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Development of multifunctional additives based on vegetal oils for high quality diesel and biodiesel

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1. Abstract

The increasing qualitative requirements of the fuels of modern Diesel engines can be satisfied by applying environmental friendly blending components of high energy content and additive-packages having high performance level. The aim of our experimental work was to produce vegetable oil-based multifunctional additives which have not only lubricity improver effect applying in fuel but other necessary properties can be achieved, too. Beside, our object was to use raw materials originated from partly renewable source meeting the biodegradability requirements. These synthesized additives showed same or even better detergent-dispersant properties compared to the traditional PIB-succinimides and also provided other functional effects such as corrosion inhibiting and lubricity effects.

Keywords: multifunctional additives, vegetable oil derivatives, lubricity, detergent-dispersant

1. Introduction

Engine fuels are comprised of ”green”, high quality blending components and highly efficient additives. Nowadays, application of high performance additives is essential to meet the required fuel properties and to protect the engine and the environment (Haynock, R. F., 2004).

Out of the numerous additive types, Deposit Control Additives (DCAs) are applied in the highest amount. Deposits may form in the fuel injector system of the engine. These deposits influence the emission, fuel economy, cold start behaviour, driveability and performance, too (Haynock, R. F., 2004, AAMA, ACEA, JAMA, 2002). DCAs are generally long chain hydrocarbons attached to a polar head group. Deposit precursors are attracted to the deposit control molecule, and become bounded into the dispersant miscelle. At normal operating temperatures the DCA is a liquid

that forms a thin film on the surface of the inlet system. The thin film is driven forward by air and fuel vapour flow, but forms a first line barrier to deposit precursors as well as a dispersant/neutraliser of the precursors protecting the metal surface. In the case of deposits on the metal surface, the liquid film slowly removes deposits by a detergent action. Diesel fuel detergents are predominantly based on polyisobutylene (PIB-amine, -succinimide, etc.) and other ashless polymeric products (Haynock, R. F., 2004; AAMA, ACEA, JAMA, 2002; Kajdas, C., 2003).

Diesel fuel injector pumps often rely on the fuel itself to lubricate. Formerly the lubrication function was provided by natural components in the diesel fuel (sulphur, aromatics and other heterocyclic, polar compounds) (Kajdas, C., 2003; Kajdas, C., 1999; Spikes, H., 1997). Due to environmental protection and human health reasons, the sulphur content of Diesel fuels was reduced to 50 ppm in the European Union beginning with 2005 and the limit will be further tightened in the immediate future ($\leq$ 10 ppm) (AAMA, ACEA, JAMA, 2002). As a result, the lubricity of diesel fuels decreased. Wear occurs on the parts of the fuel pump moving on each other. Therefore, it is very important to ensure the formation of a cover film either by physical adsorption or chemisorptions, in order to reduce the number of metal to metal contact points. Lubricity improving additives are polar compounds with long carbon chain, i.e. they are able to form a protective layer on the surface. Many types of compounds are used as diesel fuel lubricity improving additives. These may be alkenyl succinics, alcohols, acids, esters (esters of fatty acids and alcohols, bis-alkenyl-succinic ester, etc.), carboxylic acid amides, reaction products of fatty acids and aromatic triazoles, mixtures of fatty acids and tertiary amines, mixtures of nitrogen containing compounds and carboxylic acids substituted with polymeric compounds (Kajdas, C., 2003; Kajdas, C., 1999; Spikes, H., 1997).

Diesel fuels contact with the metal equipment of the fuel system. The fuel should not have any negative effect on these materials. Hydrocarbons do not cause corrosion, but the acidic compounds (i.e. naphthenic acid) and sulphur molecules in the diesel fuel are very aggressive to copper and their alloy and they can cause important “wear”, especially in case of long term stand-down. Solid and/or gel materials are formed in these reactions can deposit on different parts of the engine and can cause faults. (Haynock, R. F., 2004; AAMA, ACEA, JAMA, 2002).

Corrosion may develop on the wall of storage tanks during long term storage, especially in the presence of water. Nowadays, these corrosion effects can be prevented with suitable corrosion inhibitors. These additives build up a cover film on the metal surface. Typical corrosion inhibitors are carboxylic acids, amines and amine salts of carboxylic acids. For example: alkyl- or polyalkyl-succinics, their esters, dimeric acids and amine-salts.

