THE IMPACT OF BIOESTERS ON LUBRICITY OF DIESEL FUELS

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Abstract

The paper discusses the influence of two fatty acid methyl esters (bioesters) derived from soybean oil (SME) and from rapeseed oil (RME) on the lubricity of the petroleum diesel fuels: Ekodiesel (S:26 mg/kg, HFRR: 555 μm) and Citydiesel (S: 8 mg/kg, HFRR: 617 μm).

High-frequency reciprocating rig (HFRR) equipment was used to examine diesel fuels, neat bioesters and blends containing from 0,1 % up to 20 % of soybean ester or rapeseed ester in each reference fuel. Lubricity evaluation was based on the measurement of the diameter of the wear scar left on the oscillated ball being in contact with a stationary disc submerged in the examined fuel.

The examinations have shown that soybean ester is the most effective additive enhancing the lubricity of both base diesel fuels, but the changes in the lubricity were more dynamic for the diesel fuel with higher level of sulphur.

1. Introduction

Systematic increase of the content of fractions from the hydrodesulphurisation processes in diesel fuels is made necessary by the need to decrease sulphur content in engine fuels [1 ÷ 4]. Deep desulphurisation removes also the traces of polar nitrogen compounds which acts as natural lubricants in diesel engines [3]. This results in a decrease in the lubricity of those fuels, which manifests itself in an increased wear of various parts of the engine, particularly the fuel injection system [3 - 6]. Diesel fuels, which do not meet the requirements concerning the standardized boundary values of the lubricity parameter require the use of special lubricity enhancers [3, 5]. Data quoted in the literature on the subject suggests that this role can be fulfilled by fatty acid methyl esters derived from vegetable oils, commonly known as FAME or biodiesel on account of the fact that this is also a good fuel for diesel engines [7 ÷ 10]].

The authors examined the effect of the addition of bioesters on lubricity of two low-sulphur diesel fuels.

2. Experimental

Materials: Ekodiesel and Citydiesel base diesel fuels (from PKN Orlen) as well as bioesters (fatty acid methyl esters) derived from vegetable oils: (i) rapeseed oil (RME) from Trzebinia S.A Oil Refinery and (ii) soybean oil (SME) obtained from Institute of Petroleum Technology, Kraków. Table 1 contains the properties of the diesel fuels and Table 2 provides characteristics of the RME and SME esters. From the above-mentioned materials blends were prepared containing: 0,1 %, 0,2 %, 0,5 %, 1 %, 5 % and 20 % by weight of the RME ester or the SME ester in the Ekodiesel fuel and in the Citydiesel fuel. Diesel fuels, bioesters and the prepared blends were subjected to lubricity evaluation.

Table 1. Characteristics of the Ekodiesel and Citydiesel reference fuels.

Tests	Unit	Results	
		Ekodiesel	Citydiesel
Cetane number	—	50,0	55,1
Density (15 ºC)	kg/m3	840,1	811,0
Sulfur	mg/kg	26	8
PAH	% (m/m)	1,9	1,6
Flash point	ºC	82	61
Viscosity (40 ºC)	mm^2/s	3,048	2,099
Oxidation stability	g/m^3	5,2	5,2
Corrosiveness (Cu)	class	1a	1a
Water	mg/kg	48	21
Distillation:			
to 250 ºC recovered	% (v/v)	30,0	52,0
to 350 ºC recovered	% (v/v)	100	100
95 % (V/V) recovered	ºC	338,0	281,0
Cloud point (CP)	ºC	-7	-29
Cold filter plugging point (CFPP)	ºC	-10	-35
HFRR lubricity (WS1,4)	µm	555	617

Laboratory equipment: Lubricity examinations of the fuels were carried out with the use of the High Frequency Reciprocating Rig (HFRR, PCS Instruments) under conditions specified by Polish Standard PN-EN 12156:2001. The lubricity of the fuels was evaluated on the basis of the wear scar left on the vibrated steel ball (φ = 6 mm) being in contact with a stationary disc submerged in the examined fuel (fuel temperature: 60 ^{o}C). The test lasted 75 minutes. The diameter of the wear scar of the ball was determined in micrometers using a microscope. During the test, the computer continuously recorded changes in temperature, the coefficient of friction and the film state.

