

Influence of dodecanol addition on Cold Filter Plugging Point for the mixtures of diesel oil with ethanol

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Abstract. The article presents the results of tests which were supposed to determine the influence of dodecanol addition to diesel oil on Cold Filter Plugging Point (CFPP). Tested were the mixtures of diesel oil and ethanol, with the volumetric percentage of ethanol of 5, 10 and 15%. The maximum dodecanol addition represented 20%. Determination of the temperature at which the filter got plugged was carried out with the use of the FPP 5Ds device, and the CFPP determination was carried out in accordance with the PN-EN 116: 2015-09 standard. The test results reflect, among other things, that dodecanol addition to the mixture of diesel oil with dehydrated ethanol results in lowering the Cold Filter Plugging Point for the lowest of the tested dehydrated ethanol percentages, whereas increase in the CFPP for the other percentages. As regards the mixtures with hydrated ethanol in which 20% dodecanol addition was applied, it may be noticed that along with the growth of the hydrated ethanol content, the CFPP was decreasing.

1. Introduction

Fast civilisation development results in growing numbers of cars which are mostly driven by engines fuelled with gasoline or diesel oil. This contributes to higher demand for the said fuels, both originating from crude oil, meaning non-renewable sources. The crude oil deposits are shrinking, while the extraction and combustion of fuels results in environmental pollution. Therefore, alternative fuels have been searched for, to be environment-friendly and price-competitive compared to the oil-derived fuels as well as originating from renewable sources [1, 2]. One of the alternatives for such fuels may be ethyl alcohol. However, independent use of such chemical as a fuel results in the necessity of costly modification of the fuel systems of compression ignition engines, which have been originally fit for fuelling with diesel oil. Therefore, ethanol and methanol are used as mixtures with diesel oil [4]. The addition of ethanol to diesel fuel reduces particulate matter (PM) and nitrogen oxide (NOx) emissions, and also increases the share of renewable fuels used in transport, which should reach 10% by 2020 in this sector. In the long-term perspective, it is assumed that by 2050 CO₂ emissions in transport will be reduced by 60% [3]. The mixture of ethanol with diesel oil depends on temperature changes and the water content in the fuel, which may result in delamination of the mixture.

In order to improve stability and facilitate miscibility with diesel oil, various additives are applied, such as dodecanol (C₁₂H₂₆). Dodecanol is produced by reduction of methyl esters [13]. Dodecanol is a solid body insoluble in water, with 24°C melting point. It is characterised with good solubility in both of the aforesaid fuels, and therefore is applied as a stabiliser for the mixtures of diesel oil and ethanol [5].



Service utility of a fuel used in fuelling compression ignition engines depends on low-temperature parameters of the fuel. The less paraffin hydrocarbons in diesel oil the better the low-temperature parameters. We differentiate the following quality parameters characterising the behaviour of fuel at low temperatures:

- cloud point;
- Cold Filter Plugging Point (CFPP) or Low Temperature Flow Test (LTFT);
- flow temperature.

All of the parameters are determined in normalised conditions [1]. The most important and most frequently applied low-temperature parameter is CFPP. It is the highest temperature at which the specific volume of fuel, cooled in normalised conditions, is not able to flow through a normalized filtration system during a specific time [11]. The value determines the lowest possible temperature at which fuel may be used.

The low-temperature characteristics of fuels are determined in the EN 590 standard, in accordance with which the basis for grading fuels is the CFPP value. For temperate climate, six grades of diesel oil have been distinguished (Table 1).

Table 1. Diesel oil grades for temperate climate [10]

Diesel oil grade	Maximum value of CFPP [°C]
A	+ 5
B	0
C	-5
D	-10
E	-15
F	-20

Diesel oil grades admitted for sale in Poland in accordance with the PN-EN 590 +A1:2011 standard are intended for three seasons:

- summer season – grade B;
- transition season – grade D;
- winter season – grade F.

Apart from the fuel low-temperature properties, a major parameter is the fuel water content. Water present in diesel oil results in corroding the elements of injection devices, faster consumption of sprayers as a result of electromechanical corrosion, deterioration of fuel spraying, deterioration of diesel oil lubricity, plus reduction of fuel filters durability [1]. The percentage of water in fuel is normalised and cannot exceed 200 ppm.

2. Test devices and methods

Determination of the Cold Filter Plugging Point was made with the use of an automatic FPP 5Ds device (Fig. 1). CFPP determination was carried out in accordance with the PN-EN 116:2015-09 standard, which recommends the determination of CFPP with the use of a manual or automatic device.

