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Mathematical Modeling of Additive Concentration Forecasting for Low Temperature Diesel Fuel Characteristics Improvement

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Abstract

The determination of the hydrocarbon composition of diesel fractions (DF) is related with the most important performance characteristics of diesel fuel, such as the pour point (PP), for example. The injectivity of the main groups of hydrocarbons (HC), n-paraffins and aromatics, into a depressant are evaluated. The injectivity in the depressant additive was investigated regarding intermolecular interactions between hydrocarbons and vinyl acetate, revealing the n-paraffins crystallization suppression effect, and the dissolution of n-paraffins in aromatic hydrocarbons. Based on the results, a mathematical model was proposed to calculate the change in pour point, varying the concentration of a depressant additive, considering the intermolecular interactions of diesel fuel from different hydrocarbon compositions.

Keywords: *Diesel fuel; Hydrocarbon composition; Intermolecular interaction; Quantum-chemical calculation; Pour point; Mathematical model.*

1. Introduction

Nowadays, due to the active development of northern territories, especially in the Artic regions, more high-speed diesel and gas turbine engines are produced [1]; thus, increasing the demand for diesel fuel, meeting modern requirements, both in the Russian market and in the world [2]. Therefore, improved low temperature properties, corresponding to the climatic environment, are required in order to meet these requirements.

According to GOST 32511-2013 "Diesel fuel EURO. Technical conditions", for winter and arctic fuels, transitioning from the 0 to 4th class, the cold filter plugging point (CFPP) decreases from -20 to -44°C, and the cloud point from -10 to -34°C. Moreover, according to GOST 305-82 "Diesel fuel. Technical conditions", for temperate climate zones, in summer and winter, the diesel fuel must have a pour point of -10 and -35°C, respectively; And for cold climate zones, winter and artic, diesel fuel should have a pour point of -45 and -55°C, respectively. Furthermore, according to ASTM D 975 "Requirements for Diesel Fuel Oils", the pour point for diesel fuel type No. 1-D ranges from –18 to 0°C; and for type No. 2-D, it ranges from –6 to 21°C.

The selection of high-quality raw materials and improvement of the technology to obtain diesel fuel is necessary for fulfilling all diesel fuel requirements [3]. Low temperature properties, flammability, and lubricating properties are examples of characteristics determined from the optimization of the hydrocarbon composition of raw materials [2]. Achieving these characteristics is possible due to the use of additives: cetane-increasing, antiwear, depressant-dispersing and detergents, for example.

Since the use of imported additives is costly, regulations are necessary from an economic standpoint. Currently, the available diesel fuel products, meeting the requirements for additives, contain: alkyl nitrates [4], anticorrosive components, hydrocarbon fractions, alkyl succinimide, copolymers based on ethylenically unsaturated monomers, unsaturated fatty acids [5] (from the oleic, linoleic, or amide groups of the acid), calcium sulfonate [1] and copolymers of

higher esters of C_6-C_{28} acrylic [6]), or methacrylic acid with ethylenically unsaturated mono-mer, depressants based on: ethylene-propylene rubber, or based on the copolymerization product of maleic anhydride; and a wide fraction of 1-olefins [7-9].

In addition, depressant additives are made from: composite-polymer base components [10]; polymethacrylate-co-maleic anhydride [11]; polyoxymethylene dimethyl ethers [12]; nitrogen-containing components [13]; benzyl methacrylate-methacrylate copolymers [14]; maleic anhy-dride-co-methyl benzyl acrylate copolymers [15]; organic based manganese [16] and polymer wastes [17].

The effect of depressants in the low temperature characteristics of diesel fuel was evaluated in the present work. Since the pour point of diesel fuel is a non-additive parameter and, the required quantity of additives depends on the hydrocarbon composition and intermolecular interactions between the hydrocarbons included in the diesel fuel and its additives, these in-teractions must be considered (i.e. PP is not the sum of these values of individual hydrocar-bons included in the diesel fuel, in accordance with their percentage).

The main parameters that affect the low-temperature properties of diesel fuel are the con-centration of the additive, the content of aromatic hydrocarbons, and the content of paraffins of normal structure. The lower pour point directly depends on the lower content of n-paraffins in the mixture and the energy of intermolecular interactions.

Therefore, a mathematical model that allows the calculation of the change in the pour point, depending on the concentration of the depressant additive, and considering the hydrocarbon composition and intermolecular interactions existing between the hydrocarbons and the addi-tive is proposed.

2. Materials and methods

Samples of diesel fuel were obtained from crude oil direct distillation, while straight-run samples of DF and atmospheric gasoil (AGO) were obtained from oil refineries [18]. The inves-tigation of vinyl acetate as a depressant additive was conducted, considering the activity of polyethylene vinyl acetate in low-temperature additives.

The hydrocarbon compositions of diesel fractions were determined by gas chromatography-mass spectrometry on an Agilent 7890B (GC) – Agilent Q-TOF 7200 (MS) GC-MS device with a quartz capillary column DB-5MS (length - 30 m, internal diameter - 0.25 mm, film thickness - 0.25 mm). The conditions of analysis: evaporator temperature 300ºC, programmed temper-ature: initial temperature of 40ºC, heating 5ºC / min up to 150ºC, followed by 3ºC / min up to 310ºC, holding at 310ºC for 20 minutes. Helium carrier gas flow 1.1 mL / min. Measure-ments were conducted both in total ion and in selected ions currents (in Scan and SIM modes). The HC components were identified using the mass spectrometric libraries NIST 14, and a detailed study of mass spectrum of fragmentation and molecular ions using reference books on mass spectrometry, previously analyzed in the laboratory of samples of rock and oil ex-tracts, as well as standards provided by Chiron [18].

