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Improving the stability of bioethanol/fatty-acid-alkyl-ester/gas oil emulsions

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The aim of our research work was to prepare stable bioethanol/gas oil emulsions at low temperature (-10°C) in presence of water (1.0-3.0v/v%) by application of different additives, additive compositions and co-solvents (fatty-acid-alkyl-esters, different carbon number bioalcohols). We found that the application of 5v/v% fatty-acid-methyl-ester (FAME) as co-solvent bioethanol/gas oil emulsion containing 6v/v% bioethanol could be produced which was stable at -10°C. With the application of FAME the loss of lubricity caused by the blending of bioethanol could be compensated. With the application of an additive composition prepared from tridecanol- and polyalkyl-succinimid type additives the emulsion was stable in case of water in emulsions. Stability of the emulsions could be increased significantly by blending higher carbon number alcohol (e.g.: biobuthanol) and/or fatty-acid-alkyl-esther (e.g. fatty-acid-butil-esther) as co-solvent.

1. Introduction

In the last couple of years we have been facing several new challenges about the mobility, which is one of the most important pillars of sustainable development [Varga, 2006, Demirbas, 2007]. Among these things one of the most important factors is the production and application of biofuels [Demirbas, 2008, 2009, Varga, 2006]. In the European Union the application of biofuels has been growing in the last couple of years and this tendency will continue in the near future [Demirbas, 2008, 2009, Directive, 2003]. According to 2003/30/EC EU directive motor fuels should contain 5.75% bio-derived components in 2010. Nowadays biodiesel (fatty-acid-methyl-ester) has been spreading in a wide extent in the European Union, however bioethanol/gas oil emulsions could be one of the possible solutions to increase more the share of bio-derived components [Demirbas, 2008, Varga, 2006]. The main advantage of these emulsions is the lower exhaust gas emission (essentially hydrocarbon and particulate matter), which is caused by their higher oxygen content [Corro, 2008, Kim, 2008, Di, 2009]. Their main disadvantage is their poor stability [Lapuerta, 2007, Hansen, 2005, De-Gang, 2006, Fredriksson, 2006], which is influenced by numerous factors (e.g. hydrocarbon composition of base gas oil, water content of bioethanol, quantity and quality of emulsive additive, application of co-solvent and temperature). For solving

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these problems the aim our research work was to produce stable bioethanol/gas oil emulsions in case of low temperature (up to -10°C) and high water content bioethanol (3,0v/v%) with the application of different additives, additive compositions and co-solvents (different fatty-acid-alky-esters and different carbon chain alcohols).

2. Experimental

A prehydrogenated gas oil fraction was used for the production of bioethanol/gas oil/fatty-acid-alkyl-ester emulsions (5 mgS/kg, 1 mgN/kg, total aromatic content: 24.2%). The properties of the applied fatty-acid-methyl-ester and bioethanol satisfied the requirement of EN 14214:2003 and EN 15376:2007 standards. Characteristics of the prepared samples, base gas oil, bioalcohols and fatty-acid-alkyl-esters were determined or calculated by standard test methods. Preparation of the emulsions was carried out with magnetic agitator equipment at medium speed (600-700 rpm). The duration of the 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 following different additives and additive-compositions were used for preparing the bioethanol/gas oil emulsions: „A" – tridecanol based additive, „B" – fatty-alcohol + 5% ethylene-oxide, „C" – polyalkyl-succinimide based additive, 50-50% mixed „A" and „B" ("AB"), 50-50% mixed „A" and „C" ("AC"). Fatty-acid-butyl-ester was produced from n-butanol and vegetable oil, which is used for production of fatty-acid-methyl-ester with acidic esterification at 110°C. The additives and additive-compositions were used in 0.0-3.0% concentration referring to base gas oil, bioalcohols in 0-20v/v% and fatty-acid-alkyl-esters in 0-20v/v% concentration referring to base gas oil. The stability of samples was investigated in the temperature range of (-10) – (+20)°C, water content of bioalcohol was varied between 0.0-3.0v/v%.

