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Interactions of Depressant Additives and Straight-run Diesel Fuels Hydrocarbons

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Abstract

The article discusses the influence of the hydrocarbon composition of various straight-run diesel fuels samples on the efficiency of the depressant additives. In the course of the work, the characteristics and composition of straight-run diesel fuels of various origins were determined; blends of straight-run diesel fuels samples with depressant additives were prepared, their low-temperature properties were determined. It was found that the effectiveness of the depressant additives concerning the pour point of diesel fuel increases with an increase in the content of paraffins in the fuel composition, a decrease in the content of aromatic hydrocarbons and an increase in the average number of aromatic rings in the molecule. The effectiveness of the depressant additives concerning the cold filter plugging point of diesel fuel increases with a decrease in the content of paraffins in the fuel, and an increase in the initial boiling point. The regularities of the influence of the straight-run diesel fuels composition on the effectiveness of the depressant additives, found in the work, will make it possible to choose the most effective additives and select their optimal concentrations.

Keywords*: Diesel fuel, Depressant additive, Hydrocarbon composition, Pour point, Cold filter plugging point.*

1. Introduction

From year to year, there is a steady increase in global demand for diesel fuel (DF). The use of DF in engines of various vehicles, technological equipment and electric generators, in the process of developing the northern and arctic territories, has led to an increase in demand for low-freezing brands of DF. For the Russian Federation, this issue is especially relevant, since a significant part of the country's territories is located in cold climatic zones. Nowadays, there is a shortage of low-freezing brands of DF, the volume of produced DF at Russian refineries is distributed by brands as follows: 82.0 % – summer and off-season brands, less than 15.8 % – winter brands and only 2.2 % – arctic brands [1]. Involving biocomponents can increase the production volume of DF, however, these components usually have poor low-temperature properties [2-6]. That is why the production of high-quality low-freezing DF is one of the most important directions in the development of the modern oil refining industry. Modern standards [7-9] impose strict requirements on low-temperature properties for winter and arctic DF brands. It is possible to achieve the required characteristics by such methods as: lightening the fractional composition of the fuel, the use of low-temperature additives, as well as through the processes of catalytic processing [10-12]. However, the lightening of the fractional composition due to a decrease in the content of high-boiling n-paraffins in the DF composition leads to incomplete use of the oil potential for the diesel fraction, and an increase in the proportion of light fractions will reduce the volume of kerosene production. The implementation of the existing processes of catalytic processing to obtain low-freezing DF is economically feasible only at large refineries since it requires the use of hydrogen-burning gas and high capital costs [13]. There are developments in the field of low-tonnage autonomous processes for the production of low-freezing DF without the use of hydrogen-burning gas on zeolite catalysts [14], but these technologies have not yet been implemented on a production scale.

Thus, the most feasible and economically profitable way to obtain low-freezing DF is still the use of depressants that improve low-temperature properties [15-19]. However, the choice of additives and their concentrations is complicated by the interaction of the components of depressant additives and hydrocarbons of the diesel fraction, which significantly affects the effectiveness of the additives [20], and the DF composition significantly depending on the production technology and the feedstock. So, it was found that the lightening of the fractional composition of DF entails a decrease in the effectiveness of the depressant additives, and vice versa, the heavier fractional composition increases the efficiency of the depressants [21]. However, in fractions with the same boiling points, the content of hydrocarbon groups can differ significantly, which makes the task of identifying the regularities of the DF hydrocarbon composition influence the effectiveness of the depressant additives extremely urgent.

The work aim is to study the interaction of depressants and hydrocarbons that make up straight-run DF.

2. Materials and methods

As a research object, samples of straight-run DF obtained from various fields in Western Siberia, as well as commercial depressants for DF was used. Samples of DF were assigned numerical codes from 1 to 9, and additives – letter codes *A*, *B* and *C*. For the study, blends of DF samples with depressant additives were prepared. The additives were used in the concentrations recommended by the manufacturers.

Determination of the composition and characteristics of DF samples and their blends with depressants in the work was carried out using the following methods: the cloud point (CP) [22]; the cold filter plugging point (CFPP) [23]; the pour point (PP) [24]; the fractional composition [25]; the group hydrocarbon composition [26]; the structural-group composition [27].

