Study on the impact of co-solvent on selected properties of mixtures of diesel oil with bio-ethanol

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Introduction

The bio-ethanol is the most tested oxygen compound for use as a fuel component. In the sector of public transport it can be used: as a mixture with gasoline, as a mixture with diesel fuel, as a E95 fuel to power diesel engines, as a feedstock for the production of oxygen compounds (for fuels) as well as a carrier of hydrogen for fuel cells. Bio-ethanol is a well known component of motor gasoline. Attempts are being made use of bio-ethanol as a component of diesel fuel (in amounts up to 20% v/v) or as fuel to power the self-ignition engines. Anhydrous bio-ethanol has a low ignition temperature, low viscosity and poor lubrication properties. Cetane number of pure bio-ethanol is approximately 8 [1]. Therefore, the admixture of bio-ethanol to diesel influences fuel parameters directly related to engine work. First of all, bio-ethanol causes a deterioration of: viscosity, flash point, cetane number and lubricating properties. Another disadvantage of this compound is its limited miscibility with diesel oil. Because of its high affinity for water, even a small amount of water can disturb the equilibrium of oil and alcohol, and causes separation of the alcohol phase.

The stability of a mixture of diesel oil with bio-ethanol can be improved for example by a co-solvent addition. This substance easily mixes with both mentioned components. Co-solvent works on the principle of cross-linking agent forming a bridge between molecules. It allows the mixture becomes homogeneous. As a co-solvent can be used, inter alia, vegetable oil methyl esters, monohydric alcohols, tetrahydrofurane or ethyl acetate [2].

The aim of this study was investigation of the influence of co-solvent on selected properties of diesel oil blends with bio-ethanol.

Test samples

The research mixtures were composed of commercial diesel oil (without fatty acid methyl esters), fatty acid methyl esters (FAME) and anhydrous bio-ethanol. All components meet the quality requirements defined in the standard specifications. The selected parameters for these components are presented in Table 1.

Table 1

Properties of diesel oil, FAME and bio-ethanol

	Density at 15°C, kg/m³	Viscosity at 40°C, mm²/s	Boiling point, °C	Flash point, °C	Sulphur content, mg/kg	Water content, %m/m
Diesel oil	833	2.513	172-358	58	7.0	0.004
FAME	883	4.438	-	180	<3.0	0.006
Anhydrous bio-ethanol	791 (20°C)	-	78.4	13-14	<3.0	0.378

As co-solvents of bio-ethanol in diesel oil were tested following alcohols:

2-ethyl-1-hexanol, n-propanol, isopropanol and 2-butanol. The basic properties of the tested alcohols are summarized in Table 2.

Table 2

Physicochemical properties of co-solvents [3]

Compound	Density at 20°C, kg/m³	Boiling point, °C	Flash point, °C	Autoignition point, °C	Melting point, °C
2-ethyl-1-hexanol	830	183-185	73	-	-76
2-butanol	810	99-102	24	390	-115
n-propanol	800	97.4	15	360	-126.5
isopropanol	785	82-83	12	425	-88

Methodology

The mixtures were prepared in the laboratory by blending different volume shares of the components. The samples were stored in tightly closed containers for:

7 days at 22°C, 7 days at 15°C and 7 days at 5°C. The solubility of prepared mixtures has been estimated by their periodical visual evaluation.

Tests of lubricating properties of prepared blends of diesel oil with bio-ethanol and co-solvents were performed with using HFRR (High Frequency Reciprocating Rig) apparatus according to the methodology described in the polish standard [4], with some exceptions. These exceptions were caused by the specificity of tested mixtures. Bio-ethanol boils at about 78°C. Performing of the friction test at 60°C (in accordance with the standard) can cause the evaporation of a significant part of alcohol from the mixture. Such situation changes the properties of the blend. Therefore, tribological tests were performed at 25°C. In order to avoid excessive heating of testing fluid and evaporation of bio-ethanol due to friction, the enclosed research vessel with increased capacity up to 10 cm³ was applied. Lubricating properties of investigated mixtures were determined on the basis of the average wear scar diameter, calculated from diameters measured parallel and perpendicular to the direction of friction. Determination of kinematic viscosity was carried out in accordance with PN-EN ISO 3104 [5] at 40°C. The cetane number of experimental fuels was determined with the using Waukesh engine according to the PN-EN ISO 5165, also called CFR (Cooperative Fuel Research) engine [6].

Research results

The results of the solubility observation have shown that at tested temperatures, investigated blends of diesel oil with bio-ethanol are clear and homogeneous only to 10% of bio-ethanol content. Thus, the introduction of co-solvent is necessary. In the case of mixtures of diesel oil with bio-ethanol and co-solvent, these mixtures are stable up to 15% v/v of bio-ethanol and 5 to 10% v/v of co-solvent content.

