OPTIMIZATION OF THE OXIDATIVE CRACKING OF FUEL OIL ON CATALYSTS OBTAINED FROM KAZAKHSTAN RAW MATERIALS

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ABSTRACT

This study aimed to prepare catalysts on the base of Kazakhstan raw materials and test them in the oxidative catalytic cracking of fuel oils. It was determined the influence of air on the route of cracking reactions and establish the relationship between the parameters of oxidative catalytic cracking and the degree of conversion of high molecular weight hydrocarbons to light products. It was found that the air additives contribute to a deeper degradation of hydrocarbons of the starting material. According to the IR spectra, the oxidative cracking gasoline carried out without a catalyst contains sulfur compounds bound to the oxygen atom ($927-1,007\text{ cm}^{-1}$) and carbon (747 cm^{-1}). With an increase in the volumetric flow rate of air and processed feedstock, in the presence of a catalyst, sulfur-containing hydrocarbons are likely to be oxidized. The introduction of air additives into the reactor increases the fraction of the dehydrogenation reaction for lighter-boiling hydrocarbons (fraction $185-340^{\circ}\text{C}$) and does not affect the degree of dehydrogenation of the heavier fraction. The addition of air oxygen to the reactor when carrying out catalytic cracking on the developed catalysts makes it possible to deepen the processing of fuel oil and significantly reduce the content of sulfur-containing compounds. The presence of a catalyst promotes their destruction and removal from the gasoline fraction.

Keywords: Catalytic Cracking, Oil Fuel, Gasoline, Natural Taizhuzgen Zeolite, Narynkol Clay, Water and Gas Purification, Highly Toxic Organic Compounds.

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INTRODUCTION

Catalytic cracking is one of the most important multi-tonnage processes of modern oil refining. It allows you to get motor fuels and petrochemical raw materials from heavy oil raw materials of various quality. The constantly increasing demand for motor fuels and other products of catalytic cracking, as well as the limited resources of raw materials, make it necessary to intensify the process.¹⁻⁶ The most “vulnerable” place that restricts intensive processing of heavy raw materials is increased coking. In developed countries, the main areas of intensification of catalytic cracking are the development of highly efficient catalytic systems, reconstruction of installations and various methods of preliminary preparation of raw

materials.⁷⁻¹⁰ These methods give good results but require high costs for research, development and implementation of results.

When carrying out catalytic cracking, several sequentially - parallel reactions take place, in which both the molecules of the feedstock and the molecules formed during the reaction participate. The mechanism of most reactions of catalytic cracking is described qualitatively within the framework of the carbonium-ion theory.¹¹⁻¹⁷ Since catalytic cracking is a chain reaction, the process can be intensified by initiating radical chain reactions on the catalyst surface with various additives. The principles of new technological processes for the processing of fuel oil and liquid bitumen include the use of ozonolysis and radiolysis.¹⁸⁻²¹ The effectiveness of the effect of ozone on the conversion of fuel oil under the conditions of its visbreaking process and the possibility of reducing the temperature to 425 - 450°C was shown.²²⁻²⁴ The large conversion depth of ozonized fuel oil is due to the appearance in the system, in addition to hydrocarbon radicals, of peroxide radicals formed as a result of the decomposition of ozonolysis products of fuel oil components. After processing the gasoline fraction of ozonated oil on a zeolite-containing catalyst, the quality of the produced gasoline is improved and their yield is significantly increased in comparison with similar processing of the corresponding fraction of crude oil. The content of aromatic hydrocarbons in the catalysts decreases and the proportion of C₅ isoalkanes increases, while the octane numbers change insignificantly.^{24,25} The observed changes in the hydrocarbon composition of gasolines are a good prerequisite for obtaining more environmentally friendly fuel.