3. Results and discussion

3.1. Results of determining the characteristics of straight-run DF samples

Table 1 shows the results of determining the fractional composition, CP, CFPP and PP of the studying samples of straight-run DF.

Table 1. Results of determining the fractional composition and low-temperature properties of straight-run DF samples

Sample of DF	Temperature,°C				CP	CFPP	PP
	IBP	Volume, mL					
		10	50	90	°C		
1	160	189	248	338	-15	-21	-35
2	149	190	262	332	-12	-22	-32
3	138	161	247	330	-12	-24	-45
4	142	164	265	333	5	1	-5
5	145	159	251	312	-13	-17	-29
6	122	166	270	362	0	-2	-19
7	161	248	321	357	3	3	-17
8	145	159	264	346	-1	-7	-15
9	74	152	258	326	-1	-5	-15

From the results of determining the fractional composition, it can be concluded that the 50 % vol. boiling point of sample No. 7 does not meet the requirements [9] (requirements: no higher than 280°C), samples No. 1, 3 and 5 meet the requirements for the arctic brand of DF (requirements: no higher than 255°C), and samples No. 2, 4, 6, 8, 9 meet the requirements for summer, off-season and winter brands of DF.

The results of determining the low-temperature properties of samples of straight-run DF showed that samples No. 4, 6, 7 do not meet the requirements [9] even for the summer brand

DF (requirements: CFPP not higher than -5 °C), samples No. 8 and 9 meet the requirements to summer brand of DF, and samples No. 1, 2, 3 and 5 meet the requirements to off-season brand of DF (requirements: CFPP not higher than -15°C). The use of the investigated samples of straight-run DF fuel in winter or arctic conditions is possible only in the case of using depressants.

3.2. Results of determining the composition of straight-run DF samples

Figure 1 and Table 2 shows the results of determining the group and structural-group composition of the studied samples of straight-run DF.

Table 2. Results of n-d-M analysis and the average number of rings in the molecule of DF samples

Sample of DF	Carbon distribution, % wt.				Average number of rings in the molecule		
	C_{ar}	C_n	C_{ring}	C_{al}	R_{ar}	R_n	R_t
1	8.063	25.860	33.924	66.076	0.225	0.736	0.961
2	13.229	41.242	54.471	45.529	0.285	0.931	1.216
3	14.385	35.259	49.644	50.356	0.330	0.839	1.169
4	14.555	33.307	47.862	52.138	0.324	0.771	1.095
5	16.021	32.639	48.660	51.340	0.378	0.798	1.176
6	15.371	32.025	47.396	52.604	0.355	0.764	1.119
7	17.003	22.546	39.549	60.451	0.641	0.879	1.520
8	15.894	27.891	43.785	56.215	0.436	0.781	1.217
9	15.454	25.985	41.439	58.561	0.421	0.713	1.134

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.

