Study on Stability of Ethanol/Diesel Fuel Blend

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Abstract

According to Directive 2003/30/EC of the European Union transportation fuels shall contain biomass-derived components in at least 5.75% concentration calculated on energy content. A possibility to meet this target value is the application of ethanol/diesel fuel blends in Diesel engines facilitating the significant reduction of particulate emissions of vehicles. Application of ethanol/diesel fuel blends would be practical, since bioethanol production capacity is rapidly increasing both in the world and in the European Union.

One of the barriers of the application of ethanol/diesel fuel blends is their stability, which is influenced by temperature, water content, type of additive, bioethanol content and characteristics of the base gas oil (especially hydrocarbon composition).

The effect of temperature, water content, bioethanol concentration, application of biodiesel (RME: repeased-oil-methyl-ester) in various concentration on the stability of bioethanol/diesel fuel blends prepared from base gas oil and various additives was studied in the paper. Additionally, analytical and performance characteristics of bioethanol/diesel fuel blends was evaluated in comparison with those of diesel fuels.

It was found that preparation conditions and base gas oil composition has great influence on the stability of bioethanol/diesel fuel blends. As water content of the blends increased the stability of the blends dropped. The following changes were observed when blends containing 5% bioethanol were prepared form the base gas oil: density slightly decreased; kinematical viscosity slightly decreased; flash point significantly increased (from 75°C to 15°C); CFPP remained unchanged; Reid vapor pressure significantly increased (from 0.65 kPa to 13.4 kPa), cetane number decreased (from 54 to 50) and lubricity marginally improved due to the application of the surfactant used to establish the emulsion. The stability of bioethanol/diesel fuel blends without additive was improved in case of RME in various concentrations.

Keywords: bioethanol, bioethanol/gas oil fuel blend, biodiesel, emulsion, stability

1. 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 fuel in the production [Full Report, 2004]. Among other things, these changes were driven by the reduction of the vehicles' regulated emission, abetment of greenhouse gas emissions, tightening fuel specifications, the significantly higher of crude oil prices, efforts to reduce the dependency on imported crude oil and the increasing utilization of renewable energy sources. [Crockwell, 2005].

The use of biomass-derived fuels has been considerably increasing in the European Union in the last years and this tendency is expected to grow in the near future [Peeples, 2006]. According to Directive 2003/30/EC of the European Union transportation fuels shall contain biomass-derived components in at least 5.75% concentration calculated on energy content. Out of the biomass-based engine fuels, which are suitable to operate diesel engines, biodiesel (vegetable oil fatty acid methyl esters) become the most wide-spread in the European Union. However, the bioethanol is also important possibility to increase the concentration of bio-derived component in diesel fuel. There are several options of the application of bioethanol in diesel engines. The most important facilities are the follows:

- bioethanol/gas oil and/or biodiesel solution,
- bioethanol/gas oil and/or biodiesel emulsion,
- bioethanol injection,
- binary injection of bioethanol and diesel fuel,
- application of bioethanol alone with cetane booster additive,
- adaptation of diesel engine to use bioethanol.

In case of solution beside bioethanol and gas oil there is a co-solvent for example biodiesel. The emulsion or disperse systems are consists of phases or non- and partially miscible liquids. There are micro- (0,01-0,1μm) and macro-emulsions (0,1-10μm) based on the diameter of balls of partially dispersed liquids.

The investigation of bioethanol-diesel fuel and/or biodiesel blends or emulsions as possible fuels to be applied in Diesel engines is also of increasing importance [Lü, 2004, Weber, 2006]. This is constrained by the stability of these emulsions, which is highly dependent on temperature, water content [Fredriksson, 2006, Hansen, 2005], presence of biodiesel and/or of other co-solvent in the mixture, type and concentration of stabilizing additive and hydrocarbon composition of the base gas oil [De-Gang, 2005, Varga, 2006].

2. Experimental

The main objective of our research work was to determine the effect of temperature, ethanol content, presence of biodiesel and concentration of stabilizing additive on the stability of bioethanol/diesel fuel and/or biodiesel blends and emulsions. Besides, we studied the properties (primarily density, kinematical viscosity, lubricity, Reid vapor pressure, cold filter plugging point, etc.) of the bioethanol/diesel fuel blends in function of bioethanol content, in comparison with the specifications of the diesel fuel standard (EN 590: 2004) and with the corresponding properties of the base diesel fuel.

