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EXPERIMENTAL TESTING OF INFLUENCE OF COMMERCIAL DEPRESSANTS ON DIESEL FUELS LOW TEMPERATURE PROPERTIES

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Abstract

The types and action mechanism of depressant additions, which improves the properties of diesel fuels in low temperatures, were presented. The results of a sixteen different depressants influence on cloud point (CP) and cold filter plugging point (CFPP) of diesel fuels ONA without additions are given in following elaborate. The depressants were applied to samples of diesel fuel in concentration between 500 and 5000 ppm. The present paper shows correlation of diesel fuels ONA CFPP and ΔCFPP depression between depressants concentration. Only a part from the tested depressant additions has a significant impact on diesel fuel cloud filter plugging point at concentration recommended by their manufacturers. Moreover, some of the additions do not decrease the CFPP value. The depressants can be divided into three groups by their effectiveness: first, the ones which decreases greatly the CFPP (from 3 to 11 degrees) by adding only small amount of them (500 ppm), second, with almost no influence on CFPP values in smaller amounts (500 ppm) but reducing CFPP values in larger quantities (to 5000 ppm), third, with no influence on diesel fuels ONA CFPP even in large concentration. In conclusion, lowering the CFPP value depends on the kind of depressant and its concentration in diesel fuel and not on the diesel hydrocarbon composition with addition up to 7% of Fatty Acid Methyl Ester (FAME).

Keywords: *engine fuels, diesel fuel, low temperature properties, depressants*

1. Introduction

One of the major problems, which occurs during diesel fuels usage, is decreasing their fluidity in low temperatures. This is due to the crystallization and secretion of the n-paraffin and iso-paraffin hydrocarbons during cooling process. Appearing solid phase crystals causes a significant diesel fuel clouding. Continuing cooling down, process leads to increase in number of paraffin crystals and their agglomeration. The biggest solid phase crystals can create sediment on the walls of the storage tanks, distribution system pipes and diesel engines fuels systems including fuel filters. The crystallized n-paraffin (wax) at low temperature may cause operability problems, such as plugged filters and fuel lines and in result engine immobilization.

The cold flow properties of the diesel fuels can be quantified by [1]:

- the cloud point (CP) is defined as the temperature at which the first formations of solid phase (first n-paraffin wax crystals) are observed;
- the pour point (PP) is the lowest temperature at which diesel fuel loses its fluid properties;
- the cold filter plugging point (CFFP) is defined as the highest temperature at which a given volume of diesel fuel fails to pass through a standardized filtration device in a specified time when cooled under certain conditions.

The CFPP is generally considered to be a more direct and reliable indicator of low temperature operability than CP and PP. It determines the lowest temperature that the diesel fuel will give trouble free flow in certain fuel systems and diesel engine may be used.

To maintain a fluidity of diesel fuel in low temperature, special substances called depressants are added to them. An amount from 0.01 to 0.1% of depressant is enough to lower the temperature of the diesel fuel use. Nowadays, many substances were described and were patented hundreds of different chemical compounds as depressants. The most common are [2, 3]:

- copolymers of ethylene with monomers (usually with vinyl acetate),
- polyolefins, especially copolymers of ethylene and propylene,
- polymethyls,
- copolymers modified with a third monomer (e.g. maleic anhydride, acrylates, olefins, etc.),
- non-polymeric types.

Mostly copolymers of ethylene with vinyl acetate – EVA are used [4].

The influence mechanism of the depressants on the diesel fuels is not fully understood and is still under studies [1, 2, 3]. Dominated theories:

- depressant increases the solubility of n–paraffinic hydrocarbons with the highest crystallization temperature, during cooling process – the result is lowering the CP value,
- depressant prevents the expansion created by n-paraffins spatial structures, by adsorption of the crystals on the surface,
- depressant enter into nascent chain of n-paraffin crystals (co-crystallization theory) – molecule of additive is set in crystallising n-parafins, inhibiting the growth of these crystals – a large number of small crystals is formed.

In the second and the third option, the diesel fuel CFPP temperature is lowered. The effectiveness of depressants depends on many factors, e.g.: depressant chemical composition, hydrocarbon composition of diesel fuel, method of basic diesel fuel manufacture, fractional composition of basic diesel fuel. Finally, the impact of every depressant on diesel fuel varies, even on the basic diesel fuel. That is why option of adding a chosen depressant and its concentration is set during the diesel fuel manufacturing process in refinery so it has proper low temperature properties (depending on the planned usage of the diesel fuel).