Determination of the CFPP value was carried out for ten samples of various volumetric percentage of dehydrated and hydrated ethanol. Dodecanol addition for dehydrated ethanol was 2%, and for the hydrated ethanol – 20%, as only with such concentration a homogeneous mixture was obtained [9]. The properties of the applied dodecanol are presented in Table 2, whereas Tables 3 and 4 present the parameters of both types of ethanol used in making the mixtures with diesel oil.



Figure 1. FPP 5Gs automatic device for determination of Cold Filter Plugging Point

Table 2. Basic dodecanol characteristics, based on [8]

Name of parameter	Value	Unit
Density at 16°C	0.9	g/cm ³
Solubility in water at 25°C	0.037	g/l
Autoignition point	275	°C
Flash-point at 101.3 kPa	134.8	°C
Melting/solidification point at 101.3 kPa	24	°C

Table 3. Basic characteristics of dehydrated ethyl alcohol (ET), based on [6]

Parameter	Value	Unit
Alcohol content at 20°C	99.9	%
Density	0.7897	g/cm ³
Esters content	< 0.2	mg/100 cm ³
Methanol content	< 0.6	mg/100 cm ³
Denatonium benzoate content	1	g/100 dm ³
Water content	≤ 0.1	% (m/m)
Autoignition point	425	°C

Table 4. Technical specification of hydrated ethyl alcohol (ETW), based on [7]

Name of parameter	Value	Unit
Alcohol content at 20°C	92.0	%
Density	0.88	g/cm ³
Methanol	< 3	%
Isopropanol content	≤ 2.5	%
Acetone content	≤ 2.5	%
Autoignition point	425	°C

For preparing the mixtures, commercial cold diesel oil was used (table 5). The mixtures prepared for CFPP determination were stored at the temperature of 20±2°C, in closed containers due to the water-absorption capacity of alcohol. At that temperature, the prepared mixtures to which 5% or 10% of dehydrated ethanol was added were clear and transparent, whereas in the sample containing 15% of ethanol the mixture delaminated. No mixtures of diesel oil with ethanol (both hydrated and dehydrated) and dodecanol got delaminated. Table 5 presents the identification of samples used in the tests.

Table 5. Basic properties of diesel oil

Name of parameter	Value	Unit
Derived cetane number (DCN)	53,1	
Cetane improver (2-EHN)	78	ppm
Higher heating value	46,248	kJ/kg
Viscosity at 40 °C	2.8885	mm ² /s
Density at 15 °C	0.822	g/cm ³
Flash point, °C	58.5	°C
Water content	60,10	mg/kg
Cold filter plugging point	-20	°C
Lubricity (WSD)	408	µm
FAME content	0.6	% v/v

Table 6. Types of fuels tested for CFPP

Fuel identification	Percentage in ml v/v			
	Diesel oil	Dehydrated ethanol	Hydrated ethanol	Dodecanol
ON 100	200	0	0	0
ON+ET5	190	10	0	0
ON+ET10	180	20	0	0
ON+ET15	170	30	0	0
ON+ET5+D	190	10	0	6
ON+ET10+D	180	20	0	6
ON+ET15+D	170	30	0	6
ON+WET5+D	190	0	10	40
ON+WET10+D	180	0	20	40
ON+WET15+D	170	0	30	40

The Cold Filter Plugging Point also depends on the water content in fuel. Determination of fuel hydration was made in accordance with the PN-EN ISO 12937: 2005 standard, with the use of a coulometer operating based on Karl Fisher method. This consists in injecting a weighed sample of fuel to a vessel comprising an electrolyte. As a result of the reaction iodine is liberated on the anode. Upon titration of the whole water, iodine excess is detected by a electrometric endpoint sensor and titration is stopped. One mole of iodine reacts with one mole of water, which means that the quantity of water is proportionate to the total electric charge in accordance with the Faraday's law [12]. Increase of the ethyl alcohol percentage in diesel oil results in higher fuel hydration, and the highest quantity of water in the tested mixtures was obtained for hydrated ethanol, in accordance with the expectations.

3. Test results and analysis

Figure 2 presents the results of CFPP determinations for diesel oil and mixtures of diesel oil with dehydrated ethanol. The chart shows that all fuels fulfil the requirements of the PN-EN 590 + A1: 2011 standard for transition season fuels. The CFPP value for such fuels in the transition season must be at least -10°C. For the winter season, the CFPP value must be -20°C, and for the summer season 0°C. Only the sample comprising 5% ethanol and 2% of dodecanol addition fulfilled the requirements of the standard for winter season fuels, for which the CFPP value is -20°C.

