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INVESTIGATION AND PRODUCTION OF BIOETHANOL/GAS OIL EMULSIONS

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Directive 2003/30/EC contains the recommendation of the European Union regarding the increase of the use of bio-derived fuels. According to the directive fuels have to contain 5.75% bio-derived component – regarding the total energy content – by 2010. Nowadays in the European Union as renewable blending component biodiesel is applied in the highest amount, however further increase of its quantity is inhibited by many reasons. One possible solution for the increase of renewable gas oil blending components is the application of bioethanol/gas oil emulsions; however their spread is inhibited by their stability, analytical and performance properties. In this paper the effect of temperature and the presence of biodiesel on the stability of bioethanol/gas oil blends were investigated. Besides, analytical and performance properties of these emulsions were compared to the regulations of the diesel fuel standard (MSZ EN 590:2004) and to that of the applied base gas oil. It was found, that decrease of temperature worsened the stability of these emulsions in a great manner. Decrease of viscosity and lubricity caused by bioethanol were compensated until 6 v/v% bioethanol content by blending 5 v/v% biodiesel into the base gas oil. It was established that the decrease of cetane number caused by the bleding of bioethanol can be partially compensated by the application of high cetane number biodiesel. In conclusion, by the application of 5 v/v% biodiesel – produced by the transesterification of expediently improved sunflower oil having high cetane number – bioethanol/gas oil/biodiesel emulsion with 6 v/v% bioethanol content could be produced, that was stable at low temperature, had adequate lubricity and cetane number.

Keywords: gas oil, emulsion, bioethanol, biodiesel.

Introduction

In the last couple of years we have been facing several new challenges about the mobility, one of the most important pillars of sustainable development, both in the automobile manufacturing industry and in the oil industry [1-3]. Among other things, these changes were driven by regulated emission reduction of vehicles and that of greenhouse gas emissions, the tightening fuel specifications, the significantly higher crude oil prices, the efforts to reduce the dependency on imported crude oil and the increasing utilization of renewable energy sources [2-5].

Out of the biomass-based engine fuels, which are suitable to operate diesel engines, biodiesel (vegetable oil fatty acid methyl esters) became the most wide-spread in the European Union [6-8]. However, the investigation of bioethanol-diesel fuel and/or biodiesel emulsions as possible fuels to be applied in Diesel engines is also of increasing importance [7, 8]. This is constrained by the stability and the other problems derived from the analytical and performance properties of these emulsions [9-19].

The stability of these emulsions is influenced by several factors, which are the followings: hydrocarbon composition of base gas oils [10, 11], water content of bioethanol [12-15] and quality and quantity of emulsive additive [16]. The most important disadvantageous derived from their analytical and performance properties are: flash point, cetane number, viscosity and lubricating properties [17-19].

Due to these disadvantageous properties low quantity of bioethanol/gas oil emulsions have benn used as fuel in Diesel powered vehicles (mainly in case of urban bus or agricultural vehicles).

Various techniques involving bioethanol-gas oil fuel operation have been developed to make diesel engine technology compatible with the properties of ethanol-based fuels. They can be divided into the following categories:

- bioethanol/gas oil emulsions,
- injection of bioethanol (vaporization),
- dual injection of bioethanol and diesel fuel,
- application of bioethanol alone with cetane-booster additive,
- transformation of Diesel-engines to be operated with bioethanol.

In case of the first three options about 5–90% of diesel fuel can be substituted with bioethanol. The last two options mean the application of bioethanol alone.

In the European Union Diesel-vehicles fuelled by bioethanol could not be spread in wide range; currently these engines are used in Sweden in case of urban transport or agricultural fleets [19].

In pursuance of previous observations the main objective of our research work was to study the effect of temperature, presence of biodiesel and quantity of stabilizing additive on the stability of bioethanol/diesel fuel and/or biodiesel emulsions. Additionally the properties (density, kinematic viscosity, lubricity, Reid vapour pressure, cold properties, distillation properties, cetane number) of the bioethanol/diesel fuel micro emulsions in function of bioethanol content, in comparison with the specifications of the diesel fuel standard (MSZ EN 590: 2004) and with the corresponding properties of the base diesel fuel were investigated.