Dispersant additives are also in uses [5], which also reduce significantly the CFPP of basic diesel fuel. Those depressants creates, on the surface of crystals, a small electrical polar layer which causes mutual repulsion of crystals [4, 5], preventing from their agglomeration. Various depressants put into the same basic diesel fuel may act synergistically or antagonistically [6].

There are available many different substances, which, according to their manufacturers, may improve the low temperature properties of every commercial diesel fuel. However, taking into account previous information can show that it is not so obvious. Therefore, it was purposeful to carry out proper laboratory tests of the impact of additives on altering the low temperature properties of diesel fuel.

2. Experimental procedures

2.1. Fuel and blends

The aim of the study was to determine the influence of various depressants on changing the diesel fuels low temperature parameters.

Two diesel fuels were tested:

- commercial diesel fuel – ONA,
- basic diesel fuel – HON,

in addition, sixteen different commercial depressants, marked from 1 to 16. Depressants were set into the diesel fuel samples in concentration between 500 and 5000 ppm.

The low temperature parameters of ONA and ONA with depressants were obtained by testing the CP and CFPP values. Low temperature parameters and chosen quality parameters of tested diesel fuel are given in tab. 1.

Tab. 1. Selected quality parameters of investigated diesel samples in accordance to PN-EN 590:2013-12

Parameter	ONA	HON
Cetane number	56.0	51.4
Cetane index	52.7	50.0
Density at 15°C, kg/m^3	838.8	840.0
Kinematic viscosity at 40°C, mm^2/s	2.84	4.30
Flash point, °C	65.0	63.0
Particulate contamination, mg/kg	8.0	7.2
Water, mg/kg	111	126
Distillation: E250, % v/v E350, % v/v T95, °C	 34 94 355	 21 90 366
Cloud point (CP), °C	-5	1
Cold filter plugging point (CFPP), °C	-6	1
FAME, % v/v	6.7	0.0

2.2. Fuel low–temperature properties measurements

Cloud point (CP) was determined using an automated apparatus CPP 97-2 with head for measure of cloud point and thermostat CC 180 according to PN-EN ISO 3015 specifications. The fuel sample was cooled at the specified rate and examined in 1°C increments far the formation of insoluble materials (n-parafins crystals) measured by light scattering. The cloud point was identified as the temperature at which the n-parafins crystals were first detected at the bottom of the sample vial. As the result of the measurement was taken the arithmetic mean of at least three CP measurements of the sample, calculated with an accuracy of 0.1°C ± the expanded uncertainty. The expanded uncertainty for these measurements is 0.5°C.

Cloud filter plugging point (CFPP) determined using an automated apparatus CPP 97-2 with head for measure of cloud point and thermostat CC 180 according to PN-EN 116 specifications. The fuel sample was cooled at intervals of 1°C, an attempt was made to draw 20 cm^3 of the fuel sample into a pipette under a controlled vacuum (2.00±0.05 kPa) through a standardized wire mesh filter (45±3,1 μm). The procedure is repeated, as the specimen continues to cool, for each 1°C below the first test temperature. As the sample cools, insoluble materials (e.g. n-parafins crystals) form and begin to inhibit flow through the filter. The cold filter plugging point is defined as temperature for which the time taken to fill the pipette exceeds 60 s. As the result of the measurement was taken the arithmetic mean of at least two CFPP measurements of the sample, calculated with an accuracy of 0.1°C ± the expanded uncertainty. The expanded uncertainty for these measurements is 1.0°C.

3. Results and discussion

The measurements results of the different depressants effectiveness on the ONA diesel fuel Cloud Filter Plugging Point temperature are given in Tab. 2 – these are the CFPP average values and ΔCFPP depression (the difference between CFPP ONA and CFPP ONA with depressant), depending on the depressant concentration.

Testing the influence of the depressants on altering clouding temperature shown that none from the 16 different depressants, added to commercial diesel fuel (ONA) and to basic diesel fuel (HON), lowered the CP value – most of the results were set in the ±0.5°C expanded uncertainty. In conclusion, tested depressants do not increase the solubility of the released during cooling n–paraffin hydrocarbons with the highest crystallization temperature. They inhibit the growth and crystals agglomerations of n-paraffins and this should result in a decrease of the diesel fuel CFPP value.

