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INCREASING THE STABILITY OF BIOETHANOL/GAS OIL EMULSIONS BY A NEW EMULSION ADDITIVE

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Abstract

The application of bioethanol/diesel fuel emulsions is constrained by several factors (e.g. hydrocarbon composition of base gas oil, temperature, concentration and water content of bioethanol, presence of co-solvent, quality and quantity of the applied additive). The focus of our development work was to study the effect of a new chemical structure additive (fatty-acid-methyl-ester containing polyisobutylene-succinic derived) and co-solvent (fatty-acid-alkyl-esters and different carbon number alcohols) on the stability of bioethanol/gas oil emulsion, and to produce stable emulsions even in case of low temperature (−20°C) and presence of water (5.0% water containing bioethanol). It was found that high stability bioethanol/gas oil emulsion could be produced with 5.0 v/v% biodiesel as co-solvent in base gas oil and 4.0% new chemical structure additive, which was stable at the temperature of -20°C and in the presence of 5.0 v/v% water containing bioethanol.

Keywords: bioethanol; diesel fuel; emulsion; emulsion additive.

1. Introduction

In the last couple of years the significance of biofuels has been increased in the European Union and in the world. Therefore the mobility, which is one of the most important pillars of sustainable development, has been facing several new challenges [1,2,3].

Out of the biomass-based engine fuels, which are suitable to operate diesel engines, biodiesel (vegetable oil fatty acid methyl esters) has become the most wide-spread in the European Union. However further increasing the share of biodiesel has several disadvantages due to technical and economical reasons (up to 7.0 v/v% biodiesel is allowed by the EN 590:2009 standard). Therefore nowadays one of the main focuses of development is the partial replacement of this biofuel [4-8]. One of the possible solutions is to use bioethanol/gas oil emulsions [9], which have several advantages, namely the greater availability of raw materials of bioethanol compared to the vegetable oils, as well as the lower vehicle emissions due to the higher concentration of oxygen [10-13]. However the wide-spread use of bioethanol/gas oil emulsions is constrained by several factors derived from their stability, physical-chemical and performance properties [14-19]; however these problems can be eliminated by focused research and development work. Therefore the mentioned bioethanol/gas oil emulsions are one of the further possibilities for increasing the share of biomass-derived fuels, and for meeting the target biofuel ratio (10% in 2020), specified by the European Union.

Based on the foregoing, the main objectives of the research and development work were to contribute to the production and application of bioethanol/gas oil emulsions which are suitable in moderate climate conditions (ambient temperature, base gas oil composition, etc). In the framework of this several factors were investigated affecting the stability of the emulsions. For increasing the stability of these emulsions, an originally structured, self-developed polyisobutylene succinic derived detergent additive was applied [20, 21], which has fatty acid methyl ester as a molecule component.

2. Experimental

The bioethanol/gas oil emulsions were produced by practically heteroatom free, reduced aromatic content base gas oil, and by bioethanol satisfying the current requirements (EN 15376:2008). The properties of the base gas oil and the bioethanol were determined by standard test methods according to EN 590:2009, and EN 15376:2008 standards. The corrosion properties of the base gas oil and the emulsions were determined by the steel pin method (ASTM D 6138-07).

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
Total aromatic content, %	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 number	52.5

**CFPP: Cold Filter Plugging Point*

The emulsions were produced by an originally structured, fatty acid methyl ester containing polyisobutene-succinic-derived additive („I" additive) (Figure 1. [20,21]). The performance of this additive was compared to other commercial ones: tridecanol („II"), fatty-alcohol („III") and polyalkyl-succinimide („IV") based additives.