The components concentration was determined using the appropriate commercially availa-ble standards (C_{10}-C_{40} alkanes, tetracosane-D50, deuterium naphthalene, n-hexyl benzene, and phenanthrene), considering a 5% maximum error. Low temperature parameters of diesel fractions were determined using the INPN SX-800 low temperature indicator for oil products, before and after the addition of the additive.

Quantum-chemical modeling was conducted in the Gaussian software product intended for calculating the structure and properties of molecular systems, allowing the study of the inter-molecular interaction of hydrocarbons included in the diesel fuel with a depressant additive. Hydrocarbon-additive complexes molecules were created using the GaussView 5.0.8 software package [19]. The calculations to study the interaction of hydrocarbons with a depressant, were performed using the Pm6 quantum-chemical method under standard conditions at T = 298 K and P = 100 Pa.

3. Research method

3.1. Quantum-chemical calculation of hydrocarbons with a depressant additive

During the experiment, quantum-chemical calculations were conducted for the following molecules and complexes: n-paraffin, aromatics, depressant, "n-paraffin...n-paraffin", "n-paraffin...aromatics", "n - paraffin...depressor", "Aromatics...depressor" complexes.

The mechanism of adsorption of the additive was based on the surface of the formed *nuclei* *(*complexes consisting of two molecules of n-paraffins were considered as nuclei of n-paraffin crystals) of n-paraffins, which suppresses further crystallization processes. Furthermore, dissolution reactions (interactions) of n-paraffinic aromatic hydrocarbons were considered. Based on the results of the calculations, Table 1 presents the data on the energy and thermodynamic characteristics of the molecules and complexes obtained.

Table 1. Energy interaction values and Gibbs free energies for the complexes "n-paraffin...n-paraffin", "n-paraffin...vinyl acetate", "aromatics...n-paraffin", "aromatics...vinyl acetate"

Complex	"n-paraffin...n-paraffin"		"n-paraffin...vinyl acetate"		"aromatics...n-paraffin"		"aromatics...vinyl acetate"	
Hydrocarbon	E, [kJ]	G, [kJ/mol]	E, [kJ]	G, [kJ/mol]	E, [kJ]	G, [kJ/mol]	E, [kJ]	G, [kJ/mol]
C_{10}	7.59	36.19	7.45	34.78	-0.63	-2.24	7.27	34.70
C_{12}	7.62	39.36	7.56	39.05	-2.11	-3.45	5.92	38.74
C_{13}	7.64	40.97	3.98	45.49	-3.56	-4.50	4.00	51.44
C_{14}	7.66	42.36	4.13	42.11	-4.29	-5.02	4.13	46.56
C_{15}	7.68	43.91	3.95	46.76	-5.02	-5.54	4.15	41.94
C_{16}	7.69	45.33	3.64	49.95	-5.75	-6.06	4.77	53.27
C_{17}	7.71	46.84	3.64	49.88	-6.48	-6.58	3.59	51.21
C_{18}	7.72	48.47	4.03	50.34	-7.21	-7.12	3.59	51.24
C_{19}	7.74	49.83	3.59	49.72	-7.93	-7.63	3.87	53.65
C_{20}	7.76	51.38	4.02	50.15	-8.66	-8.15	3.61	51.51
C_{21}	7.78	53.06	3.58	49.68	-9.39	-8.67	3.59	51.16
C_{22}	7.79	54.61	3.58	49.78	-10.12	-9.19	3.59	51.08
Mean value	7.70	46.02	4.43	46.47	-6.31	-9.72	4.03	48.29

From the data presented in Table 1 is possible to confirm that the pour point increases with the increase of n-paraffins hydrocarbons content in the mixtures, since the complexes "n-paraffin…n-paraffin" possess the greatest value of interaction energy. Concomitantly, the energy of interaction of the complexes "aromatics…n-paraffins" is lower than the energy for the complex "n-paraffins…n-paraffins" (-6.31 kJ and 7.70 kJ, respectively); therefore, the presence of a higher content of aromatics in the mixture reduces the pour point of diesel fuel – result also observed in practices.

Furthermore, aromatic hydrocarbons with a higher content of relatively n-paraffins behave as a solvent for normal alkanes, reducing the PP of the mixture. When a depressant was added to the diesel system, a decrease in the energies of intermolecular interactions for n-paraffins was observed (from 7.70 kJ to 4.43 kJ).

3.2. Study of the hydrocarbon composition of samples of diesel fractions and atmospheric gas oil, and its influence in the pour point

Table 2 presents the established hydrocarbon composition of the diesel fractions and atmospheric gas oil in the experiment. The results of the diesel fractions and AGO obtained temperatures, varying the depressant additive concentration is presented in Table 3.