The data presented in tab. 2 can be used to divide the depressants into three groups by their effectiveness:

- I – the ones which decreases the CFPP greatly (from 3 to 11°C) by adding only small amount of them (500 ppm), depressants: 1, 3, 4, 7, 9, 12 and 13;
- II – with almost no influence on CFPP values in smaller amounts (500 ppm) but reducing CFPP values in larger quantities (to 5000 ppm), depressants: 2, 5, 8, 11, 14, 15 and 16;
- III – with no influence on diesel fuels ONA CFPP or very low influence (depressant 16), even in large concentration (depressants: 6 and 10).

Tab. 2. Influence of depressant concentration on CFPP value and decreasing of ΔCFPP, °C

depressant number	CFPP, °C				ΔCFPP depression, °C			
	depressant concentration, ppm				depressant concentration, ppm			
	500	1000	2000	5000	500	1000	2000	5000
1	-9	-16	-20	-	3	10	14	-
2	-7	-8	-10	-17	1	2	4	11
3	-9	-16	-20	-	3	10	14	-
4	-9	-16	-23	-	3	10	17	-
5	-9	-12	-17	-21	3	6	11	15
6	-6	-6	-6	-6	0	0	0	0
7	-14	-19	-21	-	8	13	15	-
8	-12	-17	-20	-21	6	11	14	15
9	-10	-16	-18	-	4	10	12	
10	-6	-6	-6	-6	0	0	0	0
11	-7	-9	-11	-20	1	3	3	14
12	-9	-19	-20	-	3	13	14	-
13	-17	-23	-28	-	11	17	22	-
14	-7	-8	-9	-20	1	2	3	14
15	-9	-12	-18	-21	3	6	12	15
16	-7	-8	-8	-9	1	2	2	3

The fig. 1 and 2 presents ONA cold filter plugging point and its depression in a function of selected depressants concentration from group I. Fig. 3 and 4 presents same function for depressants from II group.

CFPP value change, depending on the depressant concentration, can be described by the regression equation in the form of a polynomial:

$$CFPP = a - bs - cs^2 \tag{1}$$

and ΔCFPP depression:

$$\Delta CFPP = ds - es^2, \tag{2}$$

where:

a – CFPP value of the ONA diesel fuel,

b, c, d, e – factors dependant on the type of depressant.

The correlation coefficient (R^2) of these equations was greater than 0.964…0.999 indicating that these regression equations accurately represent the CFPP (ΔCFPP) – depressant concentration relationship for the samples tested.

More effective are depressants from I group (mainly copolymers of ethylene with vinyl acetate), which reduce intensively the CFPP value of the diesel fuel in low concentration (from 500 to

1000 ppm). By adding larger amounts of them the impact of the depression becomes smaller – a doubling the amount of depressant (2000 ppm) causes the depression between 2 and 3°C.