Among the fuel additives discussed above the derivatives of different alkene-, alkyl-, polyalkene-, polyalkyl-succinic anhydrides are applied in the highest amount. The derivatives of succinic anhydrides are usually produced in two steps: the first step is the preparation of alkenyl succinic anhydrid by ene-reacton between olefins and/or polyolefines and maleic anhydride (MA). In the second step, the intermediates synthesized through the first step are used to acylate amines, amino alcohols, alcohols etc. Possibilities for the next reactions and the properties of final products

significantly depend on the structure and purity of the resultant intermediate as well as the conversion of MA- and olefin. The main research ways targeting the improvement of the reaction parameters are the thermal or radical initiation, catalytic synthesis or their combinations (Quesada, J., 2003; Candy L., 2005; Kocsis, Z., 2003).

Fatty acid methyl esters (FAME) and/or their derivatives are able to substitute diesel fuels and/or their additives. The use of FAMEs can moderate the agricultural overproduction crises and/or reduce the import dependence of crude oil and its products. The application of esters based on vegetable oils in premium quality diesel fuels ensures environmental advantages (lower CO_2-emission, biodegradability, non-toxic, etc.). Many vegetable oils like rapeseed-, sunflower-, palm-, soybean oils, used frying oils and animal greases can be used as a source of methyl ester production, however the application of the rapeseed- and the sunflower-oils is the most wide-spread because their properties are the most similar to those of diesel fuel. Their advantage is the good lubricity and the smaller emission of particulate matter (AAMA, ACEA, JAMA, 2002; Anon, 2000). A more and more significant utilization option of vegetable oils resulting in substantial value addition is the production of additives that are useful for various industrial purposes (Hancsók, J., 2004; Beattie, R. J., 2002; Perella, J. E., 2002; Directive 2003/30/EC). This utilization option is not only motivated by their renewable nature and their superior biodegradability compared to synthetic products but also by their applicability in various chemical reactions or structural modifications because of the unique distribution of their unsaturated bonds and their reactive functional groups. Consequently, vegetable oils rich in C18 unsaturated fatty acids like oleic acid (C18:1), linoleic acid (C18:2) or linolenic acid (C18:3) and the derivatives thereof may be suitable to produce alkenil succinic anhydrides (Quesada, J., 2003).

The importance of transportation fuels and their additives that can be obtained from vegetables or from their crops, respectively, is expected to rise in the European Union, too. The proposal of the European Commission to promote biofuels was acknowledged by the European Parliament and Council. According to this, member states of the EU should blend 2.0% of biofuels based on the energy content of conventional transportation fuels and this would mean a 5.0% share in 2009 with the proposed annual increase of 0.75 absolute per cent (Bubálik, M., 2005).

Based on the foregoing, renewable fuel and lubricant components are expected to have more and more considerable role in the future. Therefore, the objective of our research work was to synthesize succinic anhydride derivatives from rapeseed oil methyl ester (RME), polyisobutylene ($\overline{M}_{nPIB}$ ~ 1000) and maleic anhydride in the presence of radical initiator followed by the acylation of tetraethylene pentamine (TEPA) with the intermediate thereby obtaining a multi-functional fuel additive. With the incorporation of RME into the molecular structure we wished to widen the functions and enhance the performance (lubricity improving group, corrosion inhibiting effect) of the succinic imide type additive family and also to increase its biodegradability.

Thermal reaction of FAME and MA was already presented in the literature (Kocsis, Z., 2003). In that process high temperature with relatively high residence time is required and gum-like byproducts are formed.

2 Experimental

2.1 Meterials and methods

2.1.1 Materials

The synthesis was carried out in two steps. Rapeseed oil methyl ester (RME, prepared in-house, the main properties of RME are given in Table 1.), polyisobutylenes (Glissopal 1000; $\overline{M}$: 1000; BASF Chemical Company), MA, aromatic solvent, and radical initiator were used in the first step. Tetraethylene pentamine and base oil (SN-150/A, Group I, sulphur content: 0,1%, viscosity index: 96)) was applied for the preparation of final products.