Table 2. Group composition of samples of diesel fractions and atmospheric gas oil

Hydrocarbon content, wt. %.	DF No. 1	DF No. 2	DF No. 4	DF No. 5	DF No. 6	DF No. 7	DF No. 8	AGO No. 1	AGO No. 2
n-paraffins	29.96	34.73	29.45	30.31	27.43	24.38	31.43	44.64	39.34
Iso-paraffins	24.08	23.58	22.40	18.76	23.56	21.20	24.10	24.12	23.18
Total paraffins	54.04	58.31	51.85	49.07	50.99	45.58	55.53	68.76	62.52
Cyclopentanes	2.38	1.68	1.84	3.05	1.34	3.45	3.11	1.30	1.12
Cyclohexanes	6.43	6.53	2.09	5.72	4.79	6.81	7.39	4.96	3.97
Decals	2.26	2.82	2.96	3.60	0.99	4.42	1.47	1.33	1.19
Others	1.01	4.76	15.31	15.01	9.51	18.46	16.10	2.00	2.17
Total naph-thenes	12.08	15.79	22.20	27.37	16.64	33.14	28.07	9.59	8.46
Monoarene	11.69	4.09	7.35	5.76	27.94	8.85	4.69	6.42	14.20
Biarene	9.73	7.80	9.51	7.78	1.99	1.53	8.49	10.76	12.98
Three aromatic	2.24	4.17	6.67	2.87	-	-	0.47	3.34	1.33
Total arenas	23.65	16.07	23.54	16.41	29.93	10.37	13.64	20.52	28.51
Resin	10.23	9.83	2.42	7.15	2.43	10.90	2.75	1.14	0.51
Total	100	100	100	100	100	100	100	100	100

Table 3. Pour point values of diesel fraction samples depending on the concentration of the depressant

Additive con-centration, % vol.	DF No. 1 PP, [°C]	DF No. 2 PP, [°C]	DF No. 3 PP, [°C]	DF No. 4 PP, [°C]	DF No. 5 PP, [°C]	DF No. 6 PP, [°C]	DF No. 7 PP, [°C]	AGO No. 1 PP, [°C]	AGO No. 2 PP, [°C]
0.0	-16.5	-13.2	-17.8	-24.3	-34.3	-28.6	-13.1	7.2	11.1
0.1	-26.1	-28.2	-30.7	-30.9	-46.5	-46.2	-155	6.4	6.2
0.2	-29.2	-38.6	-38.7	-39.3	-47.0	-53.0	-54.5	3.7	-12.1
0.3	-30.3	-42.7	-40.4	-42.5	-50.5	-53.2	**	-28.0	-32.9
0.4	-31.3	-41.7	-43.3	-45.5	-51.3	-53.5	**	-33.9	-35.2
0.5	-33.0	-42.6	-44.2	-46.3	-53.3	-55.0	**	-33.6	-35.8
0.6	-36.2	-44.2	-45.9	-47.3	-53.5	**	**	**	-33.7
0.7	-36.5	-44.5	-48.5	-50.7	**	**	**	**	-33.2
0.8	-36.7	*	-49.0	-51.3	**	**	**	**	**
0.9	-38.5	*	-50.3	-51.7	**	**	**	**	**
1.0	-36.9	-46.3	-50.5	-52.2	**	**	**	**	**

*Not detected (ND); **Above limit of detection (LoD)*

From the results in Tables 2 and 3, sample DF No. 5 presented the lowest value of PP (-34.3°C), characterized by the lowest content of n-paraffins (24.38 wt. %). Samples AGO No. 1 and No. 2, presented the highest values of PP (7.2 and 11 °C, respectively) and the highest value of the content of n-paraffins (39.34 and 44.62 wt. %, respectively). From the observed results, a relationship indicating that the higher the content of n-paraffins in DF, the greater the value of PP, can be drawn. Table 3 also indicates the greatest change in PP with the addition of a small amount of depressant (up to 0.2 % vol) in sample No. 7 (varying from -13.1 to -54.5°C); and the smallest - for sample No. 5 (changing from -34. 3 to -47.0°C).

Analyzing the group composition of DF samples, given character of PP the change is influenced by the content of aromatic hydrocarbons. Sample No. 7 presented the aromatic content being equal to 29.93% in mass, while in sample No. 5 the value was 10.37% in mass. Thus,

it can be concluded that the depressant injectivity in the region of low concentrations increases with the increase of aromatic content (higher than 20 wt.%). Although, the injectivity of the additive in the region of low concentrations was influenced by the content of n-paraffins starting at 40% in mass.

Therefore, in samples AGO No. 1 and No. 2, with a content of n-paraffins equal to 44.64 and 39.34 wt. %, respectively; changing the concentration of the depressant from 0 to 0.1 % vol. promoted a decrease in PP from 7.2 to 6.4°C and from 11.1 to 6.2°C, respectively; considering that the aromatic content in these samples exceeded 20 wt.% content. Inferring that in the region of low concentrations of the additive, the high content of n-paraffins levels the injectivity of the additive in aromatic hydrocarbons.