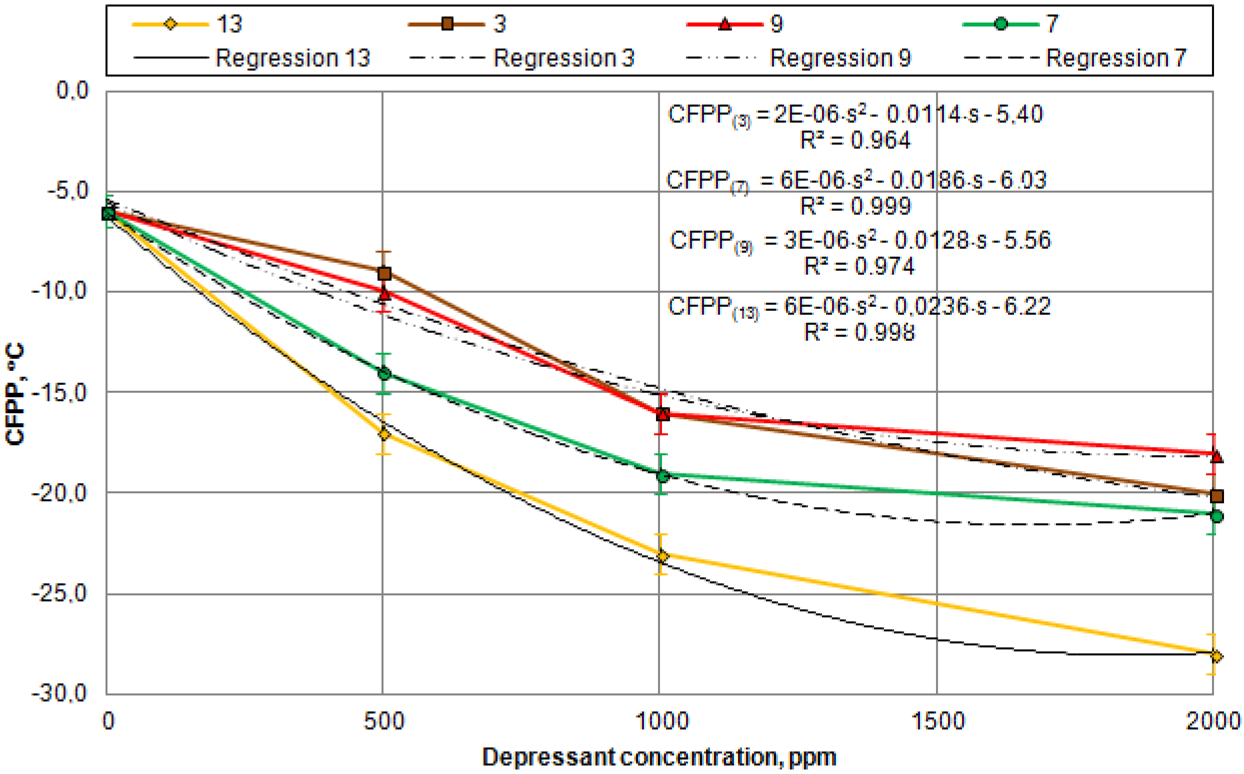

Fig. 1. ONA cold filter plugging point in a function of selected depressants concentration of group I