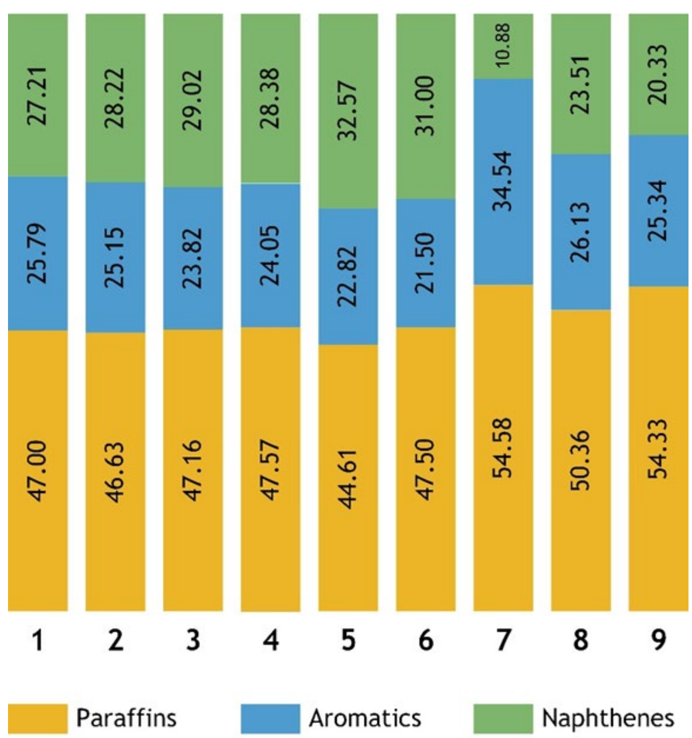

Fig. 1. Content of hydrocarbon groups in DF samples, % wt

As can be seen from the results presented in Figure 1, in the studying DF samples, paraffinic hydrocarbons are the predominant group of hydrocarbons, naphthenic hydrocarbons occupy an intermediate position, and aromatic hydrocarbons occupy the smallest proportion in the DF samples. So, the sample No. 7 is characterized by the highest content of paraffinic and aromatic hydrocarbons and the lowest content of naphthenes; sample No. 5 is characterized by the lowest content of paraffinic hydrocarbons and the highest content of naphthenes; sample No. 6 is characterized by the lowest content of aromatic hydrocarbons. From the results presented in Table II, it can be seen that the largest part of carbon atoms in the DF samples is in the alkyl substituents and the smallest in the aromatic rings. Sample No. 1 is characterized by the highest part of the carbon in the alkyl substituents and the lowest part of the carbon in the aromatic rings; sample No. 2, on the contrary, is characterized by the smallest part of the carbon in alkyl substituents and the largest part of the carbon in naphthenic structures; sample No. 7 is characterized by the highest part of the carbon in aromatic rings and the lowest part of the carbon in naphthenic structures. All studying samples are characterized by a larger average number of naphthenic than aromatic rings. Sample No. 2 leads in the average number of naphthenic rings, and sample No. 7 in the average number of aromatic rings; Sample No. 9 has the smallest average number of naphthenic rings, and sample No. 1 has the smallest average number of aromatic rings.

3.3. Analysis of the depressants effect on the low-temperature properties of straight-run DF samples

Figure 2 shows the results of determining the low-temperature properties of blends of DF samples with depressant additives.

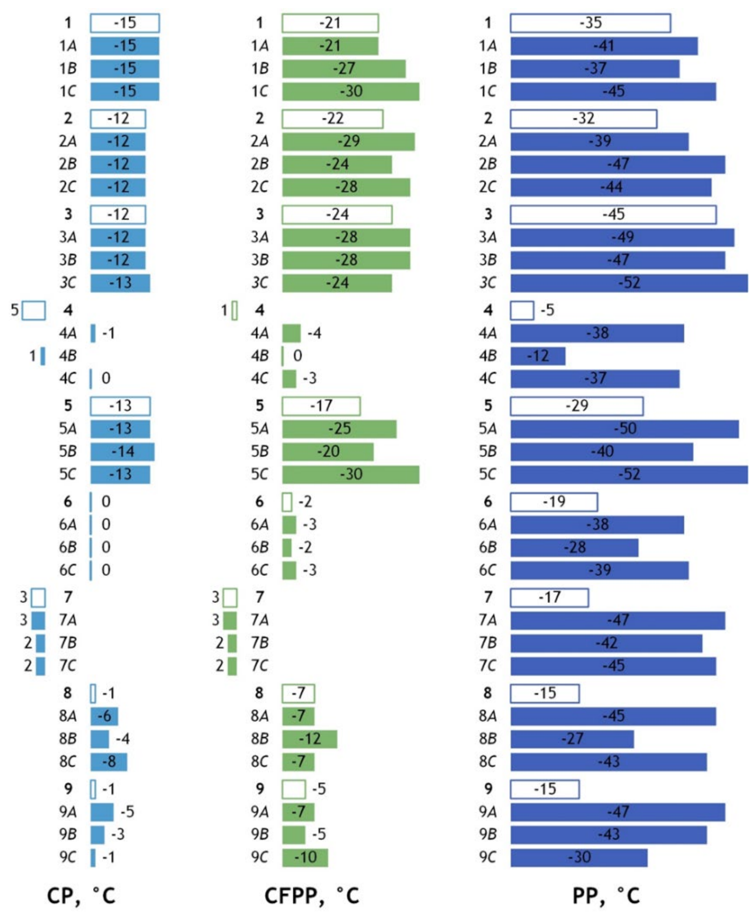

Fig. 2. Results of determining the low-temperature properties of blends from DF samples and depressant additives