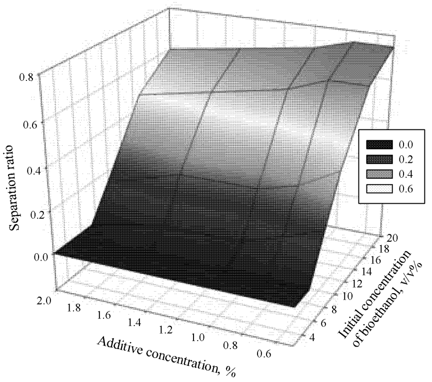
3. Results and discussion

The effect of quantity of tridecanol based "A" additive on stability of bioethanol/gas oil emulsions is shown in Figure 1. The stability of emulsions was characterized by the separation ratio (SR), which is the ratio of separated bioethanol in equilibrium condition and concentration of initial bioethanol concentration (equation 1.).

$$SR = V_{EtOH,sep} / V_{EtOH,i} , \quad (1)$$

where: SR – separation ratio, $V_{EtOH,sep}$ – separated bioethanol in equilibrium condition (v/v%), $V_{EtOH,i}$ – initial bioethanol concentration (v/v%).

The concentration of bioethanol kept in the emulsion is strongly affected by the volume of emulsive additive. The base gas oil without any additive was only able to keep maximum 3 v/v% bioethanol in solution. This value increased to 8.5% with increasing the concentration of the additive. The bioethanol kept in emulsion decreased from 8.2% to 4.6% with decreasing the temperature from 20°C to -10°C (Figure 2.). The fatty-acid-methyl-ester co-solvent significantly enhanced the stability of the emulsions, caused by the unlimited solvency of fatty-acid-methyl-ester and bioethanol. It can be observed that the reduction of temperature had a negative effect on the separation ratio of bioethanol even in the presence of fatty-acid-methyl-ester.



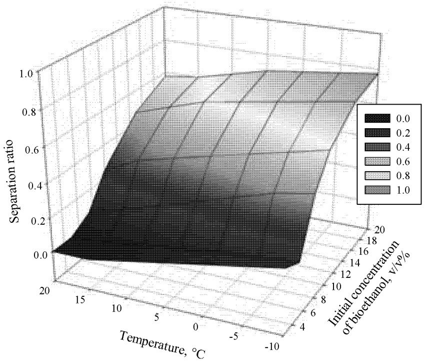


Figure 1: The changes of the stability of bioethanol/gas oil emulsions („A" additive, temperature: 20°C)

Figure 2: The changes of the stability of bioethanol/gas oil emulsions (1% „A" additive)

Without the use of additives, bioethanol did not dissolve into the base gas oil at -10°C, but the presence of 4-5v/v% fatty-acid-methyl-ester decreased the separation ratio. It could be observed that the stability of emulsions increased due to the application of fatty-acid-methyl-ester in low quantity (4-5v/v%). Minimum 4.4v/v% fatty-acid-methyl-ester containing base gas oil was able to keep 1.8% more bioethanol in emulsion under the same conditions. This observation is important, because diesel fuels containing fatty-acid-methyl-ester can be marketed only in EU (in Hungary 4.4v/v%) beginning with January 1, 2008. Fatty-acid-methyl-ester as co-solvent could improve the stability of bioethanol/gas oil/fatty-acid-methyl-ester emulsions meaning that the low temperature (-10 - +20°C) might occurring during the storage or transportation will not cause phase separation in case of bioethanol up to 8v/v%. The decrease of the positive effect caused by the aromatic hydrocarbons on stability of bioethanol/gas oil emulsions (because of the requirements of modern diesel fuels) could also be partially compensated with fatty-acid-methyl-ester.