For sample No. 5, with a content of n-paraffins of 24.38% in mass and aromatics 10.37 wt.%, when increasing the concentration of the depressant to 0.5% vol., a decrease in the pour point by 19ºC (from -34.3 to -53.3ºC), is observed. When analyzing other samples, No. 2 and No. 4, for example, similar in group composition (content of n-paraffins being 34.73 and 30.31 wt. %, and aromatics equals to 16.07 and 16.41 wt.%, respectively), an increase in the concentration of the depressant to 0.5 % vol. generates a change in the pour point by 29.4 and 22 °C, respectively from -13.2 to -42.6°C for sample No. 2 and from -24.3 to -46.3°C for sample No. 4. Therefore, an increase in the content of n-paraffins in the mixture promotes a reduction in the injectivity of the depressor in relation to diesel fuel.

3.3. Development of a mathematical model for calculating the change in pour point, dependable on the concentration of the additive, considering the hydrocarbon composition of diesel fractions and atmospheric gas oil

On the basis of a certain hydrocarbon composition, revealed patterns and quantum-chemical calculations, a mathematical model was developed aiming to determine the change in the pour point, depending on the concentration of the depressant additive. Since diesel fuel is a complex dispersed multicomponent system and, considering that the low temperature properties of diesel fuel are most influenced by the mass content of paraffins of normal structure, the following mathematical dependence on the effect of the depressant concentration in low temperature properties of diesel fuel were proposed:

$$\ln \varphi_{add} = \left[\sum \frac{\Delta H_{melt,i}}{R} \cdot \left(\frac{1}{T_{melt,0,i}} - \frac{1}{T_{pp}} \right) \cdot w_{n-par} + \frac{\Delta H_{melt,DF}}{R} \cdot \left(\frac{1}{T_{init.PP,DF}} - \frac{1}{T_{PP}} \right) \cdot \left(1 - w_{n-par} \right) \right]$$
$$\cdot f\left(C_{add}, w_{n-par}, w_{arom}, E_{int}, G_{int} \right)$$

where: φ_{add} – volume fraction of added depressant; $\Delta H_{melt,i}$ – enthalpy of crystallization (kJ/mol) for an individual n-paraffin molecule; $T_{melt,0,i}$ – melting point (K) for an individual n-paraffin molecule; $\Delta H_{melt,DF}$ – enthalpy of crystallization (kJ/mol) for diesel fuel; $T_{init.PP,DF}$ – melting point (K) for diesel fuel; T_{PP} – pour point temperature, (K) for diesel fuel; R – the molar gas constant, J/mol·K; w_{n-par} – mass content of n-paraffins in diesel fuel; w_{arom} – mass content of aromatics in diesel fuel; C_{add} – additive concentration, % vol.; E_{int} – interaction energy for complexes obtained using quantum-chemical calculation methods; G_{int} – Gibbs free energy for complexes obtained using quantum-chemical calculation methods.

The enthalpies of crystallization and melting points of n-paraffins from C_{10} to C_{22} were determined from Tatevskij [20]. The enthalpy of crystallization of DF in the calculations was considered equal to 180 kJ/mol based on the comparison of PP of pure DF with the enthalpy of crystallization of pure individual n-paraffin at a given temperature.

During the course of the work, it was found that individual molecules of n-paraffins in diesel fuel are distributed according to the Gaussian distribution law. The individual n-paraffins hydrocarbon compositions (in wt.%.) were determined for diesel fuel samples, and discoveries revealed that the maximum value of the concentration of n-paraffinic hydrocarbon from the distribution diagram of n-paraffins was within $(0,1 \cdots 0,15) \cdot w_{n-par}$, as shown in Figure 1. Furthermore, to determine the mass composition of n-paraffins, an assumption that the molecules of individual hydrocarbons in the group obey the law of the normal Gaussian distribution was made, considering the central term (peak value) equals to $0,11 \cdot w_{n-par}$.
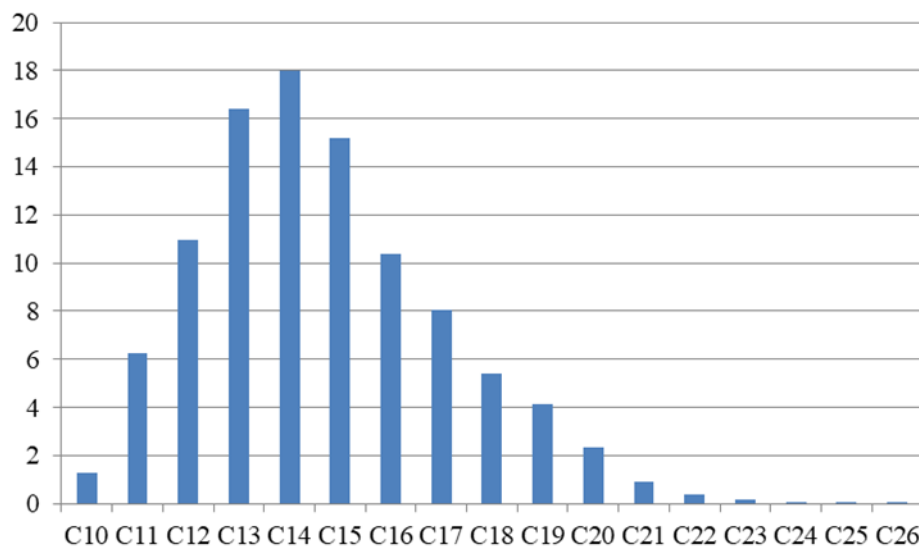
From the information of the molar masses of individual hydrocarbons from C_{10} to C_{27}, the total mass content of n-paraffins, and establishing the value of the constant difference within the Gaussian normal distribution, the molar fractions of each HC were determined by the method of successive iterations. Therefore, for hydrocarbons from C_{10} to C_{27}, the C_{18} hydrocarbon content from the peak value will be equal to:

$$w_{C18} = 0{,}11 \cdot w_{n-par}$$

However, according to the data obtained from the of n-paraffins' distribution in heavy DFs, the peak value in hydrocarbon C_{22} is:

$$w_{C22} = 0{,}11 \cdot w_{n-par}$$

Therefore, for sample DF No. 1, the mass content of n-paraffins was discovered to be equal to 32.51% (considering the distribution of mass percent of resins for each group) (assuming Gaussian normal distribution in the mixture). After, the difference in the constant value between each member of the series: $\varepsilon = 0.7$, was defined.

The mass content of the remaining hydrocarbons was determined using the formula:

$$w_{C18\pm i} = w_{C18} - \varepsilon \cdot i$$

where "i" - is the number of a member of the series.

It is established that the formation and decomposition of the complexes occurs due to the formation and rupture of van der Waals bonds. Therefore, based on the data from the injectivity of the additive and its effect in the pour point – dependable on the group composition and physicochemical characteristics –, the following calculations were accomplished:

1) The reactions of the intermolecular interaction between the *nucleus* of the crystal of n-paraffin with an additive and aromatic hydrocarbon are:

$$n - par \div n - par + additive = Complex\ 1$$
$$n - par \div aromatics + additive = Complex\ 2$$
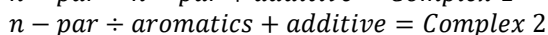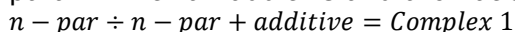
From a thermodynamic standpoint, based on Gibbs Free Energy, the rates of interactions were considered as reversible reactions, and described as:

$$w_{forw} = k_1 \cdot C_{HC}^x \cdot C_{add}^y \qquad w_{rev} = k_{-1} \cdot C_{compl.}^z$$

where: x, y and z – coefficients determined from intermolecular interactions; w_{forw} – the forward rate reaction; w_{rev} – the backward rate reaction; C_{HC} - mass content of n-paraffins and aromatics, % wt.; C_{add} - concentration of the additive, % vol; $C_{compl.}$ – mass content of complex, %wt.; k_1 – forward reaction rate constant; k_{-1} – backward reaction rate constant.

The ratio of the rates of forward and reverse reactions, are described as:

$$\frac{w_{forw.}}{w_{rev.}} = \frac{k_1}{k_{-1}} \cdot \frac{C_{n-par}^x \cdot C_{add}^y}{C_{compl.}^z} = K_{equil.} \cdot \frac{C_{n-par}^x \cdot C_{add}^y}{C_{compl.}^z}$$

The equilibrium constant of intermolecular interaction $K_{equil.}$ was considered on the basis of the chemical reaction isotherm:

$K_{equil.} = \frac{\Delta G}{R \cdot T_{PP}}$; where: ΔG – Change in Gibbs free energy, kJ/mol.

For the reaction of n-paraffins with an additive, the Gibbs free energy and the equilibrium constant were:

$\Delta G_1 = \Delta G_{int.n-par} + \Delta G_{int.n-par\ldots add} = 46.02 + 46.47 = 92.49\ kJ/mol$

$K_{equil._1} = \dfrac{\Delta G_{int.n-par} + \Delta G_{int.n-par\ldots add}}{R \cdot T_{PP}}$

where: $\Delta G_{int.n-par}$ − Variation of Gibbs free energy of interaction of normal paraffins, kJ/mol;

$\Delta G_{int.n-par\ldots add}$ − Variation of Gibbs free energy of interaction of normal paraffins and additive, kJ/mol.

For the reaction of n-paraffins with aromatic hydrocarbons, the Gibbs free energy and the equilibrium constant are equal to:

$\Delta G_2 = \Delta G_{int.n-par\ldots ar} + \Delta G_{int.ar\ldots add} = -48.81 + 48.29 = -0.52\ kJ/mol$

$K_{equil._2} = \dfrac{\Delta G_{int.n-par\ldots ar} + \Delta G_{int.ar\ldots add}}{R \cdot T_{PP}}$

where: $\Delta G_{int.n-par\ldots ar}$ − Variation of Gibbs free energy of interaction of normal paraffins and aromatic hydrocarbons, kJ/mol; $\Delta G_{int.ar\ldots add}$ − Variation of Gibbs free energy of interaction of aromatic hydrocarbons and additive, kJ/mol.

The power dependences were accomplished from the determination of the values of the energy of intermolecular interaction (in kJ) since this indicator directly affects the energy of the system. Further, the energy parameters were divided in 4 groups:

Group 1 - intermolecular interaction "n-paraffin...n-paraffin" and "n-paraffin...additive". In this group, the antagonism of two intermolecular interactions was manifested, since the action of the additive aims at "suppressing" the precipitation of n-paraffins.

$E_1 = E_{P-P \div P-Add} = E_{P-P} - E_{P-Add} = 7.70 - 4.43 = 3.27\ kJ$

where: E_{P-P} − energy of interaction between normal paraffins, kJ; E_{P-Add} − energy of interaction between normal paraffins and additive, kJ.