Analyzing the compliance of the obtained blends with the requirements of [9] for low-temperature properties, it can be seen that:

- for sample No. 1, the addition of additive *A* makes it possible to obtain DF of an off-season brand; adding additives *B* and *C* – DF of winter brand;
- for samples No. 2 and No. 5, the addition of additive *B* makes it possible to obtain DF of an off-season brand; adding additives *A* and *C* – DF of winter brand;
- for sample No. 3, the addition of additive *C* makes it possible to obtain DF of an off-season brand; adding additives *A* and *B* – DF of winter brand;
- for samples No. 4, 6, 7, the addition of additives *A*, *B*, *C* does not allow obtaining fuel that meets the requirements of [9];
- for sample No. 8, the addition of additives *A*, *B*, *C* makes it possible to obtain summer brand of DF;
- for sample No. 9, the addition of additives *A* and *C* makes it possible to obtain a summer brand of DF; the addition of additive *B* does not allow obtaining fuel that meets the requirements of [9].

Average changes in the low-temperature properties of straight-run DF samples with the addition of depressants are presented in Table 3.

Table 3. Average changes in the low-temperature properties of straight-run DF samples with the addition of depressant additives

Additive	*Δ*CP,°C	*Δ*CFPP,°C	PP,°C
A	2	3	20
B	1	2	12
C	2	4	19

From the experimental data it can be seen that the tendencies of changes in the low-temperature properties of straight-run DF samples in the presence of additives are similar for all additives – an improvement in the CFPP and PP is observed, at the same time depressants have practically no effect on the CP of DF samples. The additives had the most significant effect on the PP of DF samples. Comparative analysis shows that additives *A* and *C* are the most effective concerning the CP of straight-run DF samples, additive *C* concerning CFPP, and additive *A* concerning the PP.

The unequal efficiency of depressants concerning the low-temperature properties of straight-run DF samples is explained by the influence of the composition of the DF on the effectiveness of the depressant additives.

3.4. Analysis of the effect of the straight-run DF samples composition on the effectiveness of the depressant additives

Analyzing the obtained experimental data, it can be concluded that with an increase in the content of paraffins in DF, the effectiveness of the depressant additives concerning the PP increases, and concerning CFPP decreases. To illustrate this conclusion, let arrange DF samples in the order of increasing paraffins content (Figure 3).

The effect is clearly seen on samples No. 5 and 7. Sample No. 7 is characterized by the highest paraffin content (54.58 % wt.) and the highest average effect of depressant additives on the PP (28 °C), while sample No. 5 is characterized by the lowest paraffin content (44.61 % wt.) and the highest average effect of depressant additives on CFPP (8°C). It should also be noted the high efficiency of the additives concerning the PP of samples No. 9 and 8 (average effect 25°C and 23°C, respectively), characterized by a relatively high content of paraffins (54.33 % wt. and 50.36 % wt. respectively), as well as the high efficiency of the additives concerning CFPP samples No. 2 and 1 (average effect of 5°C for both DF samples), characterized by a relatively low content of paraffins (46.63 % wt. and 47.00 % wt. respectively).

The observed effect is explained in the mechanism of depressant additives action – adsorption on the surface of nucleating crystals and hindering their growth. Depressant additives can begin to act only when the first crystals of paraffins appear – in the case of fuels with a high paraffin content, crystals appear already with a slight decrease in temperature and trigger the action of the additive, which allows DF to not lose fluidity even at very low temperatures (high efficiency concerning the PP). However, in the case of a high content of paraffins in the fuel, the number of incipient crystals is large and leads to plugging of the standard filter element despite the use of an additive (low efficiency concerning CFPP).

