THE EFFECT OF HYDROCARBON COMPOSITION ON THE FLAMMABILITY OF DIESEL FUELS WITH TAKING INTO ACCOUNT INTERMOLECULAR INTERACTIONS

A.A. Berdnikova, M.V. Maylin, E.V. Frantsina
Scientific supervisors – Candidate of Engineering Sciences, researcher E.V. Frantsina
Linguistic advisor – Candidate of Engineering Sciences, researcher E.V. Frantsina

National Research Tomsk Polytechnic University
634050, Russia, Tomsk, 30 Lenin Avenue, tpu@tpu.ru

Cetane number (CN), conforming to modern standards is increased by the addition of ignition promoters. Concentration of cetane-increasing additives (CIA) is non-additive value influenced by the hydrocarbon (HC) composition and the intermolecular forces, acting between the molecules.

As objects of study were selected 7 samples of DF with various hydrocarbon compositions and an ignition promoter – isopropyl nitrate.

To identify Gibbs energy and the interaction energy of the main hydrocarbon groups of DF, molecules, radicals, and hydrocarbon-additive complexes were created in the GaussView5.0.8 software package and was studied using the Gaussian software product (DFT, 2273 K, 5.0 MPa [1]).

To determine the quantitative content of hydrocarbon groups, samples were separated into fractions by column liquid adsorption chromatography on activated silica gel. The paraffin-naphthenic fraction was isolated by elution with hexane, the fraction of aromatic compounds was isolated by elution with a mixture of hexane: benzene (3 : 1 (vol.)), the fraction of "resins" was washed off the column with an eluent of ethanol: benzene (1 : 1 (vol.)). The boundaries of the aromatic fraction were controlled using the formolite reaction. The obtained DF were studied by chromatography-mass spectrometry (CMS) using a quartz capillary column [2] (table 2).

Using the SHATOH-300 instrument determined the CN of DF (Tab. 3).

Table 1. Interaction characteristics for groups "hydrocarbon-additive"

Hydrocarbon group	E of interactions, kJ/mol		dG of reaction, kJ/mol	
	n-alkyl substituent	isoalkyl substituent	n-alkyl substituent	isoalkyl substituent
Paraffins	56.73	–0.15	–3.07	–71.70
Naphthene substituted	–0.18	–0.71	–18.59	–45.06
Naphthalene substituted	–0.42	–0.38	–49.56	–30.47
Benzene substituted	–0.70	–0.75	–38.98	–36.68

Table 2. The group composition of diesel fractions

Hydrocarbons, % wt.	Sample №1	Sample №2	Sample №3	Sample №4	Sample №5	Sample №6	Sample №7
Paraffins	59.15	63.22	69.32	53.05	62.76	52.63	51.01
n-paraffins	32.51	37.17	44.92	30.04	39.46	32.09	27.09
aromatics	26.21	18.53	20.81	24.15	28.64	18.20	13.10
Naphtenes + aromatics	40.86	36.78	30.67	46.96	37.23	47.36	48.97
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Table 3. Values of CN of DF depending on additive concentration

Concetration of additive, % vol.	Sample №1	Sample №2	Sample №3	Sample №4	Sample №5	Sample №6	Sample №7
	CN	CN	CN	CN	CN	CN	CN
0.0	51.00	50.00	54.00	51.90	53.50	48.00	47.90
1.0	53.40	53.00	55.00	54.20	55.00	52.00	51.30
ΔCN	2.40	3.00	1.00	2.30	1.50	4.00	3.40

The energy of interaction "n-paraffin - additive" is the highest (56.72 kJ/mol). It can be assumed that for high n-paraffin fuel (sample No.3 content 44.92% %wt of n-paraffins) the smallest concentration of the CIA will significantly increase the CN, ensuring its good pick-up to the additive.

In samples 6, 7 (Tab. 3), the content of n-paraffins is less than in sample №2, however, the increase in the CN is greater. This is due to the fact that the total content of paraffins is greater than the sum of aromatic and naphthenic HC. The interaction energies of aromatic and naphthenic HC are negative, which confirms their poor response to a CIA. For samples 1, 3, 5, the increase in CN with the addition of the CIA is minimal, despite the high content of paraffins (>55%). It is associated with a high content of aromatic HC (>20%), which have a low interaction energy (–0.43 kJ/mol).Thus, the group composition of DF will have a different effect on CN when adding CIA to the DF. This fact is associated with the different influence of HC groups and reflect the injectivity of the DF additive and the increase in the CN with a change in the concentration of the CIA.

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THE STUDY OF INHIBITORY AND DISSOLVING ABILITY OF HUMIC ACIDS

A.A. Berdnikova, E.V. Beshagina, E.V. Frantsina

Scientific supervisors – Candidate of Engineering Sciences, researcher E.V. Frantsina;
Candidate of Engineering Sciences, assistant professor E.V. Beshagina
Linguistic advisor – Candidate of Engineering Sciences, researcher E.V. Frantsina

National Research Tomsk Polytechnic University
634050, Russia, Tomsk, 30 Lenin Avenue, tpu@tpu.ru

During high-paraffin oil refining, asphaltene-resin-paraffin deposits (ARPD) are formed on the surface of oilfield equipment, reduce the efficiency of the plants and decrease the distillate yields [1]. Applying chemical methods in the fight against paraffin is limited, due to their high cost and metal consumption. A new solution is bioadditives – high molecular weight (HMW) humic acids (HA), which have depressive and surface – active properties. In this work, the ability of HA to inhibit and dissolve paraffin deposits was investigated.

As the objects of study, we selected high-paraffin oil (10.5%) from the Verkhnesalatskoye field with a density of 0.78 g/sm^3, kinematic viscosity of 1.8 mm^3/s, pour point – plus 12 °C , residue of this oil and humic acids.

Evaluation of the inhibitory ability of HA was carried out on the installation to assess the effectiveness of paraffin inhibitors according to the method of "cold rod", which includes 2 blocks. The first block is a “cold rod” immersed in a water bath, which includes 4 metal cups, U-shaped hollow tubes which are mounted into lids and connected to the refrigerant supply and exhaust system. The temperature in the cells, connected with the cold rod, are maintained by a cryostat and thermostat.

The weight of the sample was 60 g. HA were diluted in solution (0.1 N. NaOH), ratios: 1:10, 1:15, 1:20. Samples were added to oil in concentrations: 0.2% (vol), 0.4% (vol), 0.6% (vol), 0.8% (vol). The temperature of the oil in the cell was 30 °C, the temperature of the “cold" rod – mi-