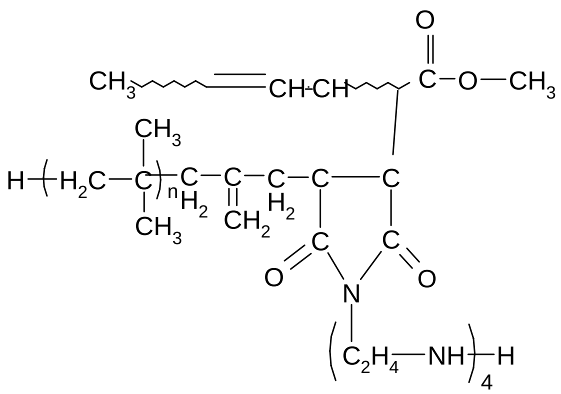

Figure 1. Molecule structure of the self-developed additive

The concentration of the additives, additive compositions, co-solvents and alcohols were changed in the following range:

- additive: based on base gas oil 0.5-5.0%,
- alcohol: based on the emulsions 1-20 v/v%,
- fatty-acid-alcyl-esters: based on base gas oil 3-20 v/v%.

The water content of the bioethanol was varied between 1.0-5.0 v/v%. The preparation of the emulsions was carried out with mechanical stirrer equipment at medium speed (3000 rpm) to produce the microemulsions. The duration of the agitation was 10 minutes in case of all samples. After the agitation, the samples were left at room temperature for 7x24 hours in a measuring tube of 100 cm^3 volume. The stability of the emulsions was investigated in the temperature range between (-20) – (+20)°C (the temperature range of moderate climate condition).

The stability of the emulsions was characterized by separation ratio (SR), which is the ratio of the separated bioethanol in equilibrium condition and the concentration of the initial bioethanol (equation 1.):

$$SR = V_{et,sep} / V_{et,i} \qquad (1)$$

where: SR – separation ratio, $V_{et,sep}$ – separated bioethanol in equilibrium condition, v/v%, $V_{et,i}$ – initial bioethanol content, v/v%.

The separation ratio is between 0 and 1, which was increased by the separation ratio, i.e. it increased the instability of the emulsions.

3. Results and discussion

First the effects of the quantity of the self-developed, originally structured, fatty acid methyl ester containing polyisobutene-succinic derived additives and other reference additives, the quantity and quality of the present co-solvents, the temperature and the water content of the bioethanol on the stability of the emulsions were investigated. The main focus was to produce a stable emulsion even in case of the moderate climate conditions (to −20°C) and in the presence of relatively high water containing bioethanol (about 5.0 v/v%).

Emulsions containing 0.5-2.0 % additive and 10.0 v/v% bioethanol were prepared to study the effect of the self-developed additive on the stability of the emulsions. It was found that the concentration of the additive had a strong effect on the stability of the emulsion (Figure 2.). Without any additive the base gas oil could keep maximum 2.5 v/v% bioethanol at +20°C, however this value was increased up to 9.5 v/v% with increasing the concentration of „I" additive up to 2.0%.

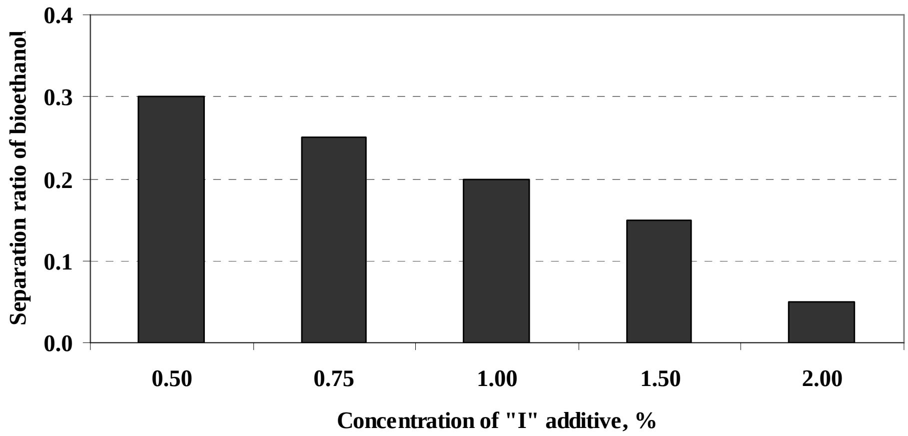

Fig. 2. Stability of bioethanol/gas oil emulsions as a function of „I" additive concentration (temperature: +20°C)