The process of cracking of a vacuum distillate on a zeolite-alumino-silicate catalyst and reforming of gasoline fractions on a modified catalyst in the presence of atmospheric oxygen with its concentration in the reactor below the lower explosive limit of the reaction mixture was studied.²⁵ Catalytic cracking of the vacuum distillate was carried out in a laboratory flow-through setup at atmospheric pressure, in an inert atmosphere and in the presence of air, which was supplied in an amount ensuring the oxygen content in the reaction mixture was not more than 5% wt. for raw materials. The presence of oxygen contributed to an increase in the yield of light fractions, however, it leads to an increase in the yield of hydrocarbon gases (to the least extent at an oxygen content of 1.3 wt. %), as well as the coke content on the catalyst. The gasoline fraction obtained in the presence of oxygen has a higher octane number (by 1.5-2.3 units) than the same fraction obtained in the absence of oxygen. This can be explained by the presence of oxygen-containing hydrocarbon compounds in it, which is confirmed by IR spectra. On the results of oxidative catalytic cracking (oxycracking) of vacuum gas oil in the presence of an industrial zeolite catalyst "omnikat", it was found that the oxidation state of hydrocarbon feedstock in the range of 0.5-1.0% promotes an increase in the yield of gasoline fraction (up to 25-27%) at increasing the depth of its transformation by 14-15% of the mass.^{26,27} The presence of air in the reaction mixture changes the route of the reactions occurring during cracking. Unlike an inert atmosphere, where the isomerization reaction of n-alkanes (57% of isoalkanes) is predominant, the oxidative destruction of vacuum gas oil enhances the process of dehydrogenation of its constituent paraffin to olefinic hydrocarbons.

So, when comparing the technological characteristics of the oxidative cracking of heavy petroleum fractions on composites of natural components with the well-known industrial processes of catalytic cracking of petroleum residues, the advantage of using air additives in the reactor during catalytic cracking becomes obvious.²⁰⁻²⁷

This work aimed to study the patterns of oxidative cracking of fuel oils on composite catalysts based on Kazakhstan's natural raw materials.

EXPERIMENTAL

Material and Methods

Commodity fuel oil and a fuel oil of the M-100 brand of the Amangeldy gas processing plant (Kazakhstan) were used as raw materials for cracking. The natural zeolite of Taizhuzgen deposit and clay of Narynkol deposit were applied for the synthesis of zeolite-containing catalysts. Initially, fractions of zeolite and clay of 60-80 microns were prepared. The zeolite was activated by ion exchange of sodium cations from the zeolite framework into lanthanum and ammonium cations.

The experimental procedure, preparation of catalysts, and general information on the starting materials are described in our previous work.^{28,29} The analysis of gaseous cracking products was carried out on a

gas chromatograph with a flame ionization detector: for hydrocarbon gases - on columns, 2 m long and 2 mm in inner diameter filled with a porralak sorbent with particle sizes 8.2-8.3 mm; for non-hydrocarbon gases - on a packed column 1 m long with NaX zeolite with a particle size of 0.25-0.5 mm. The carrier gas, argon, was supplied at a rate of 3 ml/min. The programmed temperature scan was performed for hydrocarbon gas in the range - 25-165°C with exposure at 25°C for 7 minutes; and for non-hydrocarbon gas-40-100°C, at a speed of 8°C / min.

The spectra of the sample were registered on the JNN-ECA 400 spectrometer of the company "Jeol" (Japan). The operating frequency of the spectrometer is 400 and 100 MHz on ^1H and ^{13}C cores, respectively. The survey was performed at room temperature using CDCl_3 solvent. Chemical shifts are measured relative to the signals of residual protons or carbon atoms of deuterated chloroform.^{30,31}

RESULTS AND DISCUSSION

According to NMR research, the proton spectrum of Amangeldy fuel oil (Fig.-1) contains ^1H signals of paraffinic, naphthenic and aromatic compounds, which are the main components of the mixture. Signals of methyl protons of saturated hydrocarbons (HC) are noted as a broadened singlet at 0.90 ppm. A high-intensity signal with a chemical shift of 1.28 ppm indicates a high content of protons of methylene groups of aliphatic cyclic and acyclic hydrocarbons.