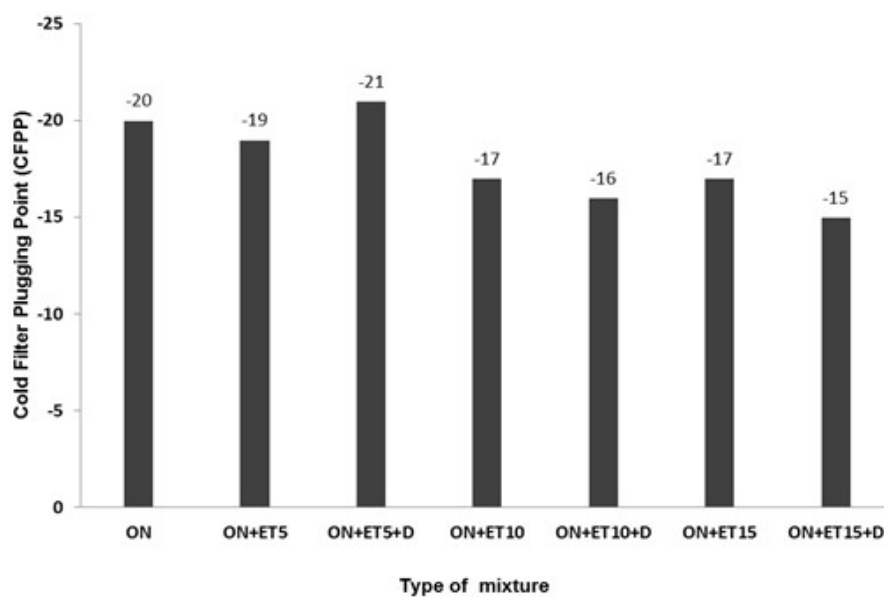


Figure 2. CFPP for the tested mixtures of diesel oil and ethanol with 2% dodecanol addition

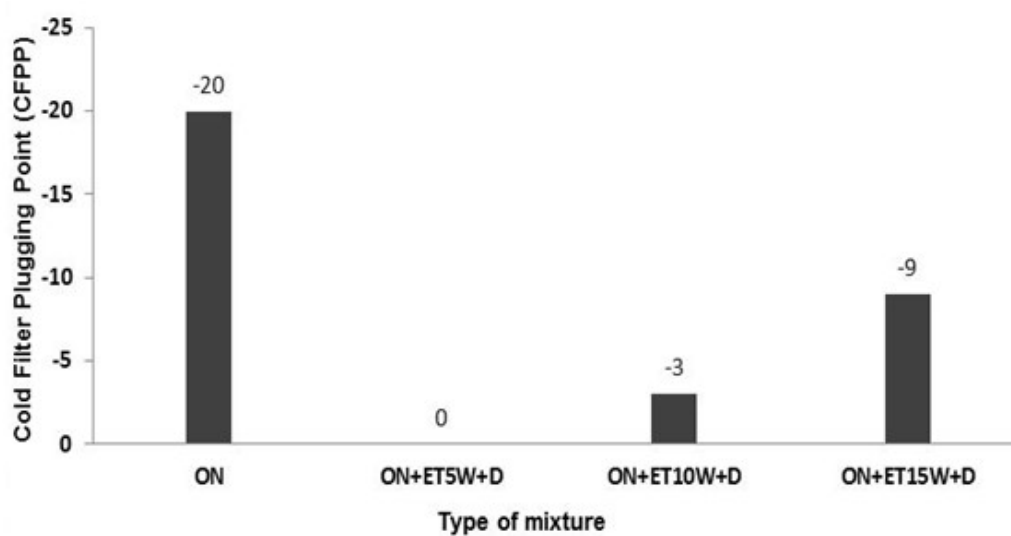


Figure 3. CFPP for the tested mixtures of diesel oil and hydrated ethanol with 20 % dodecanol addition