Beside the effect of the additive the stability was greatly influenced by the temperature, too (Figure 3.). Without the additive the separation ratio was 1.0 at the temperature of–20°C, i.e. the total quantity of bioethanol was dissolved from the emulsion. The separation ratio was increased from 0.2 to 0.75 by decreasing the temperature from +20°C to −20°C in case of 10.0 v/v% initial bioethanol content, i.e. the concentration of bioethanol kept in the emulsions decreased from 8.0 v/v% to 2.5 v/v%. Similar tendency was observed in case of 2.0% additive, but the decrease of the quantity of bioethanol in the emulsions was smaller (Figure 4.); at −20°C the residue bioethanol content in the emulsion was 4.0 v/v%, i.e. the self-developed, originally structured additive had high detergent performance.

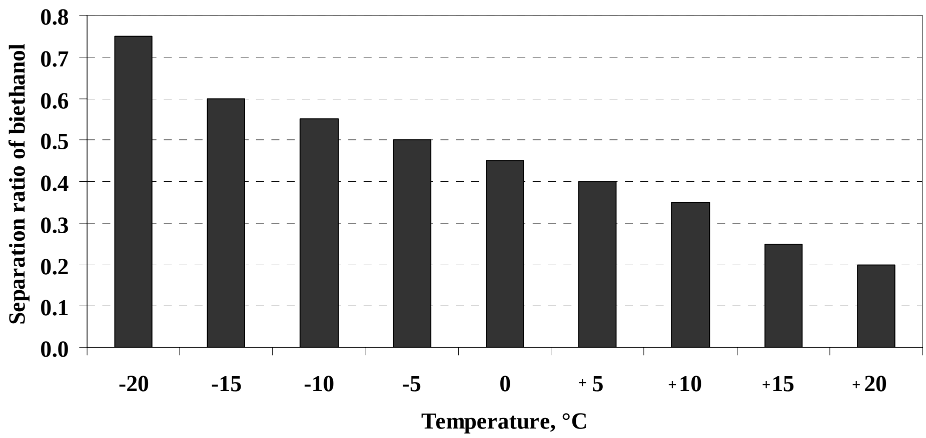

Figure 3. Stability of bioethanol/gas oil emulsions as a function of temperature (concentration of „I" additive: 1.0%)

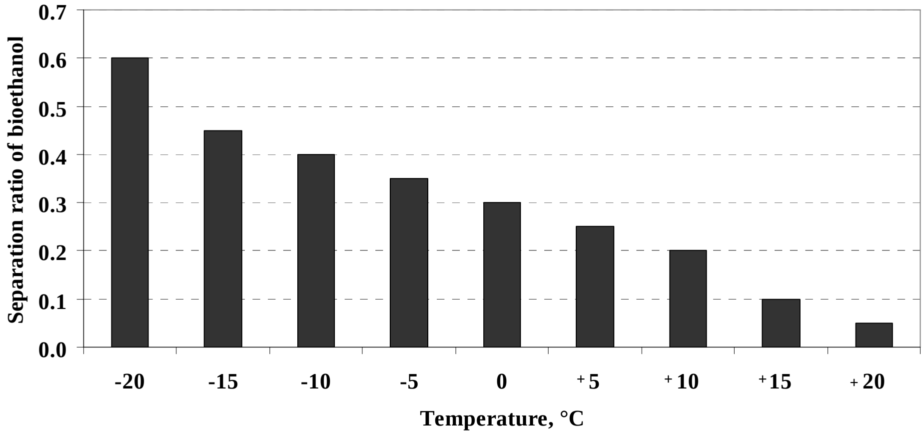

Figure 4. Stability of bioethanol/gas oil emulsions as a function of temperature (concentration of „I" additive: 2.0%)

For the comparison of the performance of the self-developed additive to reference additives the stability of emulsions was investigated by 1.0% additive and 10.0 v/v% initial bioethanol concentration (Figure 5.). It was observed that the separation ratio of the bioethanol was the lowest in case of the self-developed additive in the investigated temperature range ((–20°C) – (+20°C)), i.e. the "I" additive had the highest detergent performance. Similar tendency could be observed at 2.0 % additive concentration.