Characteristics of the base gas oil used to prepare the studied samples were summarized in table 1. Characteristics of bioethanol and biodiesel were given in table 2 and table 3.

Characteristics	**Data**
Density @ 15°C, kg/m^3	837.2
Sulphur content, ppmw	5
Nitrogen content, ppmw	1
Aromatic content, %	
mono	21.9
di	2.0
poly	0.3
total	24.2
Kinematic viscosity @ 40°C, mm^2/s	2.60
CFPP*, °C	-10
Cloud point, °C	-10
Pour point, °C	-22
Flash point (Pensky-Martens), °C	64
Distillation properties, °C	
IBP**	184
10 v/v%	219
30 v/v%	246
50 v/v%	271
70 v/v%	299
90 v/v%	335
FBP***	356
Cetane index	51.1
BMCI****	29.2
Cetane number	52.5

*CFPP: Cold filter plugging point
**IBP: Initial boiling point
***FBP: Final boiling point
****BMCI: Bureau of Mines Correlation Index

Table 1: Characteristics of the base gas oil

Characteristics	**Data**
Relative molecular mass	46.07
Carbon content, %	52.14
Hydrogen content, %	13.13
Oxygen content, %	34.73
Sulfur content, ppmw	<1
Density @ 15ºC, kg/m^3	789.3
Boiling point @ 101.3 kPa) ºC	78.5
Heating value, MJ/l	21.1
Flash point, ºC	12.8
Reid vapor pressure, kPa	15.9

Table 2: Characteristics of the bioethanol sample

A tridecanol based additive (MX 1625) was use to prepare the emulsion samples. Characteristics of the prepared samples were determined or calculated by standard test methods, which were listed in table 4.

Characteristics	Data
Ester content %	99.2
Density, @ 15°C, kg/m^3	885
Kinematic viscosity, @ 40°C, mm^2/s	4.5
Flash point, °C	132
Oxidation stability, @ 110°C, h	13
Acid value, mg KOH/g	0.3
Iodine value, g Iodine/100g	84
Cold filter plugging point, °C	-12

Table 3: Characteristics of the biodiesel sample

Characteristics	Standard test methods
Density	EN ISO 3675
Kinematic viscosity @ 40°C	EN ISO 3104
Flash point	EN ISO 2719
Cold filter plugging point	EN 116
Cloud point	EN 23015
Reid vapor pressure	EN 13016-1
Lubricity (four ball test)	ASTM D 2783-88
Sulphur content	EN ISO 20846
Aromatic content	EN 12916
Distillation properties	EN ISO 3405
Cetane index	EN ISO 4264
Cetane number	EN ISO 5165
Ester content	EN 14103
Oxidation stability	EN 14112
Acid value	EN 14104
Iodine value	EN 14111

Table 5: Standard test methods

3. Results and discussion

Preparation of the blends 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 3x24 hours in a measuring tube of 100 cm^3 closed with a glass stopper.

3.1. Study on the stability of bioethanol/diesel fuel blends and emulsions

The products prepared in the experiments were solutions, which were studied for stability. The results of the stability test in case of various concentration of the stabilizing additive are represented in figure 1 and 2. Figure 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% bioethnol in the solution. The decrease of temperature had a negative effect on the amount of dissolved bioethanol, as expected.

Beside the effect of additive concentration and temperature that of biodiesel, as a potential co-solvent, was also investigated. These results are presented in figure 3, 4 and 5. All the blends contained 15 v/v % bioethanol. The amount of biodiesel was varied between 3-21 v/v% while the additive concentration was adjusted to 0-2%. The biodiesel co-solvent significantly enhanced the stability of the blend, i.e. 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. Figure 3 shows that the blend was able to dissolve 15 v/v% bioethanol at 20°C temperature even without additive after blending 21 v/v% biodiesel. Stability of the blends necessarily increased with the concentration of the additive (figure 6).