One of the important parameters of diesel fuel is its lubricity. Changing the oil composition may improve or deteriorate this parameter. Ethyl alcohol has significantly poorer lubricity in compare to commercial diesel fuel. The average wear scar diameter on the ball lubricated with absolute bio-ethanol was 472 μm, while for ball lubricated with commercial diesel oil - 176 μm. Therefore, it can be expected that the introduction of bio-ethanol to diesel oil deteriorates the lubrication properties of the mixture. These assumptions were confirmed by the results of carried out tests. Figure 1 shows examples results of the tribological tests for compositions of diesel fuel and methyl esters of fatty acids (5% v/v) with different content of anhydrous bio-ethanol. Presented data indicate that the introduction of 5% v/v of bio-ethanol causes increase of the wear scar diameter by over 60% compared with diesel oil or diesel oil containing FAME. Another increase of the alcohol content to 20% v/v results in a 2.5 - fold increase of wear scar diameter.

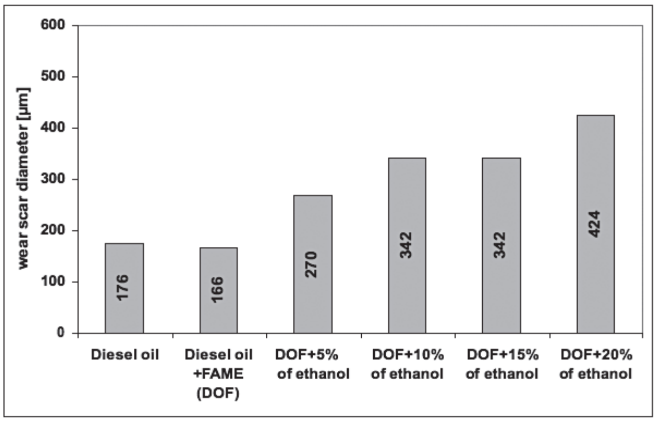

Fig. 1. Results of tribological tests of diesel fuel and blends of diesel fuel with 7% of FAME and the different content of anhydrous bio-ethanol

The wear increase due to the increase of bio-ethanol content is most likely caused by the viscosity decrease. The fuel viscosity is important for the lubrication of fuel system, especially equipped with a rotary fuel pump. Too low viscosity leads to excessive wear of fuel injection system. In Table 3 are presented the results of the kinematic viscosity measurement obtained for diesel fuel blends with different contents of bio-ethanol.

Table 3

Kinematic viscosity of selected blends of diesel with bio-ethanol

Mixture composition, %v/v	95 ON+5 FAME	100	95	90	85	80
	Bio-ethanol	-	5	10	15	20
Kinematic viscosity at 40°C, mm^2/s		2.612	2.355	2.189	2.077	2.016

The quantity of alcohol introduced into the mixture as well as the kind of used co-solvent has an influence on the size of wear. Figure 2 shows the results of tribological investigations of diesel fuel blends with 10% v/v and 15% v/v of absolute bio-ethanol and 5% v/v of different co-solvents.

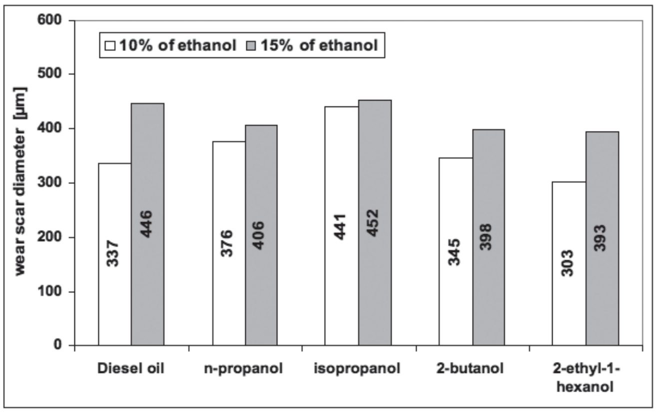

Fig. 2. The results of tribological tests of diesel oil mixtures with anhydrous bio-ethanol (10 and 15% v/v) and different co-solvents (5% v/v)

The presented data (Fig. 2) show that, influence of co-solvents is arranged in a similar trend, regardless of the concentration of bioethanol in the fuel. In both systems (10 and 15% of bio-ethanol), the worst lubricating properties showed blend with isopropanol, but the best – the mixtures with 2-butanol and 2-ethyl-1-hexanol.

The viscosity of mixtures containing tested co-solvents is similar (Tab. 4), only a blend with 2-ethyl-1-hexanol has a slightly higher viscosity in comparison to others.

Table 4

Kinematic viscosity of selected blends of diesel oil with bio-ethanol and co-solvents

Blend	Kinematic viscosity at 40°C, mm^2/s
Diesel oil (85%) + bioethanol (10%) + n-propanol (5%)	2.064
Diesel oil 85% + bioethanol (10%) + isopropanol 5%	2.057
Diesel oil 85% + bioethanol (10%) + 2-butanol 5%	2.077
Diesel oil 85% + bioethanol (10%) + 2-ethyl-1-hexanol 5%	2.174

On the base of research results of viscosity and tribological tests it has been stated that the kind of co-solvent influences lubricating properties of the mixture.