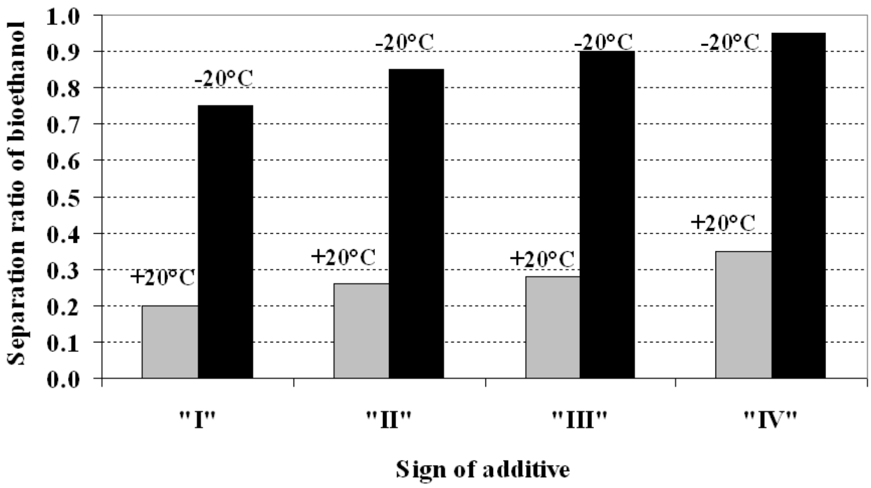

Figure 5. Comparison of the detergent performance of the additives (additive concentration: 1.0%, temperature: +20°C and –20°C, initial concentration of bioethanol: 10.0 v/v%)

For further increasing the stability of the bioethanol/gas oil emulsions the effect of co-solvents was also investigated. The most important selection criteria of co-solvents were the following:

- it should be easily mixed with gas oil,
- the presence does not cause any problem in meeting the strict requirements of gas oils (e.g. does not contain sulphur-, nitrogen- and aromatics),
- the exhaust gas does not contain poisonous agents for automotive catalysts,
- it should be compatible with other additives applied in the diesel fuels,
- preferably it should not or very slightly change the performance properties of gas oils,
- it should be compatible with the construction materials of engines (metals, alloys, etc.),
- it does not cause corrosion,
- it should be cheap and easily produced, etc.

According to the above mentioned facts the following co-solvents were investigated to increase the stability of bioethanol/gas oil emulsions:

- n-propanol,
- i-propanol,
- n-butanol,
- *tert*-butanol,
- n-1-hexanol,
- fatty acid methyl ester (biodiesel),

- fatty acid butyl ester.

It was concluded that the solvency effect of alcohol co-solvents was increased with increasing carbon number (Figure 6.). The reason of it was the better solubility of the longer non-polar hydrocarbon chain. Unlimited solvency with gas oils were observed in case of butanoles, hexanol and fatty acid alkyl esters.