Experimental

Characteristics of the applied bioethanol and biodiesel used to prepare the studied samples are summarized in *Table 1-3.*

Tridecanol based additive was used to prepare bioethanol/gas oil emulsions. Characteristics of the prepared samples, base gas oil, bioethanol and biodiesel were determined or calculated by standard test methods, which are listed in *Table 4.*

Table 1: Main properties of base gas oil

Properties	Value
Density at 15.6 °C, kg/m^3	837.2
Sulphur content, mg/kg	5
Nitrogen content, mg/kg	1
Aromatic content,%	
mono	21.9
mi	2.0
poly	0.3
total	24.2
Kinematic viscosity at 40 °C, mm^2/s	2.60
CFPP, °C	-10
Flash point, °C	64
Distillation range, °C	184-356
Cetane index	51.1
Cetane number	52.5

CFPP: Cold Filter Plugging Point

Preparation of the emulsions was carried out with a magnetic agitator equipment at medium speed (600–700 rpm). The duration of agitation was 10 minutes in case of all samples. After the agitation, the samples were left alone at room temperature for 7x24 hours in a measuring tube of 100 cm^3 closed with a glass stopper.

The tridecanol based additive was used in 0.5–2.0 m/m% concentration referring to base gas oil, bioethanol in 1–15 v/v% and biodiesel in 3–21 v/v% concentration referring to base gas oil. The stability of the samples was investigated in the temperature range of 1–20 °C.

Table 2: Main properties of bioethanol

Properties	Value
Relative molecular mass, g/mol	46.07
Carbon content, %	52.14
Hydrogen content, %	13.13
Oxygen content, %	34.73
Sulphur content, mg/kg	<1
Density at 15.6 ºC, kg/m^3	789.3
Boiling point at 101.3 kPa, ºC	78.5
Heating value, MJ/l	21.1
Flash point, ºC	12.8
Reid vapour pressure, kPa	15.9

Table 3: Main properties of biodiesel

Properties	Value
Ester content, %	99.2
Density at 15.6 °C, kg/m^3	885.0
Kinematic viscosity at 40 °C, mm^2/s	4.5
Flash point, °C	132
Oxidation stability at 110 °C, h	13
Acid value, mg KOH/g	0.3
Iodine value, g Iodine/100 g	84
CFPP, °C	-12
Cetane number	56

CFPP: Cold Filter Plugging Point

Table 4: Standard test methods

Characteristics	Standard method
Density at 15.6 °C	MSZ EN ISO 3675
Kin. viscosity at 40 °C	MSZ EN ISO 3104
Flash point	MSZ EN ISO 2719
CFPP	MSZ EN 116
Cloud point	MSZ EN 23015
Reid vapour pressure	MSZ EN 13016-1
Lubricity (four ball test)	ASTM D 2783-88
Sulphur content	MSZ EN ISO 20846
Aromatic content	MSZ EN 12916
Distillation properties	MSZ EN ISO 3405
Cetane index	MSZ EN ISO 4264
Cetane number	MSZ EN ISO 5165
Ester content	MSZ EN 14103
Oxidation stability	MSZ EN 14112
Acid value	MSZ EN 14104

CFPP: Cold Filter Plugging Point

Results and discussion

Investigation of the stability of bioethanol/gas oil emulsions

First, the effect of quantity of tridecanol based additive on stability of bioethanol/gas oil emulsions was investigated *(Fig. 1).* Fig. 1 indicates that the concentration of the additive strongly affected the volume of bioethanol kept dissolved. The base gas oil alone without any additive was only able to keep maximum 3 v/v% bioethanol in solution. This value increased to 8.5% with increasing concentration of the additive. The stability of emulsions was strongly influenced by the temperature. The decrease of temperature had negative effect on the amount of dissolved bioethanol, as it was expected. The bioethanol kept in emulsion decreased from 8.5% to 5.3% with decreasing the temperature from 20 °C to 1 °C.

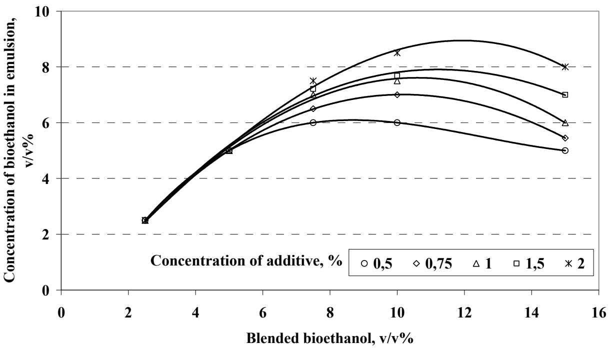

Figure 1: Stability of bioethanol/gas oil emulsions as a function of quantity of additive (temperature: 20 °C)

Beside the effect of additive concentration and temperature, as a potential co-solvent biodiesel was also investigated. These results are presented in *Figs 3-5*. The biodiesel co-solvent significantly enhanced the stability of the blend, thus a defined amount of base gas oil was able to dissolve a higher amount of bioethanol. This is caused by the unlimited solvency of bioetanol and biodiesel [10,19]. The stability of emulsions increased with increasing the quantity of the additive (Fig. 4).