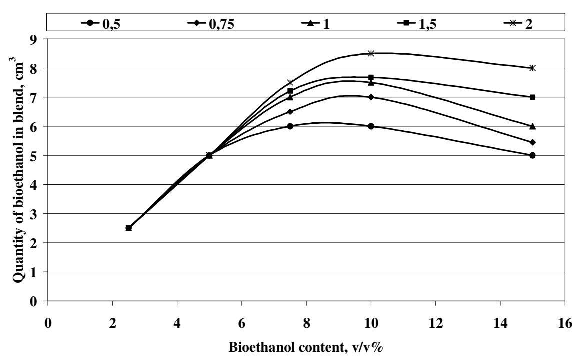

Figure 1: Stability of bioethanol/ gas oil blends (test temperature: 20°C)

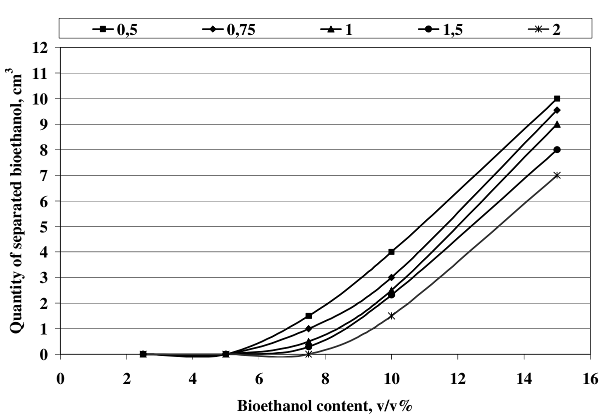

Figure 2: Stability of bioethanol/ gas oil blends (test temperature: 20°C)

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 a temperature of 1°C but the presence of 5% biodiesel facilitated the admixture at low temperature.

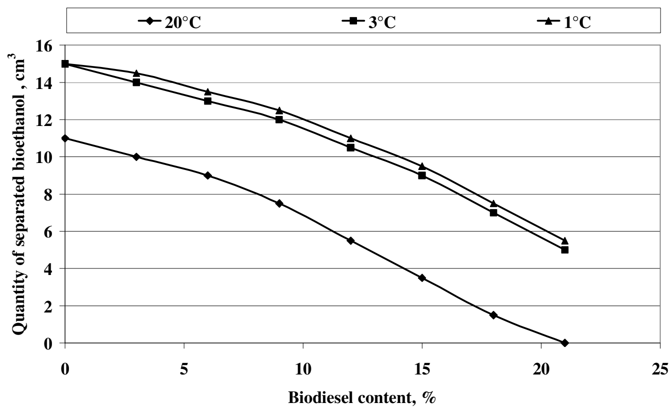

Figure 3: Effect of biodiesel concentration and temperature on the stability of bioethanol/gas oil/biodiesel blends (no additive; amount of bioethanol: 15 v/v%)

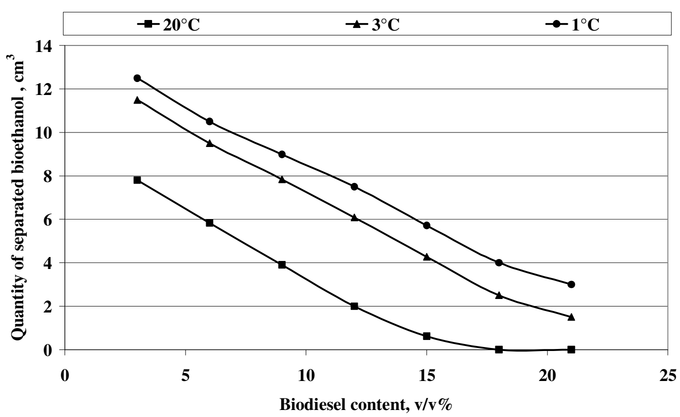

Figure 4: Effect of biodiesel concentration and temperature on the stability of bioethanol/gas oil/biodiesel blends (1% additive; amount of bioethanol: 15 v/v%)

This finding is important, because the 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 blend meaning that the low temperature might occurring during the storage or transportation will not cause phase separation.