A small amount of CH_3 groups was noted in the α -position to the aromatic ring ($\delta = 2.30\text{-}2.63$ ppm). In the range of 2.70-4.50 ppm probably the resonance of protons of the CH_2 and CH groups in the α -position of aromatic systems.^{6,28,30,31}

Of great practical interest is the development of effective technology for catalytic cracking of fuel oil without pre-desulfurization and demetallization of heavy raw materials, which are used in industrial processes.³²⁻³⁷ 84.5 wt.% of the weight of fuel oil is made up of vacuum distillate and heavier fractions (Table-1).

Table-1: Commercial Fuel Oil: Composition and Sulfur Content

Content, wt. %	Components	Sulfur Content
Fuel oil	100.00	2.10
Gasoline	0.50	-
Light gas oil	15.00	-
Vacuum gas oil	44.80	-
Heavy residue	39.70	-

The effect of small amounts of a catalyst containing 14 wt.% of Taizhuzgen zeolite and 86 wt.% of Narynkol clay, as well as additives in the reaction zone of air on the cracking of fuel oil is shown in Table-2.

Table-2: Influence of the Catalyst and Air Additives on the Cracking Process of Commercial Fuel Oil (in Suspension = 0.1 h⁻¹; 0.2 wt.% in the Raw Material of a 14% Composite, T = 450°C)

Yield, wt. %	Technological Mode			
	Air Presence			
	Inert Atmosphere		$W_{\text{air}} = 0.05 \text{ h}^{-1}$	
	Without Catalyst	With Catalyst	Without Catalyst	With Catalyst
Gas	6.50	7.60	12.90	13.60
Petrol	3.50	4.00	5.40	13.50
Light gas oil	19.60	22.10	19.80	55.30
Heavy residue	68.90	64.80	6.60	13.60
Coke	1.50	1.50	1.30	4.00
Losses	0.00	0.00	0.00	0.00
Total	100.00	100.00	100.00	100.00

As can be seen from Table-2, during thermal cracking of fuel oil, as well as catalytic cracking in an inert atmosphere, gasoline is formed in insignificant amounts, and the yield of light gas oil is 19.6-22.1 wt. %. In oxidative cracking in the absence of a catalyst, gas formation doubles, but the yield of light products does not change. Consequently, neither air additives nor the catalyst, taken separately, significantly

activate the process of destruction of high-molecular-weight fuel oil hydrocarbons. With their simultaneous action, i.e. with oxidative catalytic cracking, the yield of both gasoline and kerosene-gasoline fractions, and coke, increases 2.5 times.

(a)

(b)

Fig.-1: NMR spectra of Amangeldy fuel oil: (a) ^1H spectrum, (b) ^{13}C Spectrum.

Data on the effect of the concentration of air in the reaction mixture on the cracking of fuel oil under conditions of a high feed rate of its suspension with a composite catalyst into the reactor are presented in Table-3.

The highest yield of gasoline and light gas oil is observed when air is supplied at a speed of 0.15 h^{-1} , and an increase in the concentration of processed raw materials suppresses the destruction of high-molecular

hydrocarbons that are part of fuel oil to light hydrocarbons of gas and gasoline fractions. At the same time, the yield of the kerosene-gas oil fraction decreases slightly with an increase in the volume rate of its supply. At high concentrations in the reaction mixture of air, intense gas formation begins. Consequently, air additives contribute to a deeper degradation of hydrocarbons of the starting material. The optimal temperature for the process of cracking fuel oil at high speeds of its supply to the reactor is 470 °C. Since the initial fuel oil cracking (see Table-1) is carried out without preliminary desulfurization, it was of practical interest to determine the characteristics of the resulting products to determine the concentration of sulfur in them (Table-4).