Another important parameter of diesel oil is a cetane number. Its value affects the engine start-ability, including start at low temperatures, emission, peak cylinder pressure and combustion noise and engine durability. The introduction of new compound to the diesel oil can change the cetane number. According to PN EN 590 standard [7] the value o this number for diesel oil should be above 51. Anhydrous bio-ethanol has very low cetane number, it varies within the limits of 5÷15 [8]. Addition of it into diesel fuel lowers the cetane number. To increase a cetane number of blends of diesel oil with bio-ethanol, it is necessary to use the cetane improver (additive that improves this parameter). Figure 3 presents the dependence of cetane number of diesel fuel on ethanol content.

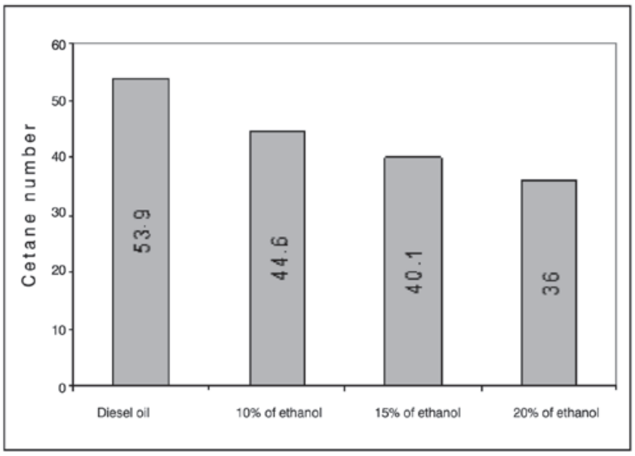

Fig. 3. The influence of ethanol content in diesel fuel on the cetane number value

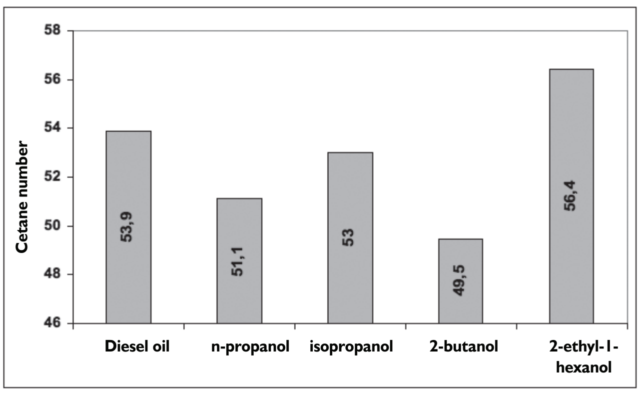

Fig. 4. The influence of 10% co-solvent content in diesel fuel on the value of the cetane number

Because co-solvents can also change the cetane number of the mixture, the authors of the article checked their effect on this parameter. In order to do it, a mixture of diesel fuel with 10% v/v content of the particular compounds were prepared and tested. The results are shown in Figure 4. Presented data indicated that only 2-ethyl-1-hexanol improve the cetane number.

The blends of diesel oil with 10% v/v of bio-ethanol and 5% v/v of particular co-solvent were also investigated. The mixture containing 2-ethyl-1-hexanol has the highest value of the cetane number and it was 49.7. These results suggest that for blends of diesel oil with 10% of bio-ethanol and 5% of co-solvents it is necessary to use the cetane improver additive.

Summary

The results can be concluded, that in the temperature range 5-22°C, diesel - bio-ethanol blends are clear and homogeneous only to 10% bioethanol content. In the case of diesel - bioethanol - co-solvent blends- the stability demonstrate mixtures containing up to 15% v/v absolute bi-ethanol and 5 to 10% v/v co-solvent.

With the increase of bio-ethanol concentration in the mixtures kinematic viscosity decreases, it corresponds with, inter alia, the deterioration of lubricating properties. The decrease of cetan number is observed, too.

On the lubricating properties and the value of the cetane number affects not only the content of bioethanol, but also the nature of the co-solvent. Among the studied co-solvents, the best effect on both parameters showed 2-ethyl-1-hexanol.

Literature

1. Li D.-g., Zhen H., Xingcai L., Wu-gao Z., Jian-guang Y.: *Physico-chemical properties of ethanol-diesel blend fuel and its effect on performance and emissions of diesel engines.* Renewable Energy 2005, **30**, 967-976.
2. Hansen A.C., Zhang Q., Lyne P.: *Ethanol-diesel fuel blends - a review.* Bioresource Technology 2005, **96**, 277-285.
3. Material safety data sheets.
4. PN-EN ISO 12156:2008, *Diesel fuel - Assessment of lubricity using the high-frequency reciprocating rig (HFRR).*
5. PN-EN ISO 3104:2004, *Petroleum products – Transparent and opaque liquids – Determination of kinematic viscosity and calculation of dynamic viscosity.*
6. PN-EN ISO 5165:2003, *Petroleum products - Determination of ignition quality of diesel fuels - Cetane engine method.*
7. PN-EN 590: 2010, *Automotive fuels - Diesel – Requirements and test methods.*
8. Odziemkowska M.: *Bioethanol as a component of biofuels for use in diesel engines.* Chemik 2010, **64**, **5**, 350-355.

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