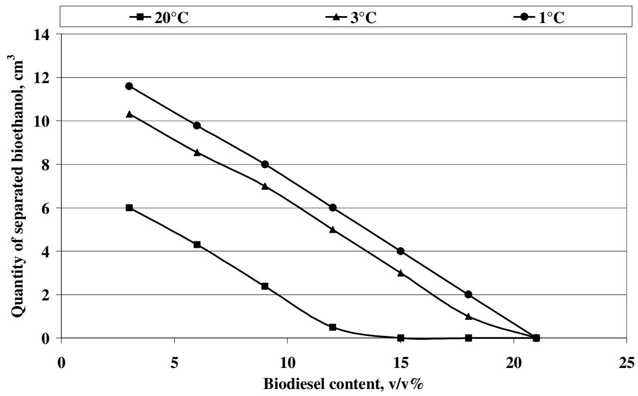

Figure 5: Effect of biodiesel concentration and temperature on the stability of bioethanol/gas oil/biodiesel blends (2% additive; 15 v/v% bioethanol)

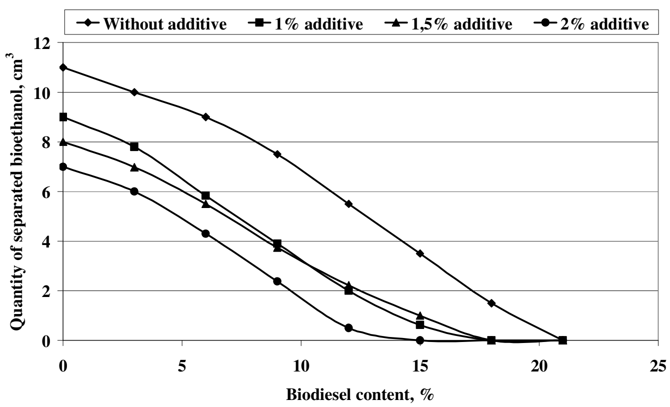

Figure 6: Effect of additive and biodiesel concentration on on the stability of bioethanol/gas oil/biodiesel blends (temperatue: 20°C; 15 v/v% bioethanol)

3.2. Study on the analytical characteristics of bioethanol/diesel fuel blends

Density of the base gas oil used for the blending was 0.8372 g/cm3 at 15°C-on. Density of the blends was lower due to the addition of ethanol having a lower density (figure 7). Density of the blends containing up to 10 v/v% bioethanol has met the specification (0.820-0.845)

Viscosity of the base gas oil measured at 40°C was 2.60 mm2/s, which dropped to 2.18 mm2/s after blendin 10 v/v% bioethanol. The presence of biodiesel slightly increased the kinematical viscosity, as expected (figure 8). The measures viscosity values have met the specifications (2.0-4.5 mm2/s) of the diesel fuel standard.

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 (figure 9). 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 the overcome this problem, the literature suggests the installation of a flame arrester in the fuel tank of the vehicle.

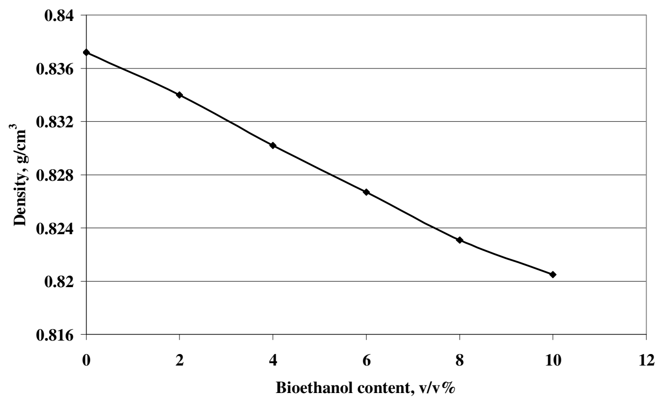

Figure 7: Effect of bioethanol content on density (15.6°C)

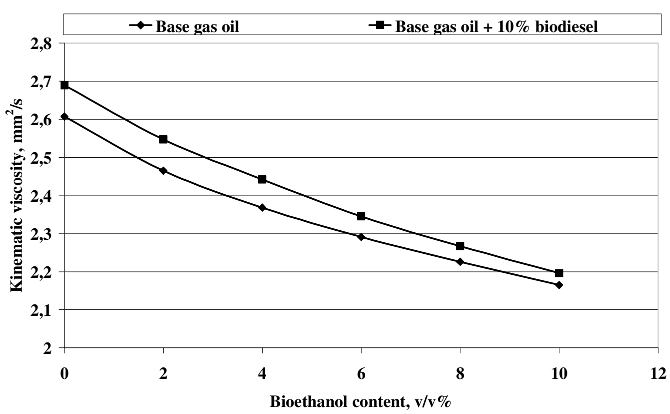

Figure 8: Effect of bioethanol and biodiesel content on the kinematical viscosity (40°C) of bioethanol/diesel fuel blends