Table-3: Influence of the Volumetric Airflow Rate on the Yield of Cracking Products of Commercial Fuel Oil ($W_{\text{suspension}} = 1.0 \text{ h}^{-1}$, 0.2 wt.% in the Raw Material of a 14% Composite, $T = 450^\circ\text{C}$)

$W_{\text{air}}, \text{h}^{-1}$	Product Yield, wt. %						Total
	Gas	Gasoline	Light Gas Oil	Heavy Residue	Coke	Losses	
0.0	1.00	0.20	18.80	77.60	2.40	0.0	100.0
0.03	4.40	1.50	25.20	67.60	1.30	0.0	100.0
0.05	2.70	1.50	27.30	66.10	2.40	0.0	100.0
0.07	3.20	1.20	39.00	54.70	1.90	0.0	100.0
0.10	3.30	1.40	39.30	53.90	2.10	0.0	100.0
0.15	1.10	3.00	42.70	51.70	1.50	0.0	100.0
0.50	6.00	1.80	23.40	67.50	1.30	0.0	100.0
0.70	10.60	1.10	38.00	49.00	1.30	0.0	100.0

Table-4: Sulfur Content in Kerosene-Gas Oil Cracking Fractions of Commercial Fuel Oil at 470°C

No	Catalyst	$W_{\text{air}}, \text{h}^{-1}$	Sulfur Concentration (wt. %) in Fractions of Light Gas Oil, $T_{\text{initial boiling point}}$	
			185-340°C	340-350°C
1	without catalyst	0	0.2	0.2
2	without catalyst	0.15	0.2	0.4
3	with catalyst	0.15	0.1	0.4

Comparing the results of the experiment (Table-4) and the initial raw material data (Table-1), it can be seen that the sulfur content in the kerosene-gas oil fraction, boiling at 185-340°C, is 20 times, and in the fraction 340-350°C - 5 times less, than in the original fuel oil.

It should be noted that in gasoline of oxidative cracking carried out at 450°C in the absence of a catalyst, compounds of sulfur bound to the oxygen atom (927-1,007 cm^{-1}) and carbon (747 cm^{-1}) were identified.³⁸⁻⁴¹ With an increase in the volume rate of air input and the raw material, in the presence of a catalyst, sulfur-containing hydrocarbons are likely to be oxidized. This is evidenced by the disappearance of the absorption band at 747 cm^{-1} , which is characteristic of valence vibrations of the C-S bond; as well as the appearance of a band at 940 cm^{-1} , showing the presence of sulfoxides in the test sample. Under the conditions of catalytic cracking in an inert atmosphere, sulfur compounds are not contained in the resulting gasoline. It can be concluded that these sulfur compounds do not oxidize, while the presence of a catalyst contributes to their destruction and removal from the gasoline fraction. For hydrocarbons of kerosene-gas oil fractions, unlike gasoline, the oxidation of sulfur-containing hydrocarbons does not occur completely, since the spectrum contains lines that characterize the S-CH₂ bond (2,627 and 740 cm^{-1}). Moreover, when air is added to the reaction zone, the intensity of the absorption band at 920 cm^{-1} corresponding to the valence vibrations S-O and S=O, increases. Based on IR spectral analysis, the course of dehydrogenation reactions of alkanes to olefins during oxidative cracking of fuel oil was established.

CONCLUSION

The article is devoted to developing catalysts based on natural Taizhuzgen zeolite and Narynkol clay (Kazakhstan) and testing their efficiency in the catalytic cracking of fuel oil. It was shown that the highest yield of gasoline and light gas oil is observed when air is supplied at a speed of 0.15 h^{-1} , and an increase in the concentration of processed raw materials suppresses the destruction of high-molecular

hydrocarbons that are part of fuel oil to light hydrocarbons of gas and gasoline fractions. The influence of the catalyst and air can be seen not only in the yield of kerosene-gas oil fractions but also in the composition of the hydrocarbons contained in them. In an inert atmosphere in the absence of a catalyst, dehydrogenation of hydrocarbons practically does not occur. A significant decrease in sulfur-containing compounds in the products has been established, the presence of a catalyst promotes their destruction and removal from the gasoline fraction.

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