It can be observed that the reduction of temperature had a negative effect on the amount of dissolved ethanol even in the presence of biodiesel. Without the use of additive, bioethanol did not dissolve into the base gas oil at 1°C, but the presence of 5% biodiesel facilitated the admixture.

Figs 2-5 indicate that the stability of emulsions increased due to the application of biodiesel in low quantity (5–7%). 4.4v/v biodiesel containing base gas oil was able to keep 1.5% more bioethanol in emulsion under the same conditions compared to the base gas oil without biodiesel.

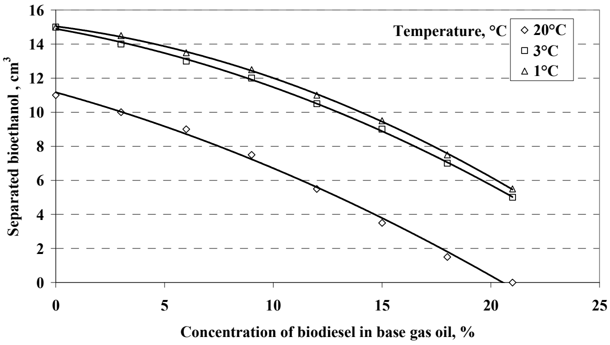

Figure 2: Stability of bioethanol/gas oil emulsions as a function of temperature (without additive, 15 v/v% bioethanol)

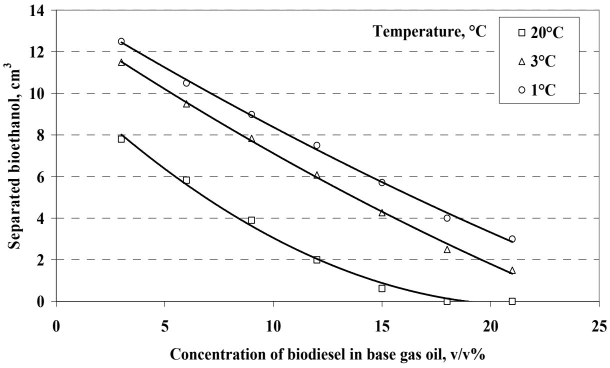

Figure 3: Stability of bioethanol/gas oil emulsions as a function of temperature (1% additive, 15 v/v% bioethanol)

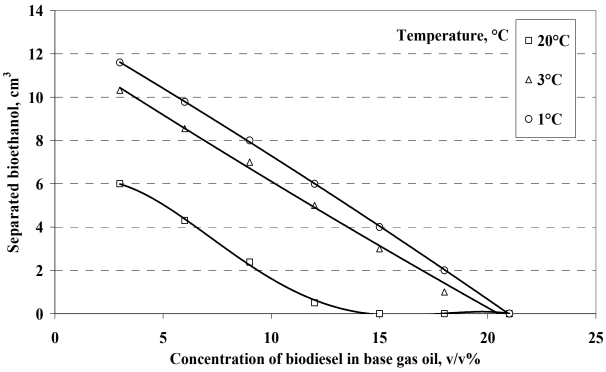

Figure 4: Stability of bioethanol/gas oil emulsions as a function of temperature (2% additive, 15 v/v% bioethanol)

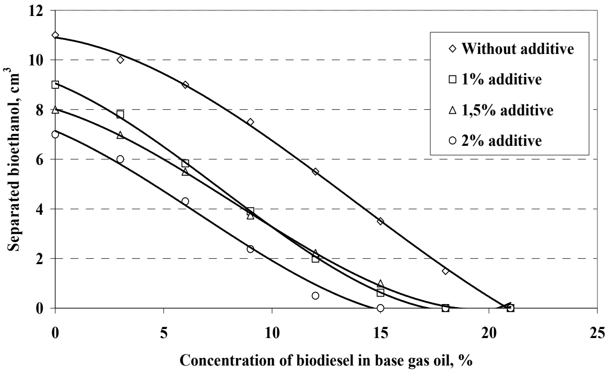

Figure 5: Stability of bioethanol/gas oil emulsions as a function of quantity of additive (temperature: 20 °C, bioethanol content: 15 v/v%)

This finding is important, because diesel fuels containing at least 4.4 v/v% biodiesel can be marketed with tax incentives in Hungary beginning with January 1, 2008. Biodiesel acts as a co-solvent and can improve the stability of bioethanol/diesel fuel emulsions meaning that the low temperature (1–20 °C) might occurring during the storage or transportation will not cause phase separation in case of bioethanol content between 1–8 v/v%.