3. Results and discussion

The diameter of the wear scar measured with the use of a microscope was corrected so that it reached the value for the normal pressure of water vapour equal to 1,4 kPa. This parameter, labelled with the symbol WS1,4, is a measure of lubricity, and, for diesel oils, its value should not be higher than 460 µm [PN-EN 590]. The results of the examinations are shown in Fig.1 and in Fig. 2.

On the basis of the results obtained from HFRR tests the relative lubricity (SWP) of the fuels was calculated. SWP was defined as a deviation from the standard expressed in % [9].

The effect of the soybean ester (SME) and the rapeseed ester (RME) on the changes of relative lubricity of the Ekodiesel and Citydiesel fuels is shown in Fig. 3. Negative values of SWP are treated as insufficient.

Data found in Table 1 suggests that the Ekodiesel and Citydiesel fuels do not meet the requirements of the relevant standard. Citydiesel (WS1,4 = 617), featured by lower sulphur content (S: 8 mg/kg) and lower final boiling point than Ekodiesel (WS1,4 = 555 µm) containing over three times as much sulphur (S:26 mg/kg), offered weaker anti-wear protection.

Table 2. Properties of the soybean methyl ester (SME) and the rapeseed methyl ester (RME)

Tests	Unit	SME	RME
Total ester	% (m/m)	95,5	97,2
Density (15 °C)	kg/m^3	885	882
Viscosity (40 °C)	mm^2/s	4,09	4,45
Flash point	°C	169	189
Cetane number	-	51	51
Sulfur	mg/kg	2	< 3
Water	mg/kg	192	186
Corrosiveness (Cu, 3h, 50 °C)	class	1a	1a
Oxidation stability (110 °C)	h	2,3	7,24
Acid value	mg KOH/g	0,46	0,27
Iodine value	gI/100 g	118	108,3
Methanol	% (m/m)	0,03	< 0,01
Linolenic acid methyl ester	% (m/m)	7,5	9,7
Monoglyceride	% (m/m)	0,10	0,22
Diglyceride	% (m/m)	0,03	0,08
Triglyceride	% (m/m)	0,13	0,04
Free glycerol	% (m/m)	0,0	< 0,005
Total glycerol	% (m/m)	0,04	0,07
HFRR lubricity (WS1,4)	μm	184	201

The soybean ester and rapeseed ester are characterised by good lubricity parameters: for soybean ester the obtained WS1,4 was 184 μm and for rapeseed ester the WS1,4 was equal to 201 μm.

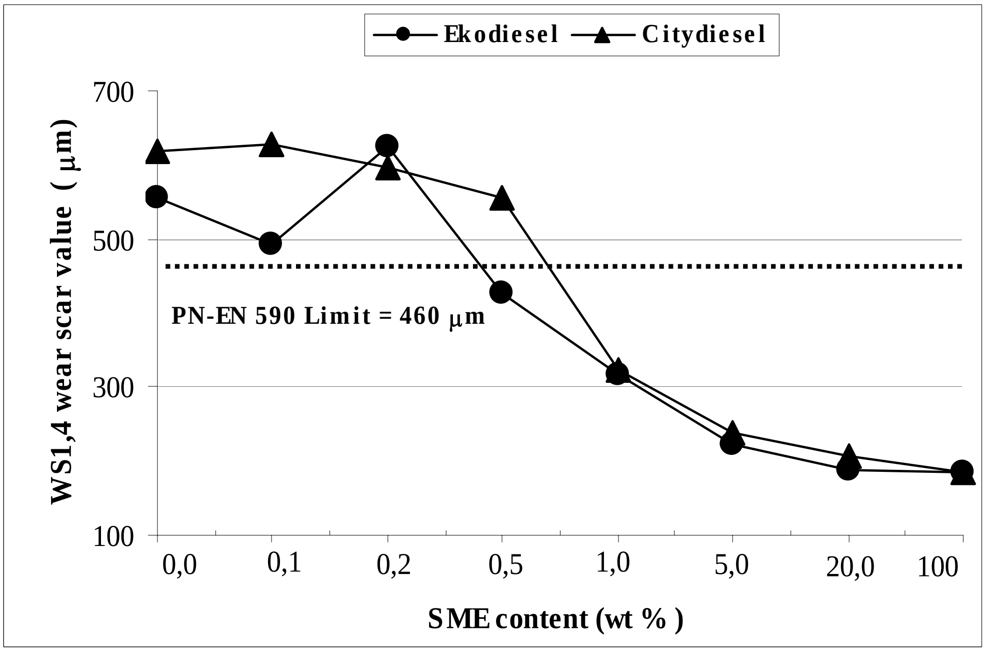

Fig. 1. Impact of the soybean methyl ester (SME) content on the HFRR lubricity of the Ecodiesel and Citydiesel diesel fuels

An increase in the ester content in diesel fuels accompanied by an improvement of the film state by HFRR and a decrease in the coefficient of friction. At the same time, the values of the corrected wear scar diameter of the test ball decrease (WS1,4 in Fig. 1 and Fig, 2) which is a proof of the beneficial effect the addition of bioesters has on lubricating ability of diesel fuels.