Table 1. The main properties of RME

Properties	RME
Ester content [%]	97.2
Density [g/cm^{3}]	0.8789
Kinematic viscosity at 40 °C [mm^2/s]	4.5
Flash point [°C]	>110
Sulphur content [%]	0.0007
Carbon residue [%]	0.26
Water-content [%]	0.017
Copper strip corrosion (3 h, 50°C), [class]	1.
Acid number [mg KOH/g]	0.3
Methanol content [%]	0.04
Monoglycerides [%] Diglycerides [%] Triglycerides[%] Free glycerines [%] Total glycerine content [%]	0.66 0.15 0.19 0.01 0.13
Iodin number [g/100g]	112
Phosphorus content [mg/kg]	0.3
Potassium content [mg/kg]	0.4

Additive-free middle distillates were used to characterize the performance properties of the additives. The base fuels (sulphur content: 4 mg/kg) have met the requirements of EN 590:2004 standard, except the corrosion and lubricity properties.

2.1.2 Methods

The analytical and performance test of the intermediates and the final products were carried out according to international and local standards and proprietary methods (Table 2.).

Table 2. Analytical and performance tests

Properties	**Methods**	**Properties**	**Methods**
Kinematic viscosity	EN ISO 3104	**Molecular structure**	IR spectroscopy
Total Acid Number	ISO 6618	**Potential DD Efficiency**	inhouse method
Maleic-anhydride content	inhouse method (titrimetic)	**Peugeot XUD-9**	CEC-PF-023
Saponification Number	ISO 6293	**Copper strip test**	ISO 2160:2000
Active material content	local standard (column chromatography)	**Steel drift test**	ASTM D 665
Molecular weight and distribution	GPC (PIB standards)	**Lubricity**	EN ISO 2156-1 ASTM D 4172

2.1.2.1 Analytical tests

The amount of substituted MA was measured by the acid number of intermediates and MA-conversion was calculated from the ratio of acid number and theoretical acid number (TAN). Analytical volumetric test was carried out to quantify the unreacted MA-content. The amount of RME (fatty-acid chains, ester groups) substituted into the intermediates was calculated from the difference between the saponification number and acid number. PIB-conversion was calculated from the active material content.

2.1.2.2 Performance tests

Two laboratory tests (detergent index and washing efficiency) were used that separately characterize DD efficiencies in screening phases. The dispersion stabilizing efficiency of DD additives was studied by a method based on centrifugation. A suspension was prepared from the base oil containing 1.5% additive and 2% carbon black. This suspension was shared with ultra sound equipment. Afterwards, the blend was diluted with kerosene and the mixture was centrifuged for 30 minutes. The blend was examined in a photometrical equipment at 530 nm. Detergent index (DI) determined on the basis of the intensity of transmitted light:

$$DI=-I_1/I_0*100$$

where, I_1: intensity of the light after transmission through the blend containing carbon black

I_0: intensity of the light transmitted through the blend free of carbon black

The washing efficiency (WE) was measured by Zaslavskii's modified method based on thin layer chromatography. The efficiency was evaluated within 0-125 mm. The results of numerous experiments attested that these two methods were suitable to estimate the potential DD efficiency (PDDE, %) in oil solutions:

$$PDDE = \frac{DI + WE}{225} * 100,$$

where DI is the detergent index, %
WE is the washing efficiency, mm
225 is the maximum value of DI+WE
(DI_{max}=100, WE_{max}=125)

Samples having the best DD efficiency were investigated by Peugeout XUD-9 engine test.
The corrosion inhibiting efficiency of the prepared additives was characterized with copper strip test and steel drift test.
The lubricity improving efficiency was measured by modified four-ball methods and HFRR (High Frequency Reciprocating Rig) test.

2.2 Results and discussion

2.2.1 Synthesis of polyisobutylene-succinic anhydrides containing rape-oil methyl ester

The polyisobutylene-succinic anhydrides containing rapeseed-oil methyl ester (ASA) were prepared in a four-neck flask equipped with a stirrer, reflux cooler, thermometer and raw-materials feeder. The reaction was carried out at atmospheric pressure and different temperatures (130-150°C) in aromatic solvent, with radical initiation and various molar ratios of the reactants. The solvent and the unreacted materials were removed at 200 °C by vacuum distillation.