Investigation of the analytical and performance properties of bioethanol/gas oil emulsions

The usability of bioethanol/gas oil emulsion is not only affected by their stability but also by their analytical and performance properties. That's why their analytical properties were also investigated according to the specifications of the diesel fuel standard (MSZ EN 590: 2004) and the corresponding properties were compared to those of the base diesel fuel.

Density of the base gas oil used for the blending was 0.8372 g/cm^3 at 15 °C-on. Density of the blends was lower due to the addition of ethanol having a lower density *(Fig. 6)*. Density of the blends containing up to 10 v/v% bioethanol has met the specification (0.820–0.845) of MSZ EN 590:2004 standard.

Kinematic viscosity of the base gas oil measured at 40 °C was 2.60 mm^2/s, which dropped to 2.18 mm^2/s after blending 10 v/v% bioethanol. The presence of biodiesel slightly increased the kinematical viscosity, as expected *(Fig. 7)*. The measured viscosity values have met the specifications (2.0–4.5 mm^2/s) of the diesel fuel standard. It can be seen that the presence of biodiesel in 5.5 v/v% concentration increased the kinematic viscosity of the base gas oil.

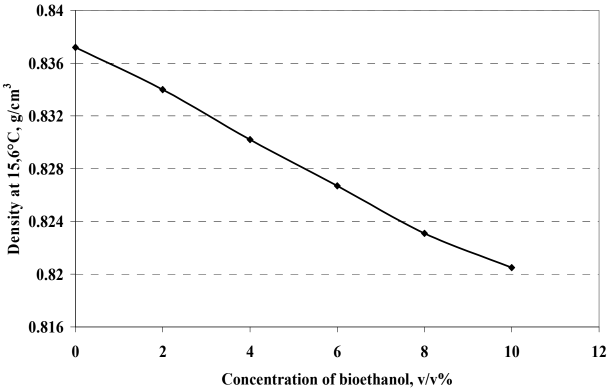

Figure 6: Change of density of bioethanol/gas oil emulsions as a function of bioethanol content

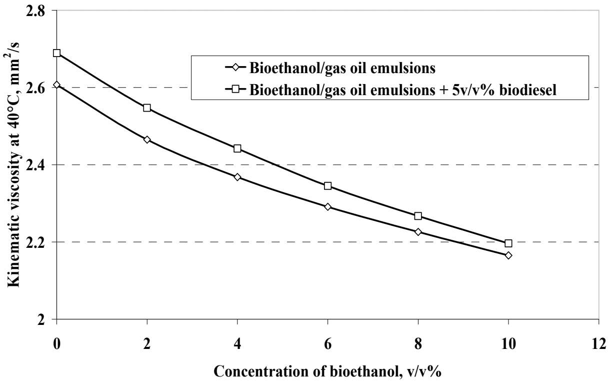

Figure 7: Change of kinematic viscosity of bioethanol/gas oil and/or biodiesel emulsions as a function bioethanol content

Flash point (as of Pensky-Martens) of the base gas oil was 64 °C, which decreased to an average of around 14 °C (± 1 °C) as a result of adding 5% bioethanol *(Fig. 8)*. This value was not affected by the presence of biodiesel. This flash point is much lower than the max. limit specified in the standard, therefore, ethanol/diesel fuel blends/emulsions have to be categorized into a higher class of flammability group than the base gas oil. As a result, the air/hydrocarbon mixture is within the range of the explosive limit at a temperature of 12–35 °C. In order to overcome this problem, the literature suggests the installation of a flame arrester in the fuel tank of the vehicle [9,10].