Group 2 - intermolecular interaction "n-paraffin...n-paraffin" and "n-paraffin...aromatics". In this group, the synergism of n-paraffins and aromatics was observed, since a high aromatic content contributes to the partial dissolution of n-paraffins and a decrease in the pour point:

$E_2 = E_{P-P \div P-A} = E_{P-A} + E_{P-P} = -6.31 + 7.70 = 1.39\ kJ$

where: E_{P-A} − energy of interaction between normal paraffins and aromatic hydrocarbons, kJ.

Group 3 - intermolecular interaction "n-paraffin...aromatics" and "aromatics...additive". In this group, the synergism of aromatics and depressants was manifested, since the effectiveness of the additive increases due to the interaction with a small portion of n-paraffins – part of n-paraffins is dissolved by aromatics:

$E_3 = E_{P-A \div A-Add} = E_{P-A} + E_{A-Add} = -6.31 + 4.03 = -2.27\ kJ$

where: E_{A-Add} − energy of interaction between aromatic hydrocarbons and additive, kJ.

Group 4 - intermolecular interaction "n-paraffin...additive" and "aromatics...additive". In this group, the antagonism of intermolecular interactions was estimated, since the distribution of the interaction of the depressant with aromatics and n-paraffins qualifies its effectiveness:

$E_4 = E_{P-Add \div A-Add} = E_{P-Add} - E_{A-Add} = 4.43 - 4.03 = 0.40\ kJ$

Further, the following equations were proposed to determine the power dependences:

1) Reaction No.1:

- $C_{HC}^x = w_{n-par}^{(E_1+E_2)\cdot(C_{add}+w_{n-par})}$;

- $C_{add}^y = C_{add}^{(E_1-E_4)\cdot C_{add}}$

- $C_{compl.}^z = \left[\left(C_{add.} + w_{n-par}\right)^{\sum E \cdot (C_{add.}+w_{n-par})}\right]^{-1}$

Where $\sum E = E_1 + E_2 + E_3 + E_4$

2) Reaction No.2:

- $C_{HC}^x = w_{ar}^{(E_2+E_3)\cdot(C_{add}+w_{ar})}$

- $C_{add}^y = C_{add}^{(E_3-E_4)\cdot C_{add}}$
- $C_{compl.}^z = (C_{add} + w_{ar})^{\Sigma E \cdot (C_{add}+w_{n-par})}$

Thus, the complete expression for the equations of intermolecular reactions was established:

$$\frac{\Delta G_{int.n-par} + \Delta G_{int.n-par\dots add}}{R \cdot T_{PP}} \cdot w_{n-par}^{(E_1+E_2)\cdot(C_{add}+w_{n-par})} \cdot C_{add}^{(E_1-E_4)\cdot C_{add}} \cdot \left(C_{add} + w_{n-par}\right)^{\Sigma E \cdot (C_{add}+w_{n-par})}$$
$$+ \frac{\Delta G_{int.n-par\dots ar} + \Delta G_{int.ar\dots add}}{R \cdot T_{PP}} \cdot w_{ar}^{(E_2+E_3)\cdot(C_{add}+w_{ar})} \cdot C_{add}^{(E_3-E_4)\cdot C_{add}}$$
$$\cdot (C_{add} + w_{ar})^{\Sigma E \cdot (C_{add}+w_{n-par})}$$

In addition to n-paraffins, the low-temperature properties are also influenced by the aromatic content, the content of resinous substances and the fractional composition [21]. Thus, lightening diesel fractional composition from 20 – 40°C leads to a decrease in PP by 10-15°C. Therefore, indicating that the "wider" the fractional composition, unchanging the remaining variables (the content of n-paraffins and aromatics), the lower the PP of diesel fuel. As previously described, aromatic hydrocarbons have an ability to dissolve paraffins of normal structure, thereby reducing PP. The solubility equation can be represented as:

$$\frac{d[\ln (K_L)]}{dT} = \frac{\Delta H}{RT} + C$$

where: K_L is the solubility constant; ΔH - the enthalpy of dissolution, kJ/mol; C – Integration constant.

Therefore, the mathematical evaluation employed the right side of the above equation, since aromatics completely dissolve normal paraffins and mixes with them without stratification. The considered enthalpy of dissolution was the energy of intermolecular interaction "n-paraffin-aromatics".

The integration constant "C" reflects the effect of fractional and group composition in the dissolution of n-paraffins, depending on the concentration of the additive, expressing the dependance of the pour point.

$$C = \left[ex \, p\left(\frac{T_{90} - T_{10}}{T_{PP}}\right) + \ln(\ln T_{PP})\right] \cdot K$$

where: T_{90} – 90 % diesel fraction boiling point temperature, K; T_{10} – 10 % diesel fraction boiling point temperature, K.

Expression T_{90}-T_{10} shows the influence of the "latitude" of the fractional composition in the PP of diesel fuel. The expression $\ln(\ln T_{PP})$ reflects the nonlinear nature of the change in the pour point. Coefficient "K" reflects the influence of the interaction of the group composition and the depressant, related to the nature of dissolution and PP, being dependable on the following cases:
- The type of diesel fuel according to PP: temperature higher than 0°C (conditionally summer); temperature from - 25 to 0°C (conditionally all-season); temperature lower than - 25°C (conditionally winter);
- The aromatic content - more than 20 wt. %;
- The resin content - above 5 wt. %.

