THESIS OF PHD DISSERTATION

IMPROVING THE QUALITY OF TRIGLYCERIDE BASED MOTOR FUELS

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INTRODUCTION AND OBJECTIVES

Importance of motor fuels produced from renewable sources is increasing worldwide. Application of fuels containing bio-components is supported by several European Union directives, 2003/30/EC (Biofuels), 2009/28/EC (Renewable Energy Directive) and 2009/30/EC (Fuel Quality Directive). Nowadays, bio-components blended to diesel fuel are almost exclusively fatty acid methyl esters (FAME) produced by the catalytic transesterification of natural triglycerides (e.g.: vegetable oils, used cooking oils). The EN 590:2010 standard allows the blending of biodiesel to diesel fuel up to 7 v/v%. According to the literature and our experience, the use of biodiesels, however can cause many problems for example higher cold filter plugging point, higher viscosity, sensitivity to hydrolysis (corrosion), poor thermal and oxidation stability, storage problems, lower energy content etc. Information about the storage stability of biodiesels and that of diesel fuels containing biodiesel components is quite limited in the literature. Such data and information is crucial in terms of the proper quality of motor fuels and the appropriate strategic storage, therefore my experimental activity was concentrating partly on the analysis of long term storage stability of biodiesel and diesel fuels with 5, 7 and 10 % biodiesel content.

Application of modern additives – in particular the detergent-dispersant additives - is essential in order to ensure the appropriate application properties of biodiesels and diesel fuels containing biodiesel components. Further development of a succinimide type detergent-dispersant additive containing fatty acid methyl ester in its structure and - following a laboratory synthesis - performance of a successful production tests in a semi-industrial pilot plant were further objectives of my work. I intended to confirm the additive effectiveness also with motor tests.

Another objective of the research work was to investigate the effect of detergent-dispersant additives on the oxidation stability of biodiesel, diesel fuel and their mixture.

I investigated also the feasibility of blending bio gas oil (mixture of iso-, and normal paraffins produced from natural triglycerides in catalytic way)- a second-generation bio motor fuel – into the diesel fuel, and analyzed the efficiency of the different detergent-dispersant additives produced by me. Bio gas oil eliminates various negative features resulting from the application of biodiesels.
EXPERIMENTAL ACTIVITY

Properties of diesel fuels, biodiesels and biodiesel containing diesel fuels were measured according to the methods determined in the EN 590:2009+A1:2010 and the EN 14214:2009 standards. The samples were stored at ambient temperature for one year in metal containers isolated from light and air, they were exposed to air only during sampling. Properties of the samples were measured every two weeks.

Oxidation of one selected biodiesel sample was studied with infrared spectroscopy. Infrared spectrums of biodiesel sample were registered before and after the Rancimat induction period measurement in order to study the reactions that occur due to thermal and oxidative treatment.

In the second part of the experimental work further development of a succinimide type detergent-dispersant additive containing has fatty acid methyl ester in its structure was performed. The novel additive contains not only fatty acid methyl esters in its structure but styrene comonomer, too. After the laboratory synthesis successful production in semi-industrial pilot plant was performed. Efficiency of the additives were proved by engine test, too. Structure of the intermediate products and additives were determined by gel permeation chromatography (GPC), infrared spectroscopy (IR) and nuclear magnetic resonance (NMR) spectroscopy.

Effect of detergent-dispersant additives on the oxidation stability of diesel fuel, and 5, 7 and 10 % biodiesel containing diesel fuel was investigated. Rancimat apparatus was applied to evaluate the effect of the additives in biodiesel containing diesel fuels; meanwhile Seta TOST device for the efficiency in diesel fuel. In the literature no information was found either on the application of these apparatus for such purposes, or on the effect of detergent-dispersant additives on the improvement of oxidative stability.
1. I determined the key parameters that have to be measured regularly in case of the long term storage of diesel fuels, biodiesels and 5, 7 and 10 % biodiesel containing diesel fuels [1, 9, 10, 14]: density, kinematic viscosity, acid number, iodine number, water content, oxidative stability.

1.1. I concluded that during long term storage the primary oxidation products of biodiesel – the allilic hydroperoxides – decompose to carboxilic acids. Furthermore the hydroperoxides can react with the allilic or bis-allilic carbon atoms of the hydrocarbon chain of biodiesel and form dimers and oligomers. In such a way number of reactive double bonds decrease. It was found that fatty acid methyl esters can decompose by hydrolisis to alcohols and carboxilic acids.

1.2. I concluded that due to eventual antagonistic effects not only the quality of the blending components has to satisfy separately the requirements of the related standards, but quality of the blends prepared from them has to be also checked before releasing them for consumption purposes.

1.3. The relationship between the iodine number and Rancimat induction period enables the prediction of the storage stability of 5 and 7 % biodiesel containing diesel fuels. In case of the 10 % biodiesel containing diesel fuels the prediction has high incertanity due to that in such concentration the oxidation stability of biodiesel component highly affects the stability of the blends.