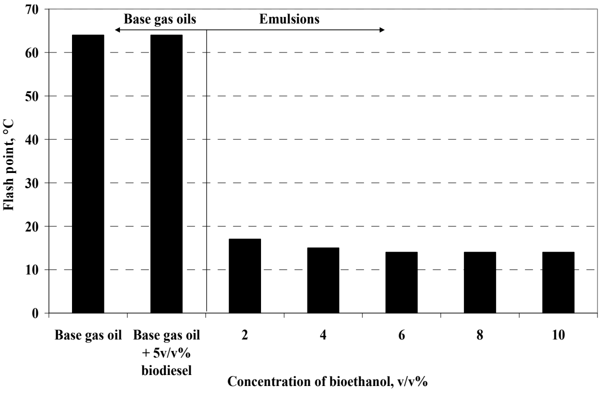

Figure 8: Change of flash point of bioethanol/gas oil and/or biodiesel emulsions as a function of bioethanol content

Normally, vapour pressure of gas oils is not measured, because it is very low. However, the blending of bioethanol has significantly increased the vapour pressure of the base fuel as already projected in the literature. Reid vapour pressure of the base feedstock was 0.6 kPa, while those of the blends containing 5% bioethanol were about 13.2 kPa in average, also in the presence of biodiesel. The about twenty times higher RVP of the gas oil/ethanol blend can even result in vapour lock formation in the fuel supply chain of vehicles.

Among cold properties the CFPP values decreased only slightly, pour point also decreased, but greatly and cloud point increased greatly as a result of bioethanol blending. CFPP values became higher by 2–3 °C in the presence of biodiesel *(Table 5)*. The increase of cloud point was caused by the growing micelles due to the lower temperature in micro emulsions.

Table 5: Change of cold flow properties of bioethanol/gas oil and/or biodiesel emulsions as a function of bioethanol content

Bioethanol content, v/v%	**CFPP, °C**	**Cloud point, °C**	**Pour point, °C**
Base gas oil	-10	-10	-22
2	-11	-8	-24
4	-11	-6	-25
6	-13	-5	-26
8	-14	-4	-28
10	-14	-2	-31

The lubricity of fuel can be an issue in the vehicles, where the lubrication of the fuel pump is provided by the fuel itself. Lubricity of the bioethanol/gas oil emulsions was studied with a four ball equipment available at our Department. The samples were examined in the four ball test under 300 N load for 1 hour. The obtained results are presented in *Fig. 9* and *10.* As expected, the ethanol has considerably decreased the lubricating properties of the base gas oil. The size of wear scar increased from 0.78 mm to 1.2 mm after blending ethanol, i.e. the anti-wear effect of the mixture substantially dropped. The temperature varied between 55.5–57 °C, which was not a significant change but increased in tendency, indicating that the anti-friction effect of the fuel mixture also worsened.

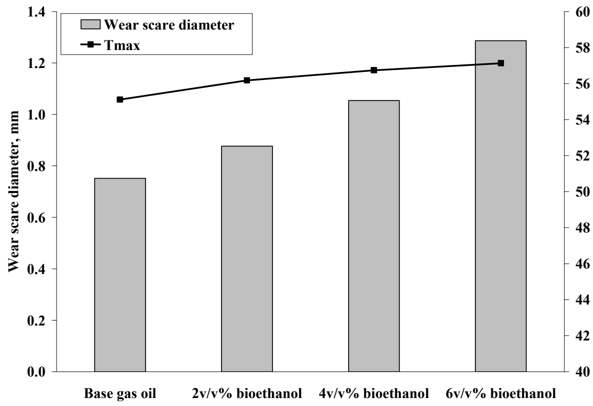

Figure 9: Change of lubricity of bioethanol/gas oil emulsions as a function of bioethanol content

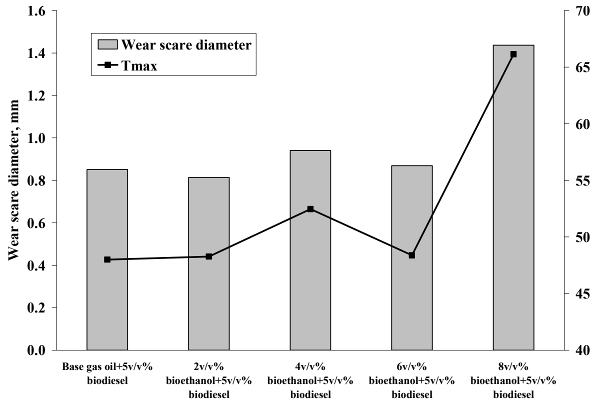

Figure 10: Change of lubricity of bioethanol/gas oil/biodiesel emulsions as a function of bioethanol content (biodiesel content of base gas oil: 5 v/v%)

The loss of lubricity could be compensated with biodiesel in case of maximum 6 v/v% bioethanol (Fig. 10).