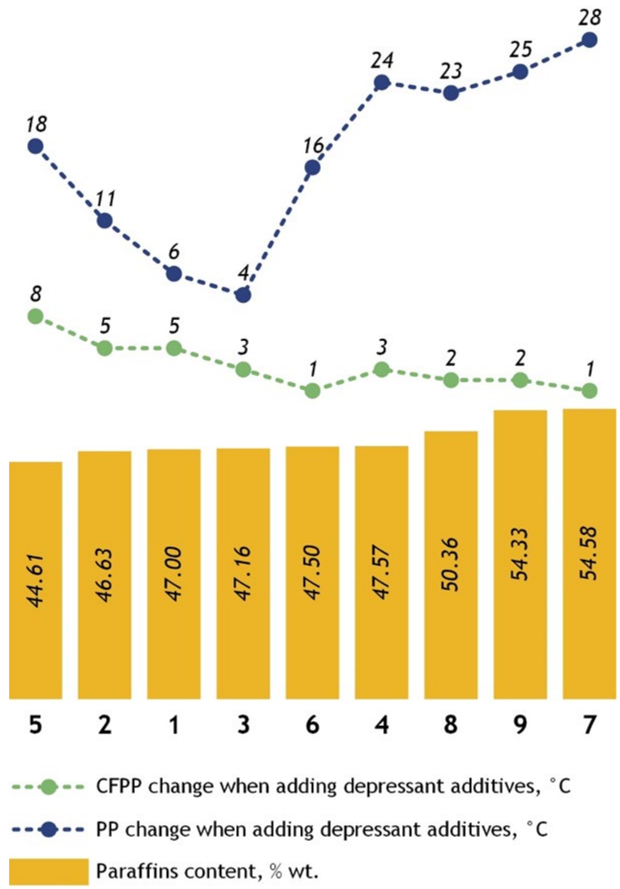

Fig. 3. Dependence of the effectiveness of depressant additives concerning the PP and CFPP on the content of paraffins in the composition of DF samples

The found effect has an important practical consequence – the possibility of increasing the effectiveness of the depressant additives concerning the PP of DF by adding small amounts of paraffinic fractions to the fuel. The search for resource-efficient ways of using paraffinic fractions is an extremely urgent task today in connection with the growth in paraffinic oil production.

Analyzing the obtained experimental data, it should also be noted the negative effect of the high content of light fractions in the composition of DF on the effectiveness of the depressant additives concerning CFPP. To illustrate the revealed effect, let consider DF samples characterized by practically the same paraffin content, but at the same time differing in the initial boiling point (Figure 4).

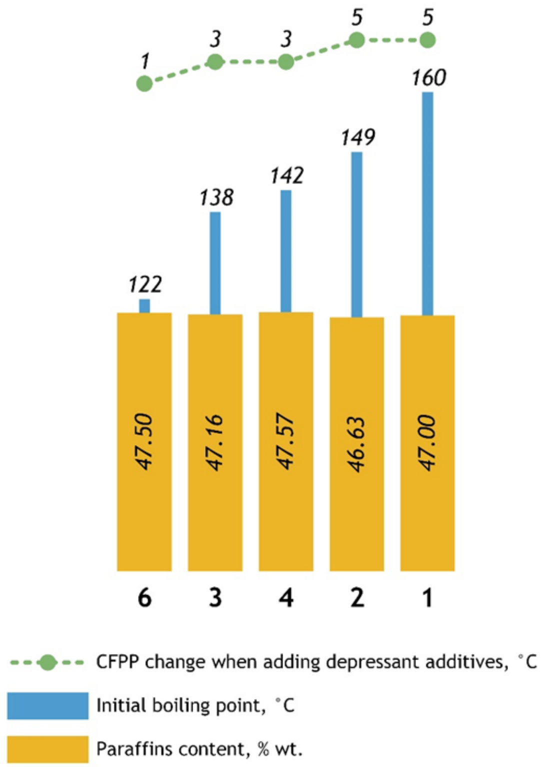

Fig. 4. Dependence of the effectiveness of depressant additives concerning CFPP on the initial boiling point of DF samples

The revealed effect is clearly seen for sample No. 6, which is characterized by a low initial boiling point (122°C). Comparing sample No. 6 with sample No. 4, it can be seen that for the heavier sample No. 4 (the initial boiling point – 142 °C) the average efficiency of the additives concerning CFPP is 2°C higher than for sample No. 6; in comparison with the even heavier sample No. 1 (the initial boiling point – 160°C), the average efficiency of the additives concerning CFPP is 4°C higher than for sample No. 6.

This effect is explained by the fact that the presence of light fractions in the composition of DF leads to a decrease in the total content of heavier hydrocarbons, which, with a decrease in temperature, crystallize in the first place and trigger the action of the additive. A further decrease in temperature leads to the simultaneous formation of a significant number of crystals and plugging of the standard filter element (low efficiency concerning CFPP).