2. I studied with infrared spectroscopy the reactions that occur due to thermal and oxidative treatment of biodiesel. Spectrums of the biodiesel were registered before and after the Rancimat induction period measurement [4]:

2.1. I observed change in the 725 cm$^{-1}$ and 967 cm$^{-1}$ wave numbers, due to a slight change in the cis-trans isomer ratio.

2.2. After the oxidation I observed a wide peak in the range of 3250 and 3600 cm$^{-1}$ wave number, due to a significant increase in the amount of carbonyl and hydroxyl compounds.

3. I further developed the succinimide type detergent-dispersant additives that have fatty acid methyl ester in their molecular structure. I established that by the application of piperazine
additives could be synthesized that have low total base number but high detergent-dispersant efficiency. Based on the results of gel permeation chromatography (GPC), infrared spectroscopy (IR) and nuclear magnetic resonance (NMR) spectroscopy analysis I concluded that the developed additives are a mixture of the following molecules [2, 3, 5, 6, 8, 11, 15, 16]:

3.1. They contain molecules, in which two PIB chains or one PIB and one FAME chain are attached to one maleic anhydride, resulting in increase apolar molecular part. These molecules can keep in dispersion larger size dirt, than those where only one PIB chain is attached to one maleic anhydride.

3.2. Compounds of polyisobutylene-di-maleic anhydride can also be found in the additives when two maleic anhydrides are connected to one PIB chain, such molecules has increase polar part. This molecule contains more nitrogen, thus it has higher total base number (TBN) resulting in a higher neutralizing effect.

3.3. The additives also contain bis-succinimide type molecules, in which on one side both FAME and PIB are attached, on the other side only PIB. These molecules have higher thermal stability.

4. I established a novel synthesis method for the incorporation of fatty acid methyl ester and styrene comonomer into the structure of the polyisobutylene maleic anhydride. the novel additives proved excellent viscosity index and lubricity improving improving effect besides their proper detergent-dispersant efficiency [6, 13].

4.1. I concluded that the most suitable feedstock ratio for the incorporation of styrene comonomer the was 1,0:1,9:0,9 = polyisobutylene:maleic anhidride:styrene.

5. I concluded that blending of bio gas oil into diesel fuel reduces the lubricity of the blend, no significant change in other properties was observed. I found that the decrease of lubricity can be almost totally compensated by the application of succinimide type detergent-dispersant additives that have fatty acid methyl ester in their molecular structure. Among the tested additives those were found to be the most suitable that had both styrene comonomer and fatty acid methyl ester in their molecular structure [12].
INDUSTRIAL APPLICATION OF THE RESULTS

I concluded that the tested detergent-dispersant additives are suitable by their structure for improving the oxidation stability of diesel fuels and diesel fuels bended with 5, 7 and 10 % biodiesel component. In case of the analyzed samples the decrease in oxidation stability can be compensated with post additization. Total base number, potential detergent-dispersant effectiveness and the oxidation stability improving effect of the analyzed additives proved to be directly proportional. Higher total base number of additives improves the acid neutralizing efficiency of the additive, the proton releasing speed equals to the formation speed of peroxide free radicals and carboxylic acids, this way the additives are capable of improving the oxidation stability of diesel fuels and diesel fuels containing biodiesel components.

In case of intermediate quality diesel fuels, the 25 g/m³ limit specified by the relevant EN 590:2009+A1:2010 was met by all additives at a concentration of 250 mg/kg, while in case of winter quality diesel fuel said limit was reached solely by additive SF-1 at a 750 mg/kg concentration.

It has been established that the additives with the same quality can also be produced in industrial scale. Production test were performed in a semi-industrial pilot plant to produce intermediate products containing fatty acid methyl ester in its structure. The pilot production test was successful, the quality of the intermediate products proved to be appropriate. It has also been confirmed that the used cooking oil content of the fatty acid methyl ester had a slight negative effect on the quality of the intermediate products and of the additives. During the application of fatty acid methyl ester without used cooking oil content the 1.0:1.1:1.4 = polyisobutylene:fatty acid methy ester:maleic anhidride molar ratio was found to be the most suitable for the synthesis, while in case of fatty acid methyl ester with 30 % used cooking oil content, the molar ratio of 1.0:0.9:1.3 = polyisobutylene:fatty acid methy ester:maleic anhidride was confirmed as proper.
ARTICLES AND PRESENTATION IN THE FIELD OF THE DISSERTATION

Revised foreign journal articles:


Article published in book in foreign language:


Submitted Hungarian patent:

Revised full text presentation in international conference proceedings in English:


Revised full text presentation in Hungarian conference proceedings in Hungarian:


Abstract in international conference proceedings in English:

OTHER ARTICLES AND PRESENTATIONS IN THE FIELD OF THE TOPIC OF DISSERTATION

Revised foreign journal articles:


Revised Hungarian journal articles in Hungarian:


Revised full text presentation in international conference proceedings in English:


Revised full text presentation in Hungarian conference proceedings in Hungarian:


### SUMMARIZED PUBLICATION ACTIVITY

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* submitted for publication

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