Beside the temperature the stability of bioethanol/gas oil emulsions was significantly influenced by the water content of bioethanol. The support of anhydrous logistic system for transportation, handling, distribution and storage of bioethanol/gas oil emulsions would be expensive. Therefore, the aim of our research work was to find an additive or additive composition to stabilize these emulsions in low temperature in case of bioethanol containing water. The highest stability of bioethanol/gas oil emulsions with „AC" additive composition could be produced. The main advantages of bioethanol/gas oil/fatty-acid-methyl-ester emulsions containing 2% of the above mentioned "AC" additive composition and 5v/v% fatty-acid-methyl-ester is their high stability in case of low temperature (-10°C) and presence of 3.0v/v% water in bioethanol (Figure 3., 4.). During the application of these emulsions it is not necessary to use anhydrous system for transportation, storage, handling and distribution even in case of low temperature. It can be concluded that due to the synergic effect of these additives this additive composition had higher performance than the emulsions containing "A" or "C" additive separately in same concentration.

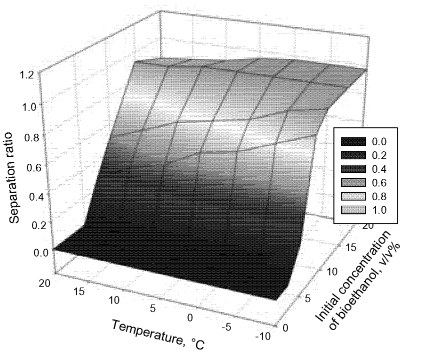


Figure 3: The changes of the stability of bioethanol/gas oil emulsions (2% „AC" additive composition, water content of bioethanol: 3v/v%)

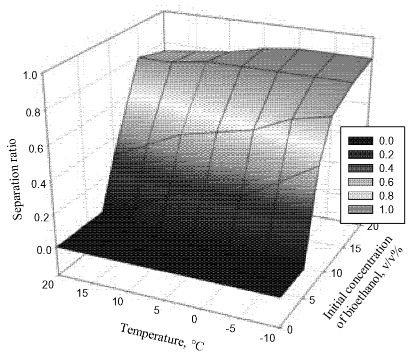


Figure 4: The changes of the stability of bioethanol/gas oil emulsions/fatty-acid-methyl-ester emulsions (2% „AC" additive composition, water content of bioethanol: 3v/v%, concentration of fatty-acid-methyl-ester: 5v/v%)

It was observed that bioethanol concentration of bioethanol/gas oil/fatty-acid-methyl-ester emulsions in equilibrium was also affected by the initial concentration of bioethanol according to equation 2 [Fernando, 2004]. Therefore miscibility of bioethanol and gas oil was described by the mean solubility (S) (equation 3.), which was calculated as the average of bioethanol concentrations remaining in the emulsions after phase separation (in equilibrium) obtained from a number of experiment with different initial bioethanol concentration in constant temperature, water content of bioethanol, concentration of co-solvent and the additive.

$$c_{et} = c_{et,i}\frac{1-SR}{1-SRc_{et,i}} \quad (2); \qquad S = \frac{\sum_n c_{et}}{n} \quad (3)$$

where: SR – separation ratio, S – mean solubility (v/v%), c_{et}– concentration of bioethanol in the emulsion in equilibrium (v/v%), n – number of experiments carried out constant temperature, water content of bioethanol, concentration of co-solvent and additive, $c_{et,i}$ – initial concentration of bioethanol (v/v%).

With mean solubility the stability of bioethanol/gas oil/fatty-acid-methyl-ester emulsions in case of different conditions could be easily compared (Figure 5.). The effect of higher carbon chain biobutanol and fatty-acid-butyl-ester on stability of bioalcohol/gas oil/fatty-acid-alkyl-ester emulsions was also investigated. It was concluded that mean solubility of biobutanol and gas oil was significantly higher than that of bioethanol (Figure 6.). Without emulsive additive the base gas oil was able to keep about 6v/v% anhydrous biobutanol at low temperature (-10°C), and this value was increased to 13v/v% with increasing temperature from -10°C to 20°C. The difference of mean solubility between bioethanol and biobutanol was same even in case of blending of fatty-acid-alkyl-ester to base gas oil.