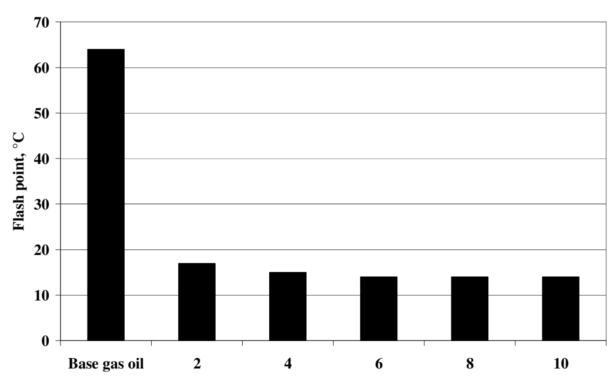

Figure 9: Effect of bioethanol content on flash point

Among cold properties the CFPP values decreased only slightly, pour point also decreased greatly and cloud point greatly increased as a result of bioethanol blending. CFPP values became higher by 2-3°C in the presence of biodiesel (Table 6).

Bioethanol concentration, 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

Table 6: The effect of bioethanol concentration on cold properties of gas oil

Normally, vapor pressure of gas oils is not measure, because it is very low. However, the blending of bioethanol has significantly increased the vapor pressure of the base fuel as already projected in the literature. Reid vapor 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 twenty times higher RVP of the gas oil/ethanol blend can even result in vapor lock formation in the fuel supply chain of vehicles. Additionally the emission due to the evaporation loss is increased by bioethanol.

Lubricity of the ethanol/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 hours. The obtained results are presented in figure 10 and 11. 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. This can be an issue in the vehicles, where the lubrication of the fuel pump is provided by the fuel itself.

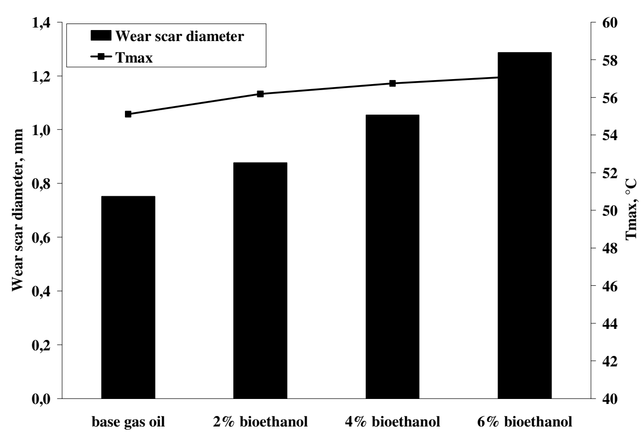

Figure 10: Lubricating properties of ethanol/diesel fuel blends

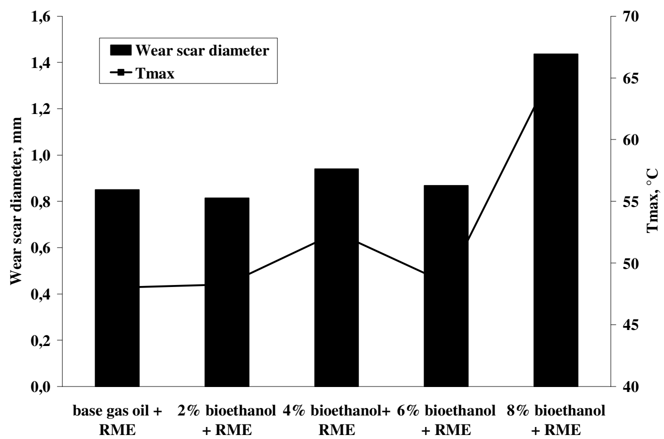

Figure 11: Lubricating properties of ethanol/diesel fuel/biodiesel blends

The loss of lubricity effect can be compensated to a certain level by adding biodiesel into the mixture. (figure 6). As the figure shows, the addition of 3% biodiesel highly improved anti-friction and anti-wear properties of the blends. In case of 8 % bioethanol, however, the much higher wear scars were experienced even with the biodiesel content.
The distillation properties of base gas oil greatly changed due to the lower boiling point of bioethanol (78.5°C at 101.3 kPa) (figure 12).