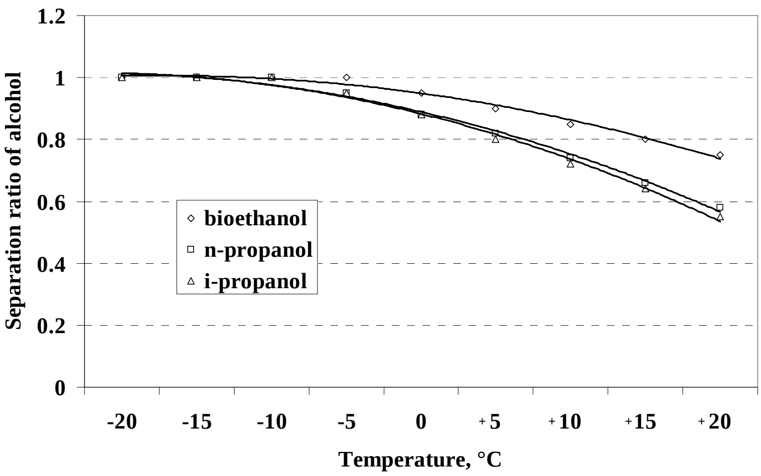

Fig. 6. Separation ratio of co-solvent in base gas oil (initial concentration of co-solvent: 10.0 v/v%; without any additive)

To further investigate the effect of co-solvents on the stability of emulsions 5.0 v/v% co-solvent containing samples were produced. It was concluded that the usage of fatty acid alkyl esters could produce the highest stability emulsions, additionally the stability increasing effect of different alcohols was increased with longer carbon chain (separation ratio was 0.65 in case of *tert*-butanol and it was 0.56 with using n-1-hexanol) (Figure 7.). The separation ratio was decreased to 0.49 unit in case of fatty acid methyl ester. However the difference was negligible between the stability increasing effect of fatty acid methyl- and fatty acid butyl esters.

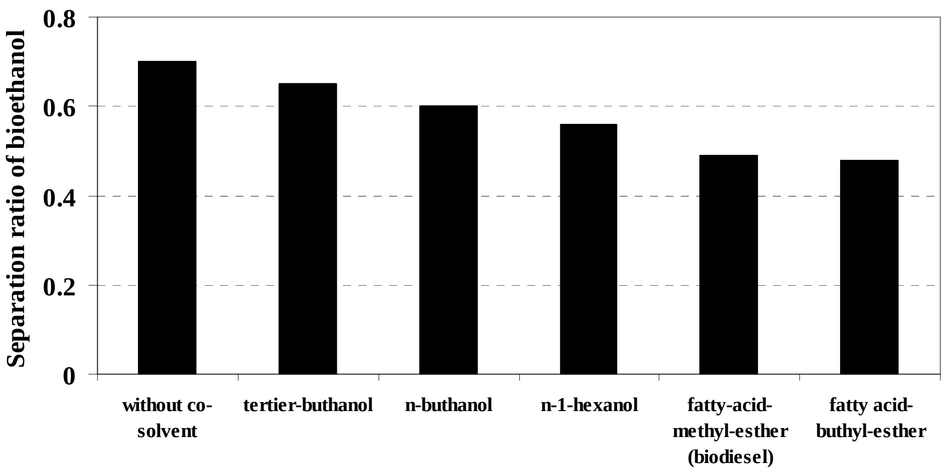

Fig. 7. The effect of co-solvents on the stability of bioethanol/gas oil emulsions (initial bioethanol concentration: 10.0 v/v%, concentration of co-solvents based on base gas oil: 5.0 v/v%, without any additive, temperature: 20°C)

This finding of the effect of fatty acid methyl ester is important, because diesel fuels containing at least 4.4 v/v% biodiesel have been marketed with tax incentives in Hungary since January 1, 2008, and the maximum allowable fatty acid methyl ester content was increased from 5.0 v/v% to 7.0 v/v% in 2009. In case of this fatty acid methyl ester content in base gas oil the separation ratio of the bioethanol in the emulsion decreased with about 0.2 unit at 10.0 v/v% initial bioethanol concentration, i.e. the kept bioethanol in the emulsion increased from 2.5 v/v% to 5.0 v/v% at +20°C.

However in case of the investigation of the effect of lower ambient temperature the separation ratio of bioethanol increased with decreasing the temperature at 10.0 v/v% initial bioethanol and 5.0 v/v% fatty acid methyl ester as co-solvent concentration (Figure 8.).

These results suggest that beside the co-solvent surfactant additive stable bioethanol/gas oil emulsions are also needed to be produced.