Furthermore, based on the data from Table 3 and the injectivity of the depressor to DF of different group compositions, the value of the coefficient "K" is not constant: fluctuating within the following concentration ranges:
- Area No. 1 of the highest injectivity (for diesel fractions with a temperature $T_{90} > 400 \, \text{℃}$) – K_1 concentration range from 0 to 0.1% vol., inclusive;
- Area No. 2 of high injectivity (for diesel fractions with $T_{90} \le 400$ °C) and low injectivity (for diesel fractions with $T_{90} > 400$ °C) – K_2 concentration range from 0.1 to 0.2% vol., inclusive;
- Area No.3 - linear injectivity - K_3 concentration range from 0.2 to 1% vol., inclusive.

Nevertheless, for winter fuel, the following dependencies correlations were derived for the coefficient "K":
- Aromatic content below 20 wt. % and resin content lower than 5 wt. %,

$$K_1 = w_{ar} - (w_{n-par} + w_{ar}) \cdot \varphi_{res}; \quad K_2 = K_1 + (w_{n-par} + w_{ar}) \cdot \varphi_{res} + C_{add}; \quad K_3 = K_2 + C_{add}$$

where: φ_{res} - resin content.

• Resin content over 5 wt. %.

$$K_1 = w_{ar} + (w_{n-par} + w_{ar}) \cdot \varphi_{res} - w_{ar} \cdot \varphi_{res}; \quad K_2 = K_1 + C_{add} \cdot w_{n-par}; \quad K_3 = K_2 + C_{add}$$

For all-season diesel fuel, the following functional dependences of the "K" coefficient were obtained:

• Content of aromatics higher than 20 wt. %:

$$K_1 = w_{ar} + w_{ar} * (w_{n-par} + w_{ar}); \quad K_2 = K_1 - C_{add} \cdot w_{res}; \quad K_3 = K_2 + C_{add} \cdot w_{res}$$

• Resin content higher than 5 wt. %:

$$K_1 = (w_{n-par} + w_{ar}) + (w_{n-par} + w_{ar}) \cdot w_{res}; \quad K_2 = K_1 - C_{add} \cdot w_{res}; \quad K_3 = K_2 + C_{add}$$

Aromatic content above 20 wt. % and resin content > 5 wt. %. The area of high injectivity corresponds to the concentration ranging from 0.1 to 0.3 % vol., inclusive:

$$K_1 = (w_{n-par} + w_{ar}); \quad K_2 = K_1 - C_{add} \cdot w_{res}; \quad K_3 = K_2 - C_{add}$$

For summer diesel fuel, the functional dependences of the "K" coefficient were obtained for aromatic content over 20 wt. %:

$$K_1 = w_{n-par} \cdot w_{ar} + (w_{n-par} + w_{ar}) \cdot (w_{n-par} - w_{ar})$$

$$K_2 = K_1 - w_{n-par}^2 \cdot (w_{n-par} - w_{ar}) - C_{add}$$

$$K_3 = K_2 + \left(\frac{w_{n-par} \cdot w_{ar}}{w_{n-par} + w_{ar}}\right)^2 + C_{add}$$

Thus, the final form of the model for predicting the low-temperature properties of diesel fuels is:

$$ln\varphi_{add} = \left[\sum \frac{\Delta H_{melt,i}}{R} \cdot \left(\frac{1}{T_{melt,0,i}} - \frac{1}{T_{PP}}\right) \cdot w_{n-par} + \frac{\Delta H_{melt,DF}}{R} \cdot \left(\frac{1}{T_{init\,PP,DF}} - \frac{1}{T_{PP}}\right) \cdot (1 - w_{n-par})\right]$$
$$\cdot \left[\frac{\Delta G_{int.n-par} + \Delta G_{int.n-par...add}}{R \cdot T_{PP}} \cdot w_{n-par}^{(E_1+E_2)\cdot(C_{add}+w_{n-par})} \cdot C_{add}^{(E_1-E_4)\cdot C_{add}}\right.$$
$$\cdot (C_{add} + w_{n-par})^{\sum E \cdot (C_{add}+w_{n-par})} + \frac{\Delta G_{int.n-par...ar} + \Delta G_{int.ar...add}}{R \cdot T_{PP}} \cdot w_{ar}^{(E_2+E_3)\cdot(C_{add}+w_{ar})}$$
$$\left. \cdot C_{add}^{(E_3-E_4)\cdot C_{add}} \cdot (C_{add} + w_{ar})^{\sum E \cdot (C_{add}+w_{n-par})}\right] \cdot \left[\frac{E_{P-A}}{R \cdot T_{PP}} + \left[exp\left(\frac{T_{90} - T_{10}}{T_{PP}}\right) + ln(ln\,T_{PP})\right] \cdot K\right]$$

Based on the resulting model, the values of PP, presented in Table 3, were calculated for the available DF in the range of additive concentration from 0.1 to 1.0 % vol., with a 0.1 step.