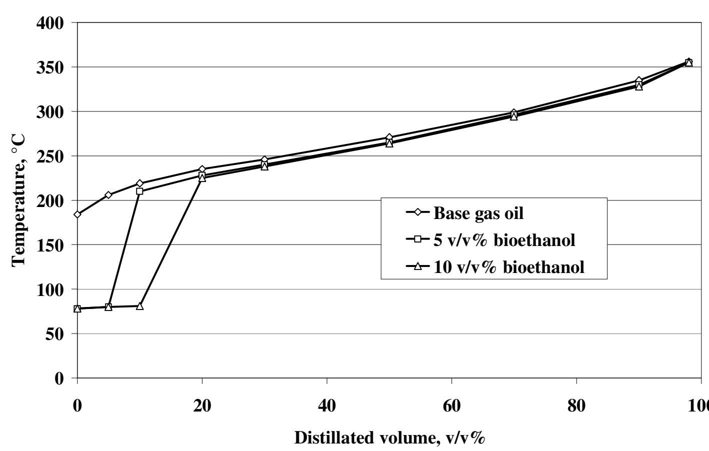

Figure 12: Distillation properties of ethanol/diesel fuel/biodiesel blends

Cetane number is an important property of diesel fuels. Due to the blending of bioethanol with gas oil the cetane number deacreased by 5-6 units (figure 13). Due to the loss in cetane number use of cetane boosters (ethyl-hexyl-nitrate) is needed.

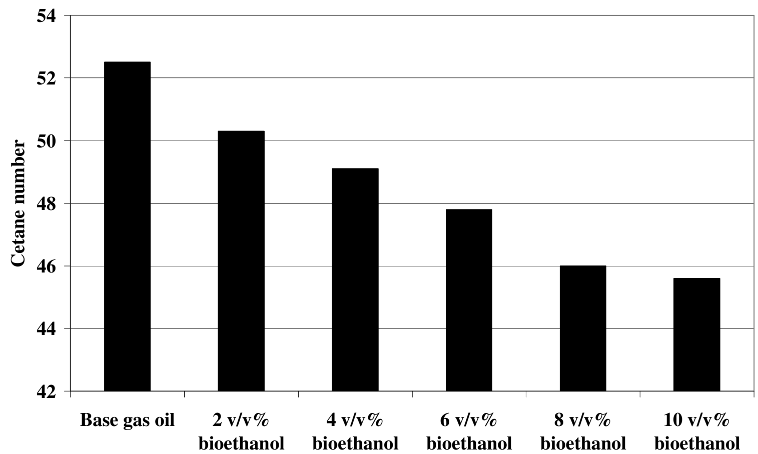

Figure 13: Cetane number of ethanol/gas oil/biodiesel blends

The performance of diesel engine is affected by the energy content of diesel fuel. The heating value of bioethanol/gas oil blends with different concentration of bioethanol is summarized in the table 7. It is clear the heating value of bioethanol is lower than that of base gas oil by 42%. This means the increase of fuel consumption. .

Blends	Heating value, MJ/dm^3	Loss of heating value, %
Base gas oil	38.2	-
5 v/v% bioethanol	36.4	0.5
10 v/v% bioethanol	35.2	3.8
15 v/v% bioethanol	34.4	6.0
Bioethanol	21.2	42.1

Table 7: The change of heating value of bioethanol/gas oil fuel blends as a function of bioethanol content

4. Summary

The application of gas oil/bioethanol blends as automotive fuels will probably increase in the next decade, primarily in the bus fleet of urban mass transportation. Stability issues of these blends (low temperature, water content, etc.) can be partly solved by co-blending biodiesel, which act a co-solvent in the dissolving of bioethanol in gas oil.

Utilization of bioethanol/gas oil blends as automotive fuels is also hampered by the very dissimilar characteristics of the blends and diesel fuels. The most important ones are probably the vapour pressure and flash point, which might be handled by installing flame arresters in the vehicles fuel supply system. The loss of kinematical viscosity and lubricity can be partly regained by co-blending biodiesel and/or with the application of stabilizing additive.

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