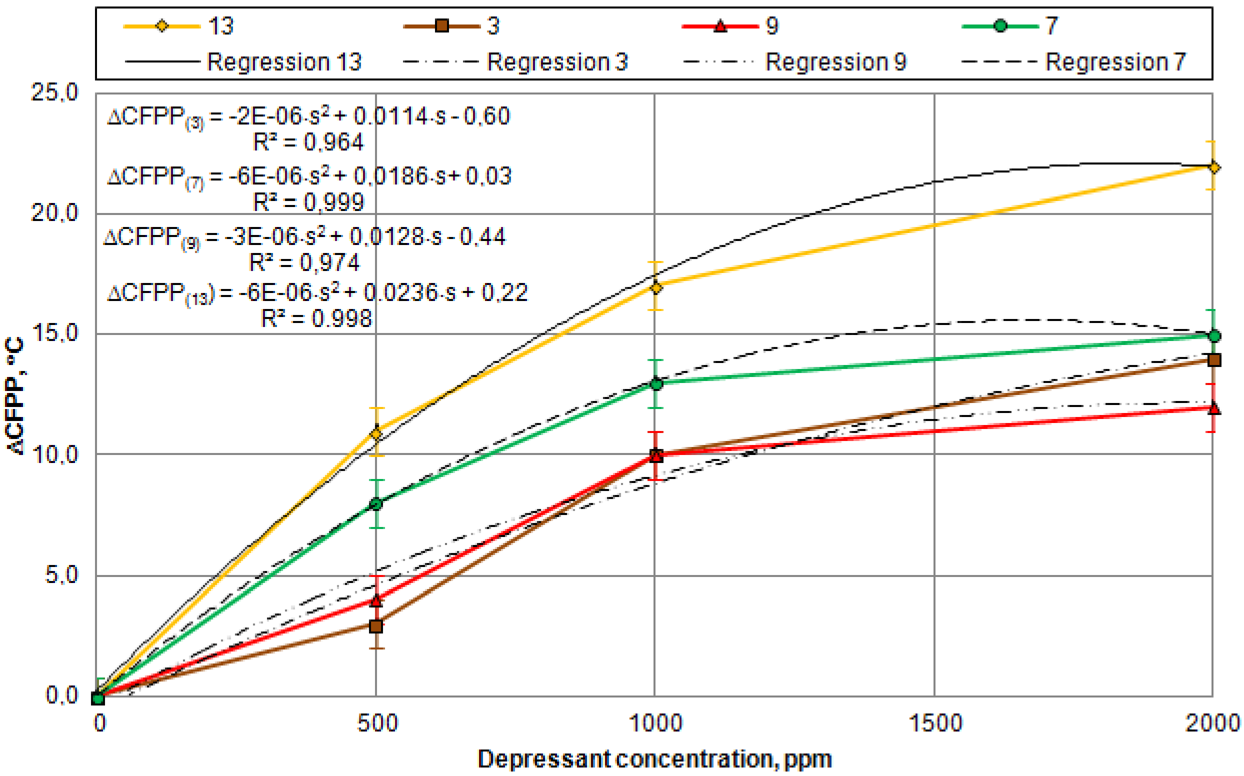

Fig. 2. ONA decrease of cold filter plugging point in a function of selected depressants concentration of group I

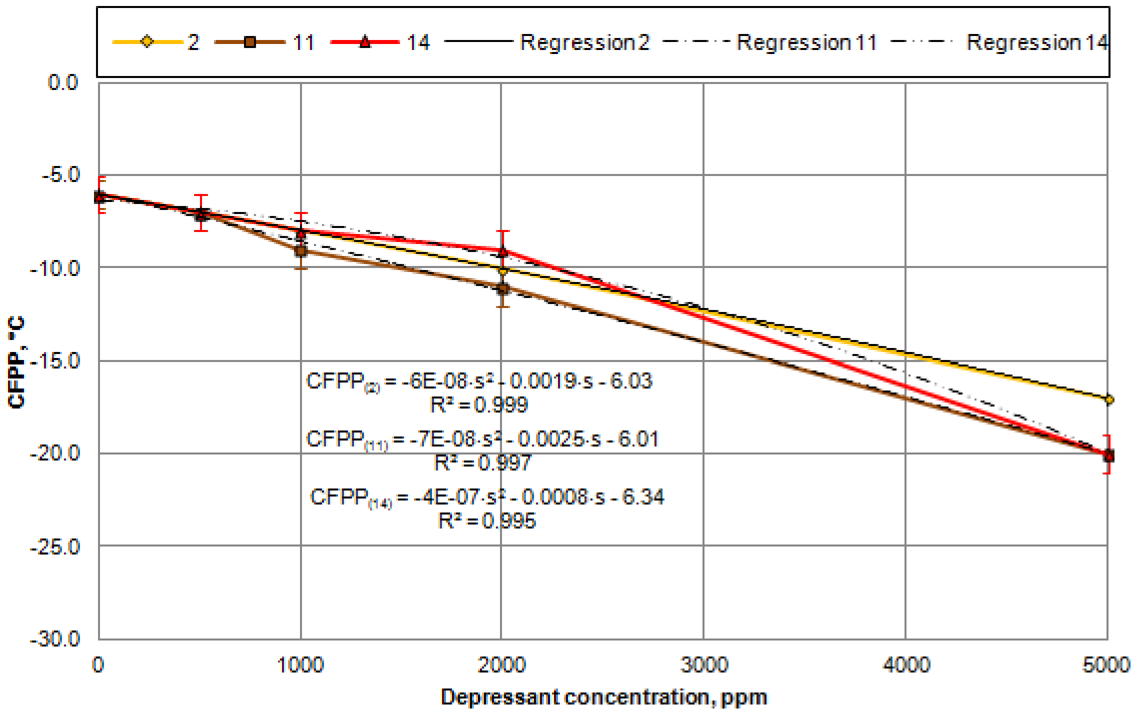

Fig. 3. ONA cold filter plugging point in a function of selected depressants concentration of group II