However, none of the bioesters increased lubricity of diesel fuels to the acceptable levels (less than 460 µm WS1,4 wear scar) at concentrations less than 0,5 %. At such concentrations of the SME ester or the RME ester there is little observable improvement in lubricity of the Ekodiesel and Citydiesel fuels as shown in Fig.1 and in Fig. 2.

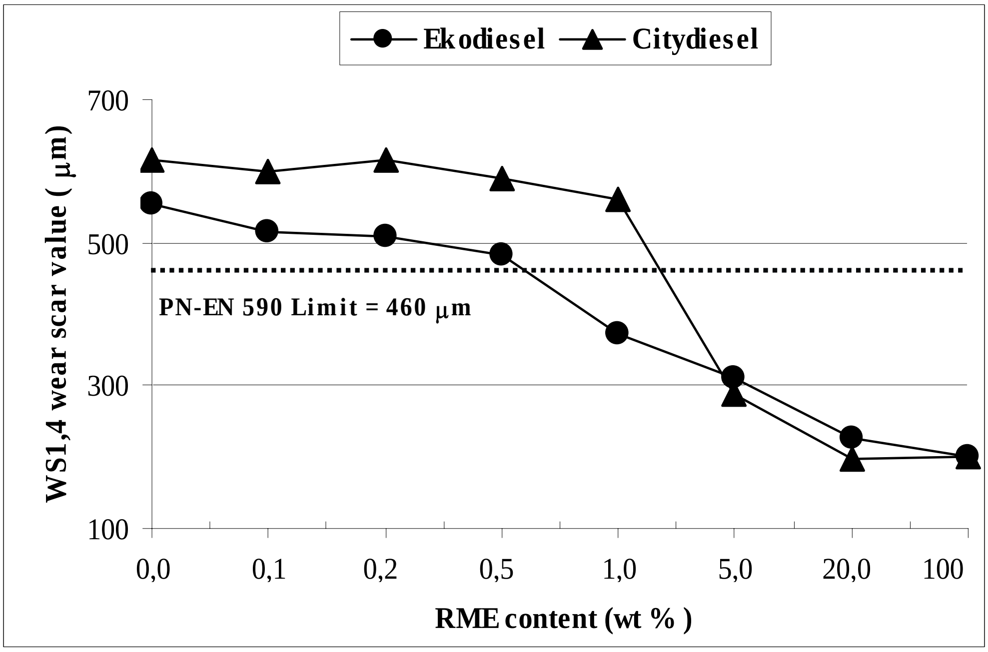

Fig. 2. Impact of the rapeseed methyl ester (RME) content on the HFRR lubricity of the Ecodiesel and Citydiesel diesel fuels

Results given in Fig. 1 and in Fig. 2 as well as in Fig. 3 prove that the SME ester is a better lubricity enhancer. The blend containing 0,5 % of SME in the Ekodiesel fuel is featured by WS1,4 lower than the boundary value of 460 µm, which corresponds to an improvement of the relative lubricity (SWP) by 7 % when compared to the boundary value (Fig. 3a)). However, with the addition of SME equal to 1 %, the SWP value increases up to 31 %, while the blend of Ekodiesel with the rapeseed ester requires a 5 % addition of RME in order to obtain similar value of SWP, i.e. 32 % (Figure 3 b).