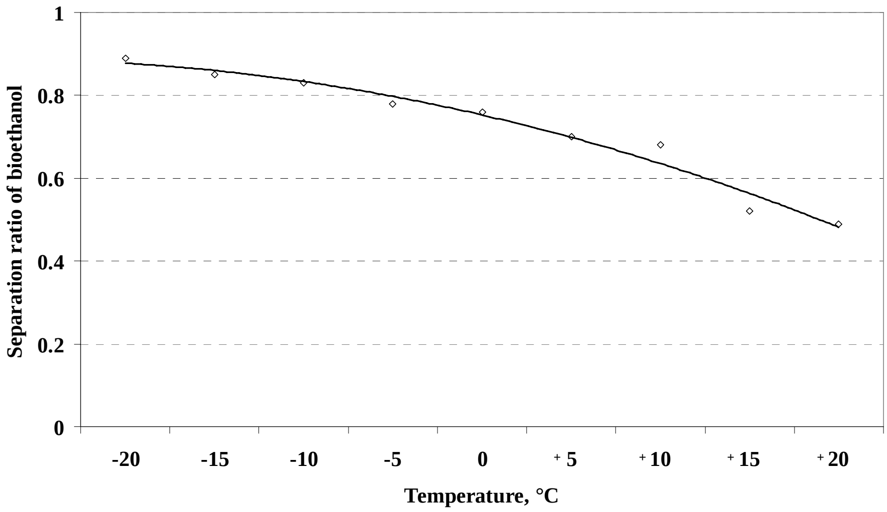

Fig. 8. Separation ratio of bioethanol as a function of temperature in case of fatty acid methyl ester containing emulsions (initial concentration of bioethanol: 10.0 v/v%, concentration of co-solvent based on base gas oil: 5.0 v/v%, without emulsifier additive)

The dependence of the stability of bioethanol/gas oil emulsions on water content of bioethanol was investigated by emulsions containing 5.0 v/v% fatty avid methyl ester as co-solvent, 0.5-2.0% „I" additive, and 1.0-5.0 v/v% content bioethanol (the initial concentration of bioethanol was 10.0 v/v%). Based on the results it was concluded that (Figure 9. and 10.) the water content of the bioethanol highly decreased the stability of the emulsions; i.e. at +20°C the separation ratio of the bioethanol increased from 0.0 to 0.6% in case of 0.5% additive, and increased from 0.0 to 0.35 in case of 2.0 %additive if the water content of the bioethanol was increased from 0.0 v/v% to 5.0 v/v%. The separation ratio of the bioethanol was also increased in a high extent with decreasing the temperature from +20°C to −20°C.

However, the curve in Figure10. illustrates that synergistic interaction occurred in case of combining the fatty acid methyl ester co-solvent and the emulsifier additive; for example at -20°C the kept bioethanol in the emulsion was 6.2 v/v%, however it was only 4.0 v/v% (Figure 4.) or 1.0 v/v% (Figure 8.) when applying the co-solvent and the additive separately.