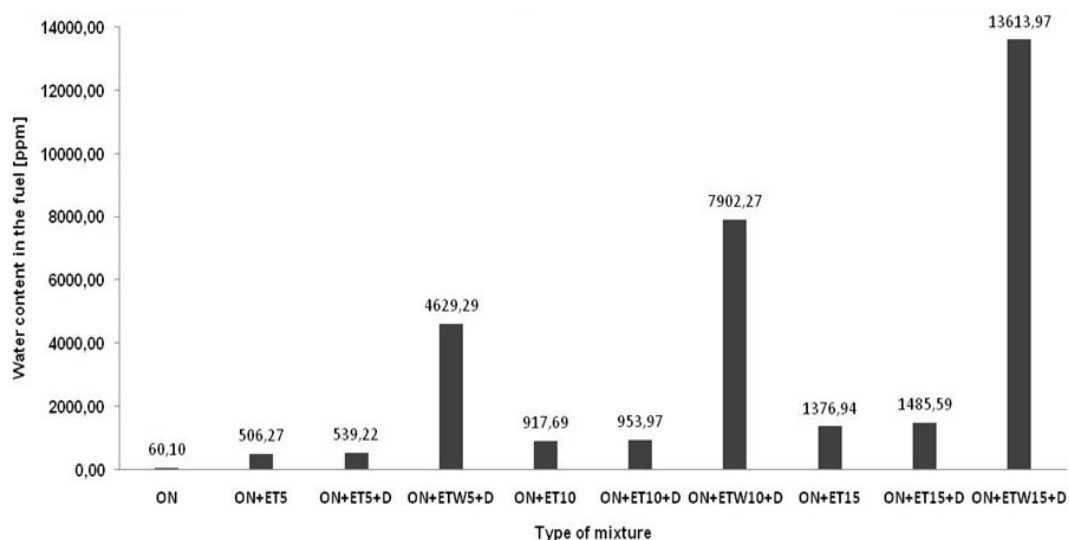


Figure 4. Water content in the tested mixtures

Figure 4 presents a comparison of the water content in the tested mixtures. An addition of ethanol and dodecanol resulted in increased fuel hydration. This derives from the water-absorption capacity of ethyl alcohol. Water content increases along with the increased percentage of alcohol in diesel oil. Dodecanol addition has also resulted in higher water content in the tested samples.

As it may be seen on the chart, water content for commercial diesel oil was 60.10 ppm. As soon as ethanol was added, water content grew in the tested fuel. For the samples containing dehydrated ethanol the highest water content was noted for the sample identified as ON+ET15 (1,376.94 ppm). Dodecanol addition resulted in further water content increase. The highest water content was reflected by the sample identified as ON+ET15+D, for which water content reached 1,485.59 ppm. Among all tested fuels the highest water content was reflected by the mixtures with hydrated ethanol. The maximum value, i.e. 13,613.97 ppm, was determined for the mixture identified as ON+ETW15+D.

4. Conclusions

Use of 2% (v/v) dodecanol addition in case of small percentages of dehydrated ethanol in diesel oil results in lowering the Cold Filter Plugging Point. Along with the growth of ethyl alcohol content, the CFPP was growing. With regard to the achieved value of CFPP -21°C , in accordance with the PN-EN 590 + A1: 2011 standard, the sample of fuel identified as ON+ET5+D fulfilled grade D requirements for temperate climate. Other mixtures with dehydrated ethanol and dodecanol addition, may be classified in grade E for temperate climate, in accordance with the aforesaid standard.

As regards the mixtures with hydrated ethanol in which 20% dodecanol addition was applied, it may be noticed that along with the growth of the hydrated ethanol content, the CFPP was decreasing. This may result from a change in the viscosity of the mixtures and the impact of higher dodecanol concentration. For the purpose of explaining that phenomenon, it would be needed to determine the viscosity of the mixtures. The obtained CFPP values classify the fuels in grade C as regards the samples containing 10% and 15% of hydrated ethanol, whereas the mixture containing 5% of hydrated ethyl alcohol falls in grade B.

All of the samples with dehydrated ethanol, for which CFPP was determined may be used in winter season. Improvement of low-temperature parameters for such fuels may still be achieved by the use of additives lowering the CFPP (e.g. hydrocarbon-based depressants, isoalkanes, or cycloalkanes).

The mixtures of diesel oil with hydrated ethanol and dodecanol may be used only in summer season, because much higher CFPP values were determined for them compared to the similar mixtures

with dehydrated ethanol. For the mixtures to be used in fuelling of compression ignition engines, additives lowering the CFPP would have to be applied.

Ethyl alcohol additionally resulted in higher water content in fuel. This derives from the alcohol water-absorption capacity. Along with the water content increase the CFPP was increasing. As regards mixtures containing small percentages of dehydrated ethanol (up to 5%) in the diesel oil as well as the dodecanol addition, CFPP values were improved despite the increased water content in the tested mixture.

Summing up, dodecanol addition results in Cold Filter Plugging Point decrease only for small concentrations of dehydrated ethanol in diesel oil.

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