity peaks A^0 =1.17-1.08-1.03.

According to Table-5, it can be seen that the olefin content in gasoline is relatively low, 29.11-29.21 wt.%, and the content of isoparaffins and aromatic compounds is relatively high, which helps to increase the octane number of the target product - gasoline. The octane number of gasoline (according to the research method) is in the range of 91.5~91.8, that is, it meets the needs of producing high-quality

gasoline at oil refineries. Table-6 shows the correspondence ratios of heavy metals in the catalyst during processing.[10,11]

Table-5: Properties of Gasoline Using a Catalyst During Calibration

Results			Stage I, selections			Stage II, selections		
			1	2	3	4	5	6
GOST 17323	Mass fraction of mercaptan sulfur, % wt.		0,0041	Not measured				0,0030
	Hydrogen sulfide content		absent	Not measured				absent
GOST 2177	Fractional compound	Initial boiling point, °C	28	29	29	29	27	29
		Distillation temp. 5%,°C	38	38	33	39	37	39
		Distillation temp. 10%,°C	43	43	40	44	43	44
		Distillation temp. 50%,°C	93	93	91	94	92	92
		Distillation temp. 90%,°C	174	175	175	172	172	172
		Distillation temp. 95%,°C	191	191	192	188	189	188
		Temp. end boiling point, °C	210	211	209	205	205	205
		Output,%	98	98	96	98	98	98
GOST 8226	Octane number according to the research method.		91.6	91.5	91.5	91.6	91.7	91.8
GOST 20884	Sulfur content, mg/kg		331.0	347.0	348.0	350.0	342.2	256.0
GOST 3900	Density at 20°C, kg/m³		722	721	722	723	719	719

Table-6: Correspondence Ratio of Heavy Metals in the Equilibrium Catalyst and Heavy Metals in the Raw Material When Processing Raw Materials FROM The Kumkol and Aktobin Deposits

Specific catalyst consumption, kg/t	Kumkol deposit-100%				Kumkol and Aktobin deposits (70%:30%)				
	Ca	Ni	Na	V	Ca	Ni	Na	V	Fe
	4 ppm	19 ppm	7 ppm	1 ppm	12.91 ppm	17.07 ppm	86.06 ppm	3.4 ppm	12.19 ppm
1,0	4000	19000	7000	1000	12910	17070	86060	3400	12190
1,5	2667	12667	4667	667	8607	11380	57373	2267	8127
2,0	2000	9500	3500	500	6455	8535	43030	1700	6095
2,5	1600	7600	2800	400	5164	6828	34424	1360	4876

From Table-6 it follows that when processing atmospheric components with a mixture of components 70% Kumkol and 30% Aktobe, compared with the value according to the agreement, the content of proven metals in the equilibrium catalyst obviously increases under different conditions of consumption of the catalytic factor, especially the content of sodium, vanadium, etc. increases etc., the activity of the catalyst decreases, which leads to contamination of the catalyst with brittle metals, which deteriorates the quality of the product. From the results of the analysis of the physicochemical properties of the equilibrium catalyst, it can be seen, as shown in Fig.-5 and 6 the content of sodium and calcium oxide in the equilibrium catalyst continued to increase. Calcium in the equilibrium catalyst exists in the form of calcium oxide and is alkaline, readily binding or blocking the acid site of the catalyst, causing deactivation of the active site of the catalyst.

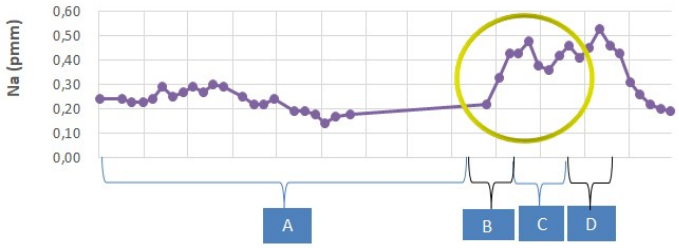

Fig.-5: Indicators of Changes in Sodium Content When Tested in the Catalyst Composition

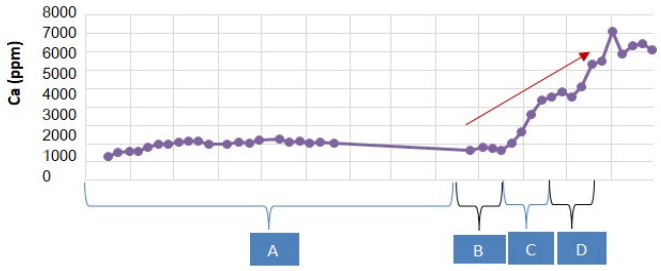

Fig.-6: Indicators of Changes in Calcium Content when Tested as Part of the Catalyst Composition

CONCLUSION

The results of the studies showed that when processing compounded atmospheric residues consisting of a mixture of Kazakhstani oils, the general characteristics of the tested regenerated catalyst do not deteriorate and have a high ability to convert heavy oil. The catalysts are resistant to the deactivating properties of heavy metals, while simultaneously increasing the yield of high-octane gasoline, which is relevant for modern oil refineries and provides the prospect of producing gasoline that meets the requirements of EURO 4 and EURO 5 standards.[12,13] According to the physic-chemical characteristics of the raw material, it should be noted that the density and index of coke deposits on the catalyst have minimal values. The results of the analysis of the equilibrium catalyst proved that, despite the high content of heavy metals in the feedstock, the catalyst retains a sufficiently active surface, which makes it possible to increase the service life of the catalyst.[14,15] Thus, the results obtained allow us to conclude that it is advisable to carry out catalytic cracking of fuel oil on a micro-spherical zeolite-containing catalyst in a reactor ending in a forced fluidized bed, which in turn helps to increase the depth of oil refining. The data obtained also make it possible to further use the research results in the design and modernization of complex production catalytic cracking units RFCC, R2R, and G-43-107M as part of existing oil refineries.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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