The found effect also has an important practical consequence – the simultaneous involvement of light fractions and depressants to improve the low-temperature properties of DF has a negative effect and is impractical.

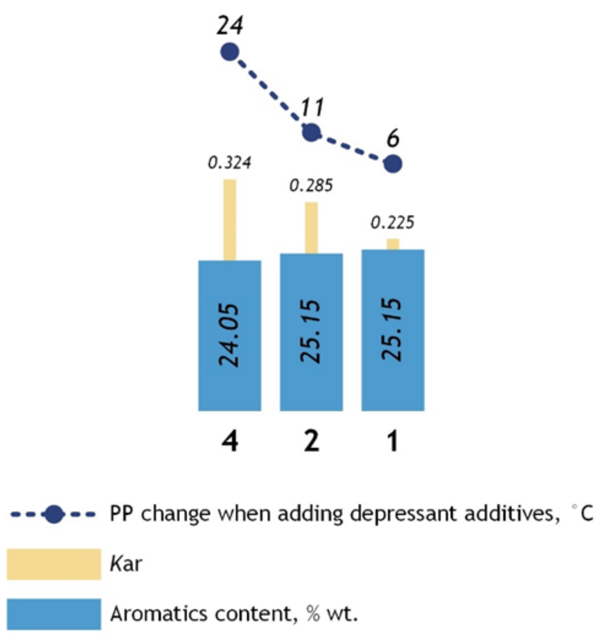

Fig. 5. Dependence of the effectiveness of depressant additives concerning PP on the content, and structure of aromatic hydrocarbons in the composition of DF samples

Analysis of the effectiveness of depressants concerning the PP of samples No. 1, 2, 4 (Figure 5) revealed the following effect: the effectiveness of the PP depressants increases with a decrease in the content of aromatic hydrocarbons in the DF and an increase in the average number of aromatic rings in a molecule.

Thus, in a series of samples No. 4, 2, 1, the content of aromatic hydrocarbons increases, the average number of aromatic rings in the molecule decreases, and the average effect of depressants on the PP decreases.

This effect is explained by the fact that the molecules of aromatic hydrocarbons are polar and attract depressants to themselves, thereby preventing the interaction of additives with incipient paraffin crystals (reducing the effectiveness of the additives), while polycyclic aromatic hydrocarbons are less polar and have a less negative effect.

4. Conclusion

The use of the studied samples of straight-run DF in winter and arctic conditions is possible only in the case of using depressants. It has been established that the addition of depressants for straight-run DF samples No. 1, 2, 3, 5 makes it possible to obtain off-season and winter brands of DF. The addition of depressants for straight-run DF samples No. 8 and 9 makes it possible to obtain a summer brand of DF. The addition of depressants for straight-run DF samples No. 4, 6, 7 does not make it possible to obtain fuel that meets the requirements of the standards.

It was revealed that the investigated depressants have practically no effect on the CP of straight-run DF samples. It was shown that the most effective concerning the CP of straight-run DF samples are additives *A* and *C* (average reduction by 2°C), concerning CFPP – additive *C* (average reduction by 4°C), concerning the PP – additive *A* (average decrease by 20°C).

The effectiveness of the depressant additives concerning the PP of DF increases with an increase in the content of paraffins in the DF composition, a decrease in the content of aromatic hydrocarbons, and an increase in the average number of aromatic rings in the molecule. The effectiveness of the depressant additives concerning CFPP of DF increases with a decrease in the content of paraffins in the DF composition, an increase in the initial boiling point of DF. The revealed regularities are explained by the mechanism of interaction between depressant additives and hydrocarbons that make up straight-run DF.

An important practical effect of the revealed regularities is the possibility of increasing the efficiency of the depressant additives concerning the PP of DF by adding small amounts of paraffinic fractions to the fuel. In addition, it has been shown that the simultaneous involvement of light fractions and depressants to improve the low-temperature properties of DF has a negative effect and is impractical.

The revealed regularities of the influence of the straight-run DF composition on the effectiveness of the depressant additives will make it possible to choose the most effective additives and select their optimal concentrations.

Acknowledgements

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List of symbols

DF	*diesel fuel;*
CP	*cloud point;*
CFPP	*cold filter plugging point;*
PP	*pour point;*
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.*

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