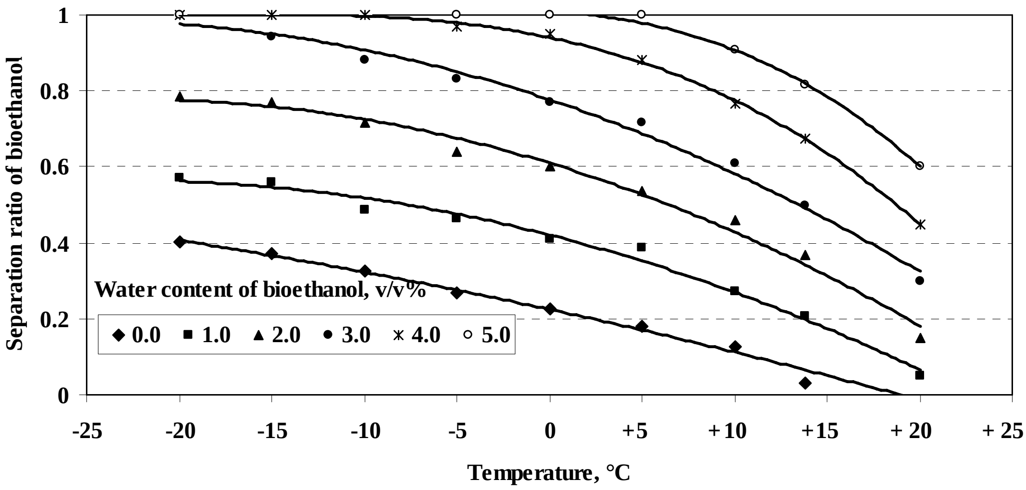

Fig. 9. Change of water containing bioethanol/gas oil emulsions as a function of temperature (initial bioethanol concentration: 10.0 v/v%, „I" marked additive concentration: 0.5%, fatty acid methyl ester concentration based on base gas oil: 5.0 v/v%)

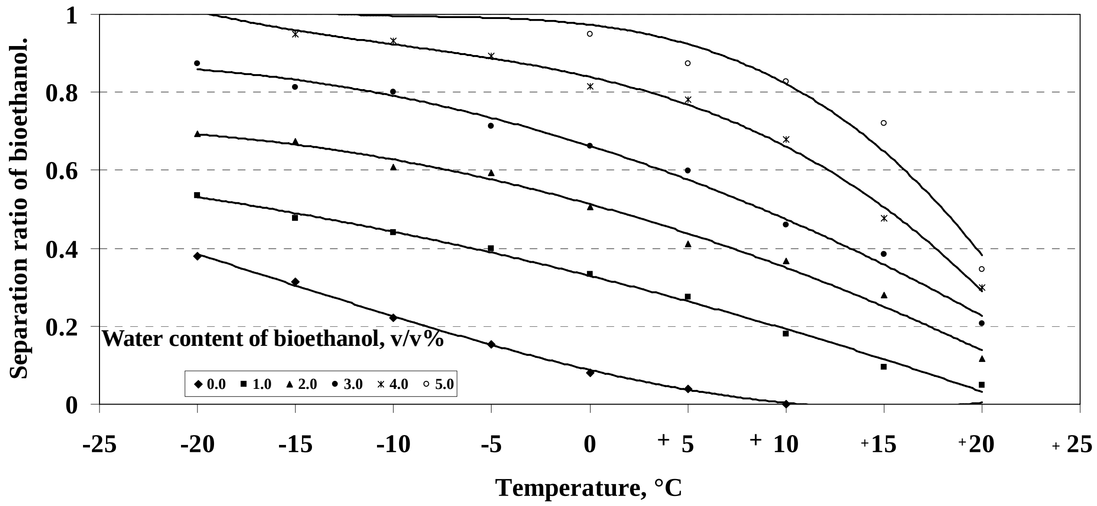

Fig. 10. Change of water containing bioethanol/gas oil emulsions as a function of temperature (initial bioethanol concentration: 10.0 v/v%, „I" marked additive concentration: 2.0%, fatty acid methyl ester concentration based on base gas oil: 5.0 v/v%)

The joint negative effect of the increasing water content and the decreasing temperature may partly be compensated by increasing the concentration of the emulsifying additive. The separation ratio decreased from 1.0 to 0.9 with increasing the „I" additive concentration from 0.5 to 2.0% at -20°C and 5.0 v/v% bioethanol concentration (Figure 11.). The rate of decrease was higher in case of increased additive concentration. It is apparent that bioethanol/gas oil emulsion with a separation ratio of 0.5 could be produced by 4.0% application of the self-developed, originally structured („I" marked) additive. This means that at -20°C and even in case of 5.0 v/v% water containing bioethanol more than 5.0 v/v% bioethanol was kept in the emulsion. This conclusion was checked with the favourable composition emulsion, which was stable after 1 week of storage time.

