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CATALYTIC HYDROPROCESSING IN OIL REFINING

IMPROVEMENT OF STRAIGHT-RUN DIESEL FUEL LOW-TEMPERATURE PROPERTIES ON THE ZEOLITE CATALYST

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Introduction

- The strategic task of developing the Arctic territories and the Northern Sea Route is extremely important, which requires the provision of transport, equipment, and power generators with high-quality low-freezing fuels.
- The proportion of low-freezing diesel fuel of winter and arctic grades is not more than 17% of the total volume of produced in Russian diesel fuel, with a demand of at least 30%.
- The delivery of low-freezing fuel obtained at major refineries enterprises to remote areas with a harsh climate sharply increases the final cost of fuel.
- The need for development of low-tonnage hydrogen-free catalytic technology for processing diesel fuels, which primarily requires the search and create a new catalyst.
- Production of high-quality motor fuels, in particular diesel fuel, is one of the most important tasks of the Russian Federation oil refining industry.

Materials and methods

In this study, the diesel fraction derived from oil atmospheric distillation unit one of the Western Siberia fields (the Russian Federation), was selected as the feedstock for the processing on a zeolite catalyst.

To carry out the process a ZSM-5 type zeolite catalyst, produced by PJSC "Novosibirsk Chemical Concentrates Plant" (KN-30 brand) was used.

The feedstock diesel fraction and the products obtained during its processing on a zeolite catalyst were characterized according to the requirements of USS 305-2013 "Diesel fuel. Specifications".

Experimental

The diesel fraction processing was carried out on a laboratory catalytic unit of continuous type (the photo of the catalytic unit is shown In picture 1).

Before testing, the zeolite catalyst was mechanically crushed and sorted by particle size. In this work, a catalyst with 0.5-1.0 mm particle diameter was used. The catalyst sample with a volume of 10 cm^3 was loaded into a reactor, after that, it was calcined for 8 hours at a temperature of 500 °C in a nitrogen flow for activate and remove residual organic substances and adsorbed moisture from the active surface of the catalyst.

Figure 1 – Laboratory catalytic unit

Composition and characteristics of the feedstock diesel fraction and the product obtained by processing on zeolite catalyst

The main characteristics of the diesel fraction and the product obtained by processing the diesel fraction on a zeolite catalyst at temperature of 375 °C, a pressure of 0.35 MPa, and a feedstock volumetric flow rate of 0.5 ml/min are presented in Table 1.

Table 1 – Main characteristics of the diesel fraction and the obtained product

Characteristic	Diesel fraction	Obtained product
Density at 15 °C, kg/m^3	836.5	833.0
Kinematic viscosity at 20 °C, mm^2/s	4.148	2.167
Dynamic viscosity at 20 °C, mPa/s	3.455	1.803
Cetane index, points	49.2	46.7
Molecular weight, g/mol	198.02	150.47
Sulphur content, mg/kg	3911	3741
T_{cp}, °C	-4	less -70
CFPP, °C	-5	-51
T_{pp}, °C	-16	less -70

T_{cp} – cloud point, CFPP – cold filter plugging point, T_{pp} – pour point

The group, and structural-group compositions, as well as the content of n-paraffins of the diesel fraction and the obtained product are presented in Tables 2-5.

Table 2 – Group hydrocarbon composition of the diesel fraction and the obtained product

Hydrocarbon group	Content, % wt.	
	Diesel fraction	Obtained product
Aromatics	25.55	36.15
Naphthenes	23.98	40.55
Paraffins	50.47	23.30

Table 3 – Structural-group composition of the diesel fraction and the obtained product

Characteristic		Diesel fraction	Obtained product
Carbon distribution, % wt.	C_{ar}	13.695	23.084
	C_n	27.148	29.043
	C_{ring}	40.843	52.127
	C_{al}	59.157	47.873
Average number of rings in the molecule	R_{ar}	0.348	0.633
	R_n	0.689	0.805
	R_t	1.037	1.438

C_{ar} – the content of carbon in aromatic rings, % wt.; C_n – the content of carbon in naphthenic structures, % wt.; C_{ring} – the content of carbon in ring structures, % wt.; C_{al} – the content of carbon in alkyl substituents, % wt.; R_{ar} – number of aromatic rings; R_n – number of naphthenic rings; R_t – total number of rings.

Table 4 – Content of n-paraffins in the diesel fraction and the obtained product

Sample	Content, % wt.				
	Total	up to C_{10}	C_{11-20}	C_{21-30}	C_{31+}
Diesel fraction	37.429	10.916	23.873	2.543	0.098
Obtained product	12.952	9.486	3.467	0.000	0.000

up to C_{10} – the content of n-paraffins with the number of carbon atoms in the chain is not more than 10, % wt.; C_{11-20} – the content of n-paraffins with the number of carbon atoms in the chain from 11 to 20, % wt.; C_{21-30} – the content of n-paraffins with the number of carbon atoms in the chain from 21 to 30, % wt.; C_{31+} – the content of n-paraffins with the number of carbon atoms in the chain 31 and more, % wt.

