Table 3. TDC of some reactions with o-xylene

№	Reaction	ΔH, kJ/mol	ΔS, kJ/mol•K	ΔG, kJ/mol
1	penten + 2 propen = o-xylene + 3 methane	–230.62	22.00	–244.88
2	penten + 3 ethene = o-xylene + 3 methane	–352.12	–75.60	–303.13
3	penten + propen + butene = o-xylene + ethane + 2 methane	–224.56	28.68	–243.14
4	penten + 2 ethene + propen = o-xylene + ethane + 2 methane	–332.35	–82.38	–278.97
5	2 penten + propen = o-xylene + 2 ethane + methane	–217.31	36.49	–240.95
6	penten + 4 ethene = o-xylene + propane + 2 methane	–441.21	–185.80	–320.89
7	penten + 3 propen = o-xylene + 3 ethane	–292.8	–95.93	–230.64
8	penten + 3 ethene + propen = o-xylene + butane + 2 methane	–428.54	–199.79	–299.08
9	penten + 2 propen + butene = o-xylene + propane + 2 ethane	–293.94	–88.29	–236.73
10	penten + 5 ethene = o-xylene + pentane + 2 methane	–536.83	–307.05	–337.86
11	2 penten + 2 propen = o-xylene + butane + 2 ethane	–293.73	–87.69	–236.90
12	penten + 4 ethene + propen = o-xylene + butane + propane + methane	–517.70	–309.98	–316.83

375 °C (648 K) and a pressure of 25 atm. (2.5 MPa). Tables 1–3 show list of some received reactions and their TDC.

The obtained results show that the flow of all the reactions is thermodynamically possible (ΔG < 0).

References

1. *Akhmedova H.W, Dadashov S.S, Mamedov S.E et al. Conversion of straight-run gasoline fraction in high-silica zeolite // Chemistry and Technology of Fuels and Oils, 2016.– №3(595).– P.28–31 (in Russ.).*
2. *Ochterski J.W. Thermochemistry in Gaussian. Gaussian, Inc., 2000.– 19 p.*

UPGRADING ON ZEOLITE – EFFECTIVE WAY TO OBTAIN LOW COLD-TEST DIESEL FUELS

E.I. Martyanova, I.A. Bogdanov
Scientific supervisor – PhD-student I.A. Bogdanov
Linguistic advisor – PhD-student I.A. Bogdanov

National Research Tomsk Polytechnic University
634050, Russia, Tomsk, 30 Lenin Avenue, martyanova.1999@yandex.ru

Despite the increase in diesel fuel production in 2018 to 77.5 million tons (an increase of 0.6 million tons compared to 2017), the share of the diesel fuel of Arctic brand in the production structure does not exceed 5 % [1]

Today, the most common method for improving the low-temperature properties of fuels is using of depressant additives, but this method is not universal, since the effectiveness of the additive depends on the composition of the fuel [2].

An alternative method is the catalytic dewaxing process. However, applying a catalyst containing noble metals and a hydrogen-containing gas in this process limits the implementation of the process at small-scale oil refineries. Therefore, it seems promising to develop processes for the upgrading of diesel fractions on zeolite catalysts, without using of hydrogen-containing gas.

The authors of the work carried out the process of upgrading straight-run diesel fraction on a laboratory catalytic unit, using a KN-30 brand zeolite catalyst. The process was carried out at the following technological parameters: process temperature – 375 °C, pressure – 0.35 MPa, feedstock speed velocity – 0.5 ml/min.

The aim of the work is studying the group hydrocarbon composition, low-temperature and physicochemical properties of the raw straight-run diesel

Table 1. Characteristics of the raw diesel fraction and product obtained by upgrading on a zeolite catalyst

Characteristics			Raw diesel fraction	Product
Group composition	Aromatic	% wt.	25.55	36,15
	Paraffins		50.47	23,30
	Naphthenes		23.98	40,55
Cloud point		°C	–4	<–70
CFPP			–5	–51
Pour point			–16	<–70
Density at 15 °C		kg/m^3	836,5	835.0
Kinematic viscosity at 20 °C		mm^2/s	4,148	2.167
Sulphur content		mg/kg	3911	3741

fraction and the product obtained during the upgrading on a zeolite catalyst.

The aniline method was used to determine the group composition. The results of determining the characteristics of straight-run diesel fraction and obtained product are presented in the Table, characteristics of the obtained product had been compared with the requirements of the standard [3].

From the obtained results, the favorable effect of the realized upgrading using zeolite catalyst on the low-temperature properties of the raw diesel fraction, is evident. The change in the limiting cold filtering plugging point, (CFPP) was 46 °C. This is due to the fact that the content of paraffin hydrocarbons in the sample decreased by about half.

In addition to significantly improved low-temperature properties, the values of which, after upgrading, make it possible to attribute the obtained product to the Arctic brand of diesel fuel, the product meets the requirements [3] and in other indicators: the density value meets the requirements for diesel fuel of Winter, Inter-season and Summer brands; the value of kinematic viscosity meets the requirements of any diesel fuel brands.

The sulfur content in the product exceeds the values allowed in the standard [3], however, it should be noted that upgrading raw diesel fraction on the zeolite catalyst made it possible to reduce the sulfur content by 170 mg/kg. To reduce the sulfur content in the product, it is advisable to carry out hydrotreating, which can be implemented both before and after the upgrading process.

To obtain a product that meets the density requirements [3] for the Arctic brand of diesel fuel, it is necessary to experimentally determine the optimal technological parameters for the upgrading process on a zeolite catalyst.

References

1. *Analytical Center under the Government of the Russian Federation, statistical compilation “Russian Fuel and Energy Complex – 2018”. [Electronic resource].– URL: https://ac.gov.ru/, Access mode: free.– Date of appeal: 02.25.2020.*
2. *Orlova A.M., Bogdanov I.A., Nikonova N.P., Kirgina M.V. // Petroleum and Coal, 2020.– V.62.– Iss.1.– P.142–148.*
3. *USS 305-2013 “Diesel fuel. Specifications” [Electronic resource].– URL: http://vsegost.com, Access mode: free.– Date of appeal: 02.25.2020.*