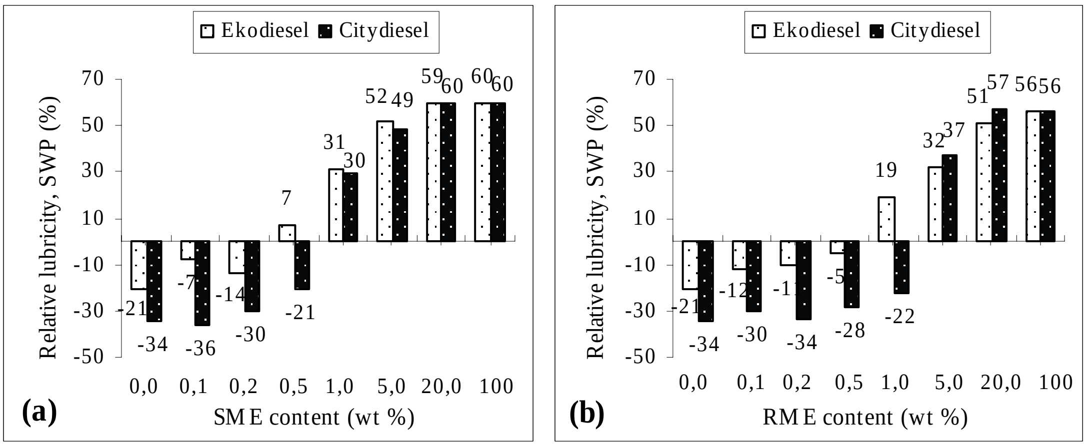

Fig. 3. Impact of the soybean methyl ester (SME) content (a) and the rapeseed methyl ester content (b) on the relative lubricity of the Ekodiesel and Citydiesel diesel fuels

The higher effectiveness of the soybean ester than that of the rapeseed ester as regards lubricating ability of conventional diesel oils was also recorded by Galler and Goodrum [7]. The above-mentioned authors proved that esters with the number of carbon atoms C18 and C20 are characterized by the best lubricity. Moreover, in the case of the same number of carbon atoms in the ester molecule, the esters with a higher number of double bonds in the ester molecule exert a more beneficial influence on lubricating properties of diesel fuel. Data found in Table 5 suggests that esters with two (C18:2 = 51,9) and three (C18:3 = 7,1 %) double bonds between carbon atoms constitute a dominant group of compounds in the soybean ester (SME), while the rapeseed ester (RME) contains mainly the C18:1 ester (60,1 %) and the C18:2 ester (18,4 %).

Table 3. Fatty acids profile of the soybean (SME) and the rapeseed (RME) methyl esters

Fatty acid methyl ester	Methyl ester content [wt %]	
	SME	RME
C16:0 (methyl palmitate)	11,1	4,0
C16:1 (methyl palmitoleate)	< 0,1	0,4
C18:0 (methyl stearate)	4,5	1,5
C18:1 (meyhyl oleate)	24,3	60,1
C18:2 (methyl linoleate)	51,9	18,4
C18:3 (methyl linolenate)	7,1	10,3
C20:0 (methyl arachdate)	0,3	0,8
C20:1 (methyl eicosenoate)	0,1	2,6
C20:2, C20:3 and C20:4	< 0,1	0,3
C22:0 (metyl behenate)	0,3	0,2
C22:1 (metyl erucate)	< 0,1	1,5
C24:0 (mehtyl lignocerate)	0,3	< 0,1
C24:1 (methyl nervonate)	0,1	< 0,1

An analysis of the plots presented in Figure 3, enables a conclusion that the Ekodiesel, characterized by a better lubricity (WS1,4 = 555 μm), was more sensitive to the ester addition than the Citydiesel (WS1,4 = 617 μm). With the same amount of the soybean ester (SME) or the rapeseed ester (RME), the changes in relative lubricity of the Ekodiesel were greater than those of the Citydiesel fuel. For instance: the relative lubricity of the blend containing 5 % of SME in the Ekodiesel (WSP = 52 %) was higher by 3 % than that of the 5 % blend of SME in the Citydiesel fuel (SWP = 49 %). A greater difference of lubricity (ca 5 %) occurred in the case of analogous blends containing the rapeseed ester.

Relative lubricity of the diesel fuels containing the 20 % additive of the SME ester or the RME ester is close to the value characterizing neat esters.

4. Conclusions

1. The methyl esters (SME, RME) derived from vegetable oils in compositions with low-sulphur diesel fuels have a beneficial effect on fuel lubricating ability, which manifests itself in a decrease of the corrected wear scar of the tested ball in the HFFR test.
2. The soybean ester turned out to be a better lubricity enhancer for petroleum diesel fuels than the rapeseed ester; a smaller concentrations of the SME ester in the blends with base diesel fuels resulted in an increase of the lubrication ability.
3. Characterized by higher sulphur content and better lubricity, the Ekodiesel was more susceptible to changes in the lubricating ability due to ester additives than the Citydiesel.

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