The distillation properties of base gas oil greatly changed due to the lower boiling point of bioethanol (78.5 °C at 101.3 kPa) *(Fig. 11).*

Cetane number is an important property of diesel fuels. Due to the blending of 10v/v% bioethanol with base gas oil the cetane number decreased by about 10 units *(Fig. 12).* The loss of cetane number would be compensated by:

- use of high cetane number base gas oil,
- cetane booster additives (ethyl-hexyl-nitrate),
- higher carbon- and cetane number and more soluble alcohol (biobutanol, cetane number: 36),
- high cetane number biodiesel produced from improved vegetable oil.

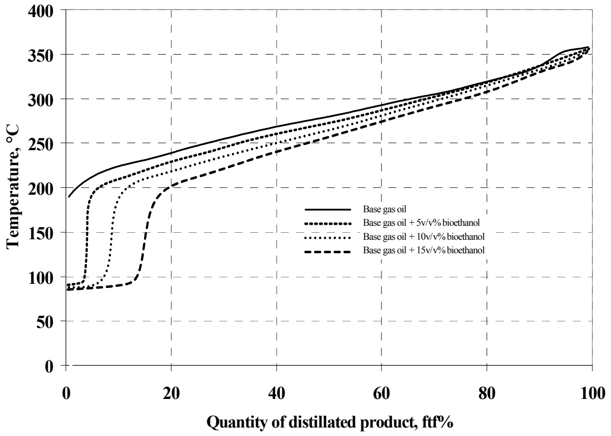

Figure 11: Change of the distillation properties of bioethanol/gas oil and/or biodiesel emulsions as a function of bioethanol content (biodiesel content of base gas oil: 5 v/v%)

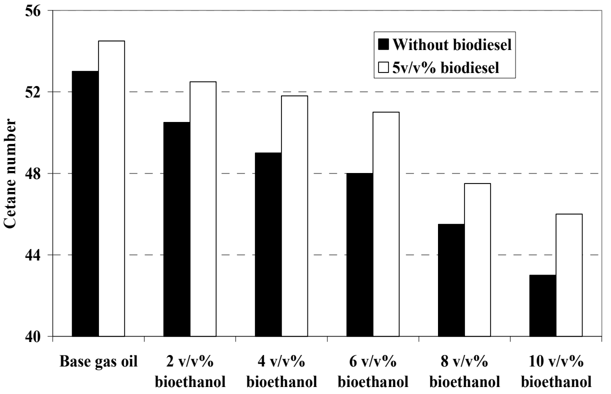

Figure 12: Change of cetane number of bioethanol/gas oil and/or biodiesel emulsions as a function bioethanol content (biodiesel content of base gas oil: 5v/v%)

Cetane number of 6v/v% bioethanol containing bioethanol/gas oil emulsion could be increase from 48 to 51 units by the application of high cetane number biodiesel produced from improved vegetable oil.

Summary

Application of bioethanol/gas oil emulsions as fuels will probably increase in the European Union in the following decades mostly in the urban bus fleets and in the agricultural vehicle fleets.

We established that stability problems of bioethanol/gas oil emulsions can be partially compensated by the application of biodiesel. 6 v/v% bioethanol containing bioethanol/gas oil/biodiesel emulsions were stable at lower temperature due to the 5 v/v% biodiesel applied in the base gas oil.

Analytical and performance properties of bioethanol/gas oil emulsions were in many cases different from that of the base gas oil and that of the regulations of the MSZ EN 590:2004 diesel fuel standard.

We established that the decrease of kinematic viscosity and lubricity of bioethanol/gas oil/biodiesel emulsions containing 6 v/v% bioethanol were compensated by blending 5 v/v% biodiesel into the base gas oil. Furthermore, it was found that the decrease of cetane number caused by the blending of bioethanol can be partially compensated by the application of high cetane number biodiesel.

In case of blending 6 v/v% bioethanol density and kinematic viscosity of bioethanol/gas oil emulsions satisfied the requirements of the MSZ EN 590:2004 standard. However, flash point and Reid vapour pressure values of the emulsions were off the limits. In order the overcome this problem, the literature suggests the installation of a flame arrester in the fuel tank of the vehicle

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