Table 4. Calculated and experimental values of the pour point of diesel fractions

Additive concentration, % vol.	DF No. 1			DF No. 2			DF No. 3			DF No. 4		
	PP, [°C]	PP, [°C] (calc.)	Δ, [°C]	PP, [°C]	PP, [°C] (calc.)	Δ, [°C]	PP, [°C]	PP, [°C] (calc.)	Δ, [°C]	PP, [°C]	PP, [°C] (calc.)	Δ, [°C]
0.0	-16.5	-	-	-13.2	-	-	-17.8	-	-	-24.3	-	-
0.1	-26.1	-26.6	0.5	-28.2	-25.2	3.0	-30.7	-28.1	2.6	-30.9	-32.9	2.0
0.2	-29.2	-28.9	0.3	-38.6	-34.6	4.0	-38.7	-37.4	1.3	-39.3	-38.2	1.1
0.3	-30.3	-32.0	1.7	-42.7	-39.6	3.1	-40.4	-42.8	2.4	-42.5	-44.2	1.7
0.4	-31.3	-32.1	0.8	-41.7	-41.4	0.3	-43.3	-44.5	1.2	-45.5	-45.9	0.4
0.5	-33.0	-36.3	3.3	-42.6	-42.7	0.1	-44.2	-45.9	1.7	-46.3	-47.0	0.7
0.6	-36.2	-37.0	0.8	-44.2	-43.6	0.6	-45.9	-47.0	1.1	-47.3	-47.9	0.6
0.7	-36.5	-37.2	0.7	-44.5	-44.3	0.2	-48.5	-48.0	0.5	-50.7	-48.5	2.2
0.8	-36.7	-37.1	0.4	*	-	-	-49.0	-48.9	0.1	-51.3	-49.1	2.2
0.9	-38.5	-36.9	1.6	*	-	-	-50.3	-49.8	0.5	-51.7	-49.6	2.1
1.0	-36.9	-36.5	0.4	-46.3	-46.0	0.3	-50.5	-50.6	0.1	-52.2	-50.0	2.2

Additive concentration, % vol.	DF No. 5			DF No. 5			AGO No. 1			AGO No. 2		
	PP, [°C]	PP, [°C] (calc.)	Δ, [°C]	PP, [°C]	PP, [°C] (calc.)	Δ, [°C]	PP, [°C]	PP, [°C] (calc.)	Δ, [°C]	PP, [°C]	PP, [°C] (calc.)	Δ, [°C]
0.0	-34.3	-	-	-28.6	-	-	7.2	-	-	11.1	-	-
0.1	-46.5	-43.1	3.4	-46.2	-44.7	1.5	6.4	8.2	1.8	6.2	2.5	3.7
0.2	-47.0	-45.8	1.2	-53.0	-54.6	1.6	3.7	4.2	0.5	-12.1	-12.4	0. 3
0.3	-50.5	-48.7	1.8	-53.2	-56.4	3.2	-28.0	-31.2	3.2	-32.9	-32.2	0.7
0.4	-51.3	-49.8	1.5	-53.5	-57.2	3.7	-33.9	-32.0	1.9	-35.2	-33.0	2.2
0.5	-53.3	-50.6	2.7	-55.0	-57.8	2.8	-33.6	-32.7	0.9	-35.8	-33.7	2.1
0.6	-53.5	-51.4	2.1	**	-	-	**	-	-	-33.7	-34.3	0.6
0.7	**	-	-	**	-	-	**	-	-	-33.2	-34.8	1.6
0.8	**	-	-	**	-	-	**	-	-	**	-	-
0.9	**	-	-	**	-	-	**	-	-	**	-	-
1.0	**	-	-	**	-	-	**	-	-	**	-	-

*Not detected (ND); **Above limit of detection (LoD)*

From Table 4, the maximum error did not exceed 4 ºC, being within the acceptance range of a diesel fuel pour point preliminary assessment, for industrial and laboratory conditions, in the absence of an analyzer. Therefore, proving the applicability of the model. Furthermore, the developed model will serve as basis for a complex model which will consider the mutual influence of cetane-increasing, depressant and antiwear additives in the properties of the fuel, improving its accuracy.

4. Conclusions

The interaction of complexes "aromatics...n-paraffins" energy is lower than the energy of intermolecular interaction of "n-paraffins...n-paraffins" (7.70 kJ and -6.13 kJ, respectively). Therefore, the presence of a higher aromatic content in the mixture reduces the pour point of diesel fuel;

An increase in the content of n-paraffins in diesel fuel promotes a decrease in the injectivity of the depressor in relation to diesel fuel;

The injectivity of the depressant, in the region of low concentrations, is directly dependable from the aromatic hydrocarbons content, when the concentration surpasses 20 wt.%;

The injectivity of the additive is dependable on the content of n-paraffins and aromatic hydrocarbons. In the low concentration regions of the depressant additive, a content of n-paraffins higher than 40 wt.%, negatively influence in the injectivity of the additive, even with aromatic hydrocarbon content above 20 wt. %.

For diesel fractions with an initial pour point lower than -33ºC, minimum concentrations ranging from 0.2 to 0.35 wt.% of a depressant, are essential to achieve the required pour point. A mathematical model for the calculation of the pour point variation, dependable on the group composition of the diesel fuel and the concentration of the depressant additive, with an error not exceeding 4ºC, has been developed.

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