The influence of processing temperature on the composition and characteristics of the obtained products

To determine the regularities of the process temperature effect on the composition and characteristics of the obtained products, some tests were carried out under conditions of process temperature variation. The temperature of the processing on the zeolite catalyst was varied in the range 375-475 °C with a step of 50 °C. Table 5 shows the full technological parameters of the processing on the zeolite catalyst.

Table 5 – Technological parameters of the processing on the zeolite catalyst

Temperature, °C	Pressure, MPa	Volumetric flow rate, ml/min
375	0.35	0.5
425		
475		

Table 6 shows the results of determining the characteristics of the products of diesel fraction processing on a zeolite catalyst under conditions of the varying process temperature.

Table 6 – Characteristics of the products of diesel fraction processing on a zeolite catalyst

Characteristic	Product at process temperature, °C		
	375	425	475
Density at 15 °C, kg/m^3	833.0	851.0	851.5
Kinematic viscosity at 20 °C, mm^2/s	2.167	2.829	2.056
Dynamic viscosity at 20 °C, mPa/s	1.803	2.398	1.743
Cetane index, points	46.7	44.4	41.8
T_{cp}, °C	less -70		
CFPP, °C	-51	-58	-49
T_{pp}, °C	less -70		

Table 7 shows the results of determining the fractional and group composition, as well as the sulfur content in the products of diesel fraction processing on a zeolite catalyst under conditions of the varying process temperature.

Table 7 – Composition of the products of diesel fraction processing on a zeolite catalyst

Content		Product at process temperature, °C		
		375	425	475
Hydrocarbon group, % wt.	Aromatics	36.15	45.57	39.50
	Paraffins	23.30	33.91	20.67
	Naphthenes	40.55	20.52	39.82
Sulphur content, mg/kg		3741	3442	2989
Fractional composition		**Temperature, °C**		
Volume, ml	IBP	39	53	55
	10	123	58	138
	20	162	178	162
	30	191	209	199
	40	230	239	234
	50	255	260	257
	60	281	284	280
	70	302	310	309
	80	341	339	342
	90	356	359	360

Conclusion

1. The processing of diesel fraction has been implemented in a laboratory catalytic unit using a zeolite catalyst of the ZSM-5 type. The results of determining the composition and characteristics showed that the feedstock diesel fraction in terms of low-temperature properties can not be used in winter and arctic conditions. The predominant group of hydrocarbons in the composition of the feedstock diesel fraction are paraffins (50.47% wt.), the content of n-paraffins is also high (37.429% wt.).

2. It was established that processing the diesel fraction on a zeolite catalyst at a temperature of 375 °C, a pressure of 0.35 MPa and a volumetric flow rate of 0.5 ml/min allows reducing the density, viscosity, and sulfur content. The product cetane index decreases slightly (by 2.5 points), while there is a significant improvement in low-temperature properties (a decrease in CFPP by 46 °C). The yield of the product is 98% vol. According to its performance characteristics, the obtained product meets the requirements for the arctic diesel fuel grade, which makes it suitable for use in arctic conditions.

3. It was shown that the predominant group of hydrocarbons in the composition of the obtained product are naphthenes (the content of naphthenic hydrocarbons increased in comparison with the feedstock diesel fraction by more than 1.5 times); the content of paraffins in the product decreased by more than 2 times (up to 23.30% wt.); the content of n-paraffins decreased almost 3 times (up to 12.952% wt.); the content of aromatic hydrocarbons increased by 10.6% wt. The change in the composition of diesel fraction in the process (a decrease in the content of normal paraffins in the product, especially long-chain n-paraffins) explains such a significant improvement in low-temperature properties. Based on the composition of the obtained products, it was established that with the considered technological parameters of the process, diene synthesis reactions with the formation of naphthenes occurred most actively. There are hydrogen transfer reactions in olefins with the formation of aromatic hydrocarbons and hydrogen that explains the decrease in the sulfur content in the obtained product due to the hydrogenation reactions.

4. The influence of the processing temperature on the composition and characteristics of the obtained products studied. It was established that with an increase in the temperature of the process, an increase in the density of the product, a decrease in the cetane index and sulfur content are observed. The maximum content of naphthenes is observed at a process temperature of 375 °C, the minimum value of CFPP, the maximum content of aromatic and paraffinic hydrocarbons is observed at a process temperature of 425 °C. It was shown that the formation of naphthenes through diene synthesis reaction is favored by lower temperatures of the processing, an increase in temperature to 425 °C favors the occurrence of the hydrogen transfer reaction with the formation of aromatic hydrocarbons. A decrease in the sulfur content in the products with an increase in the process temperature is due to the increased role of hydrogen transfer reactions with the formation of aromatic hydrocarbons and hydrogen, followed by hydrogenation of sulfur-containing compounds.

5. It was established that the optimal technological parameters for the implementation of the processing on a zeolite catalyst, which make it possible to obtain arctic diesel fuel that does not require additional compounding and meet the requirements for arctic diesel fuel by its performance characteristics, are the temperature of 375 °C, the pressure of 0.35 MPa, and the volumetric flow rate of 0.5 ml/min. The implementation of the process of hydrogen-free processing of diesel fuels on a zeolite catalyst is possible in a low-tonnage version, which will provide remote areas with high-quality low-freezing fuel.

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