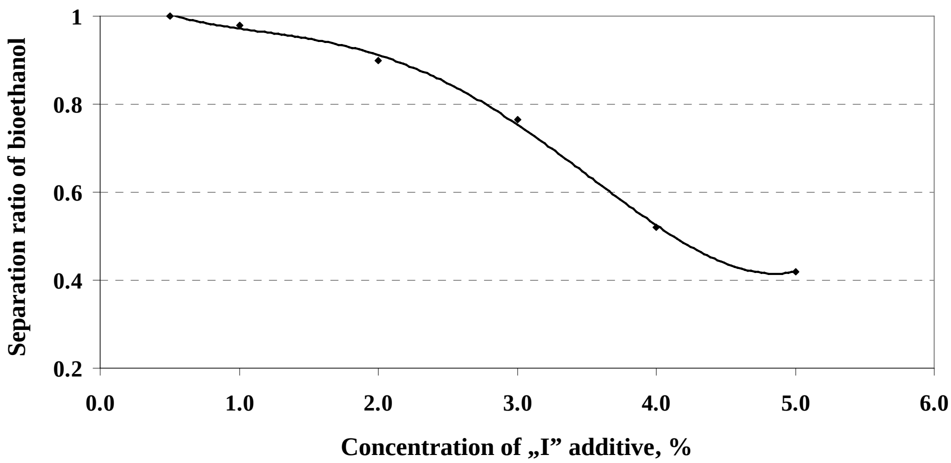

Fig. 11. Change of water containing bioethanol/gas oil emulsions as a function of temperature (initial bioethanol concentration: 10.0 v/v%, water content of bioethanol: 5.0 v/v%, marked „I" emulsifier additive, fatty acid methyl ester concentration based on base gas oil: 5.0 v/v%, temperature: -20°C)

As a result it was concluded that stable bioethanol/gas oil emulsions could be produced, which can be used at lower ambient temperature (to -20°C), with 4.0% originally structured emulsifier additive, 5.0 v/v% fatty acid methyl ester and 5.0 v/v% bioethanol (which has a relatively high water content: 5.0 v/v%). A major advantage is that it is not necessary to apply expensive dewatered bioethanol and/or the stability of the emulsions can be kept easily in case of transport, storage and distribution. In addition, corrosion tests also proved that the applied originally structured additive had a high anti-corrosive effect (Table 2). The main advantage of this function of the additive is that it prevents the corrosive effect of the water containing bioethanol, compared to common diesel fuels.

Table 2.Results of steel pin corrosion test with emulsions

Emulsion content	Corrosion rate	Corrosion degree
Base gas oil+5 v/v% FAME + 5 v/v% (5 v/v% water containing) bioethanol	Corrosion	1
Base gas oil+5 v/v% FAME + 5 v/v% (5 v/v% water containing) bioethanol +4,0% „I" additive	Non corrosive	0

4. Conclusion

In the last couple of years the significance of biofuels has been increased in the European Union and in the world. Therefore the mobility, which is one of the most important pillars of sustainable development, has been facing several new challenges, mainly in the field of the continuously increasing ratio of bio-derived blending components. One of the possible solutions to increase the share of biofuels is to use bioethanol/gas oil emulsions. However the wide-spread use of these emulsions is constrained by several factors derived from their stability, physical-chemical and performance properties.

Based on the foregoing, the main objectives of the research and development work were to contribute to the production and application of bioethanol/gas oil emulsions, which are suitable in moderate climate conditions (ambient temperature, base gas oil composition, etc).

According to the storage stability results it was concluded that even in case of 5.0 v/v% water containing bioethanol and lower ambient temperature (-20°C) stable bioethanol/gas oil emulsions could be produced by using heteroatom free and reduced aromatic content base gas oil, 5.0 v/v% high oleic acid containing fatty acid methyl ester (based on base gas oil), 4.0% originally structured emulsifier additive (based on base gas oil) and 5.0 v/v% bio-ethanol (based on the emulsion) by mechanical stirrer method. The mentioned emulsion has no corrosion effect, because the applied surfactant additive has an anticorrosion function, too.

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