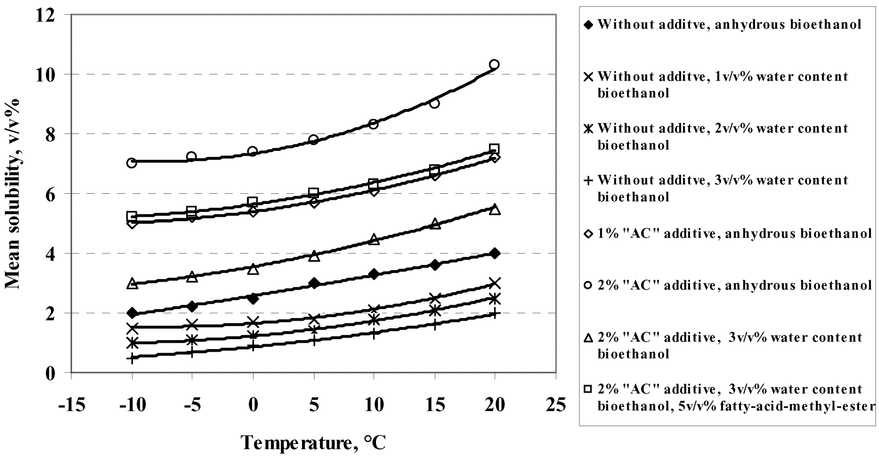


Figure 5: Stability of bioethanol/gas oil/fatty-acid-methyl-ester emulsions having different compositions as a function of temperature

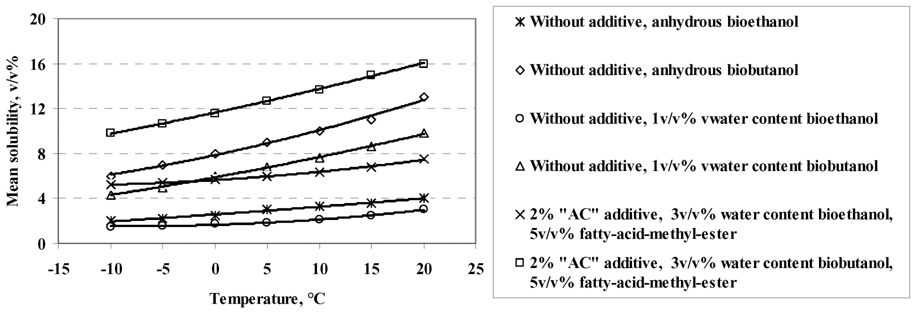


Figure 6: Stability of bioalcohol/gas oil/fatty-acid-alkyl-ester emulsions as a function of temperature

4. Conclusions

In this paper the improvement of the stability of bioalcohol/gas oil/fatty-acid-alkyl-ester emulsions was investigated. The aim of our experiments was to produce stable bioalcohol/gas oil/fatty-acid-alkyl-ester emulsions even in case of low temperature and high water content bioalcohol.

It was concluded that the mean solubility can be applied to compare the solubility of different bioalcohols and gas oil in case of investigated composition. With this value the effect of initial bioalcohol concentration on stability of emulsions could be easily eliminated. The stability problems of bioalcohol/gas oil emulsions could be partially compensated with fatty-acid-alkyl-esters. At temperature of -10°C stable bioethanol/gas oil/fatty-acid-methyl-ester emulsion could be produced with 6v/v% fatty-acid-methyl-ester even in case of 3v/v% water containing bioethanol. During the application of these emulsions it is not necessary to use anhydrous system for transportation, storage, handling and distribution even in case of low temperature. According to the results of our experimental work the main conclusions are the followings:

- the stability of emulsions greatly decreased with increasing water content of bioethanol and decreasing temperature,
- stability of emulsions is affected by the initial concentration of bioethanol, therefore the miscibility of bioethanol and gas oil was determined by the mean solubility (according to the references),
- the emulsive performance of „AC" additive composition increased by the synergic effect between the two additives,
- the mean solubility of biobutanol was significantly higher than that of bioethanol under same conditions, therefore the application of biobutanol has numerous advantages,
- stability of bioalcohol/gas oil/fatty-acid-alkyl-ester emulsions was increased more with fatty-acid-butil-ester than with fatty-acid-methyl-ester under the same conditions due to their higher solubility caused by longer alkyl-chain of bioalcohol.

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