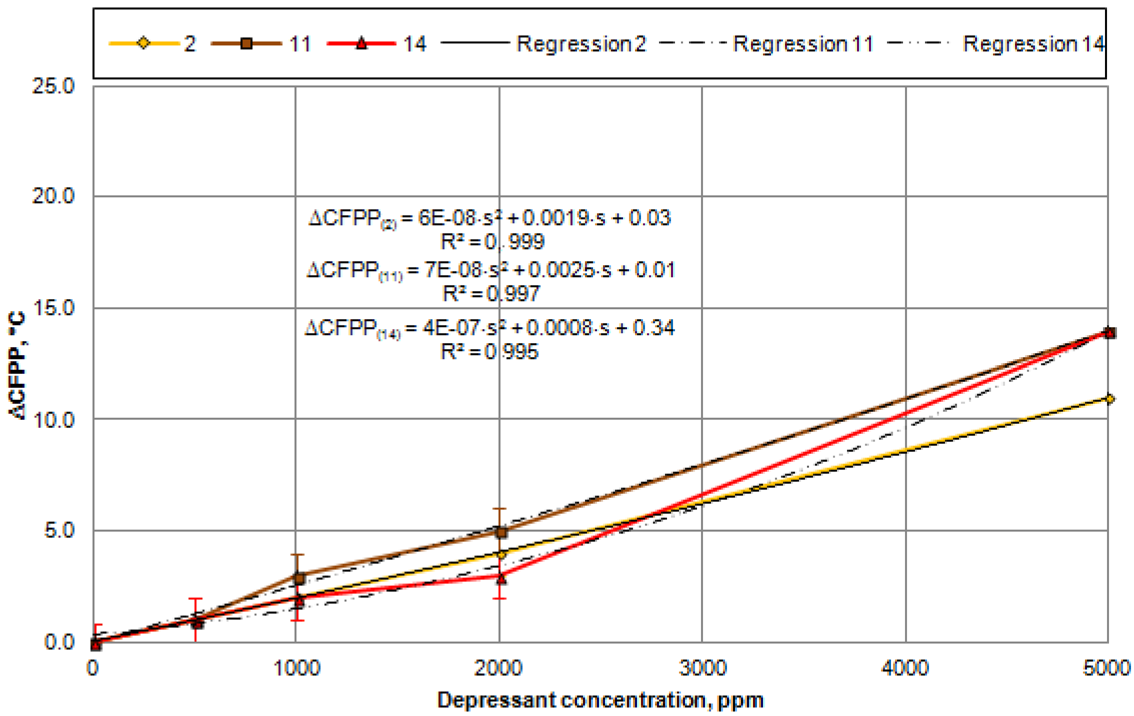

Fig. 4. ONA decrease of cold filter plugging point in a function of selected depressants concentration of group II

On the other, depressants from the II group operate less efficiently. Their influence on lowering the CFPP value in low concentration is imperceptible but increases in larger amounts, approximately in a linear relationship of the ΔCFPP and concentration. To receive a similar effect, of lowering the diesel fuel CFPP, the more than twice of the group II depressant is needed in comparison to the group I.

In Tab. 3 the impact results of the No. 3 depressant on the diesel fuels without depressants (ONA & HON) are given. HON had less aromatic hydrocarbons than ONA but contained more paraffins and naphthenes. The difference in their composition had no influence on the ΔCFPP depression and it was the same form them both in similar depressant concentration.

Presence of the Fatty Acid Methyl Esters (FAME) in ONA (up to 7%) had no influence on the depression (ONA had almost 7% of the FAME and HON consisted only hydrocarbons derived from petroleum processing).

Tab. 3. Impact of No. 3 depressant on CFPP value of selected diesel fuels, °C

diesel fuel	low temperature parameter, °C	temperature, °C			
		depressant concentration, ppm			
		0	500	1000	2000
commercial ONA	CP	-5	-5	-5	-5
	CFPP	-6	-9	-16	-20
	ΔCFPP	—	3	10	14
basic HON	CP	1	1	1	1
	CFPP	1	-4	-9	-12
	ΔCFPP	—	5	10	13
commercial ONF, [3]	CP	-9	—	-9	-9
	CFPP	-21	—	-26	-29
	ΔCFPP	—	—	5	7

4. Conclusions

1. To achieve proper low temperature properties of diesel fuels many different depressant additions and dissipating additions are used.
2. The low temperature properties of diesel fuel are created in the refinery during its production. In addition, they can be improved, during the usage of diesel fuels, by adding depressants.
3. The effectiveness of different depressants varies and depends on factors such as chemical composition, amount (concentration) of depressant in diesel fuel and method of manufacture in refinery (adding depressants during production).
4. Only a part from available depressant additions reduces significantly the diesel fuel CFPP value in concentration recommended by their manufacturers. Some of the depressants have no effect on CFPP.
5. Hydrocarbon composition of diesel fuels has almost no impact on the effectiveness of the depressants.
6. Empirical equations to predict the CFPP and ΔCFPP depression of commercial diesel fuels as a function of depressant concentration have been developed.

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