The effect of temperature, the change of molar ratio of the raw materials, the amount of solvent and initiator on the properties of the intermediates was investigated. Main properties of some typical intermediates were given in Tab. 2. The intermediates contained unreacted MA (Table 3.) and unreacted PIB, meanwhile RME was not present since no vibration bands characteristic for ester bonds were found in the IR spectra of intermediates remaining after the removal of the active component. This was confirmed by GPC analysis, because the peak around 300 typical for RME could not be observed.

Table 3. Main properties of the some typical intermediates

Properties	**ASA-1**	**ASA-2**	**ASA-3**	**ASA-4**
Appearance	Bright	Bright	Bright	Cloudy
Active material, %	63.3	63	69.3	59,6
Kinematic viscosity at 100 °C, mm^2/s	136.6	181.9	186.3	195,84
TAN, mg KOH/g	67.9	71.3	76	80,4
MA content mg/g	2.32	2.1	1.6	3,64
SN, mg KOH/g	68.8	89.7	91.7	126,6
SN-TAN, mg KOH/g	0.9	18.4	15.7	46,2
MA conversion, %	79.2	76.5	76.0	86.0

In accordance with the active material content, the PIB conversion varied between 60 and 70 %. Number average molecular mass of polyisobutylene used as feed was 1000 while that of rapeseed oil methyl ester was about 300. Number average molecular weight of intermediates was in the range of 1400-1700. Polydipersity was in the range of 1.66-1.84.

The figures above suggest that the polyisobutylene and also one or two RME compounds linked into the molecular structure. This was also confirmed by the homogeneous and clear appearance of the intermediates.

Based on the results of our experiments the most advantageous parameters of the synthesis were determined: <30% amount of solvent (based on the amount of reaction mixture), <15% amount of initiator (based on MA), <180 °C reaction temperature, 4-7 h reaction time.

2.2.2 Synthesis of final products

Selected intermediates were used to acylate polyethylene polyamines. The additives were prepared under inert N_2 atmosphere in a five-neck flask equipped with a stirrer, reflux cooler, thermometer and N_2 feeder. Polyethylene polyamines were added to the intermediate containing base oil (SN-150/A) at continuous stirring. The acylating reactions were carried out at 165-185 °C under mild vacuum with a reaction time of 4-6 hours (according to well known methods in the synthesis of polyalkylene succinics). Unreacted polyamines were removed at 200 °C by vacuum distillation.

PIB-, MA-, and the RME conversions were the main aspects of the selection of the intermediates for the synthesis of the final products. The PIB-conversion is cahacterized by the active material content (varied between 59.6 and 69.3%), the MA-conversioon by the ratio of acid number and theoretical total acid number (varied between 76.0 and 86.0) and the RME-converion by the difference between saponification number and acid number (varied between 0.9 and 46.2 mgKOH/g). The intermediates were diluted with base oil (150 N) to reduce their viscosity, and tetraethylene pentamines were acylated by using 1.0:1.0 TEPA/ASA molar ratio. Main properties of some typical succinic derivatives (SID) were given in the Table 4.

Table 4: Main properties of the some typical final products

Properties	SID-1	SID-2	SID-3
Intermediate	ASA-1	ASA-2	ASA-3
Acylating agent	TEPA		
Kinematic viscosity at 100 °C, mm^2/s	402,7	374,8	351,8
3% additive(containing 75% active material) in basic oil			
Kinematic viscosity at 40 °C, mm^2/s	35,8	37	36,8
Kinematic viscosity at 100 °C, mm^2/s	6,08	6,07	6,09
Extended viscosity index	116	110	111
DI, %	100	100	100
WE, mm	78	72	80
PDDE, %	79	76	80
Corrosion properties (10-30 ppm additive in gas oil)			
Copper strip corrosion	1A	1A	1A
Steel drift corrosion	0	0	0
Lubricity tests (200 ppm additive in gas oil)			
HFRR wear scar, µm	333	345	343
Fourball wear scar, µm [5]	713	730	726

2.2.3 Performance of succinic derivatives in diesel fuel

The synthesized additives were dissolved in SN-150/A base oil in 3% concentration for the DD efficiency tests. (Figure 1.). The results of their washing effect and potential DD effect showed that efficiency of traditional succinics could be achieved.

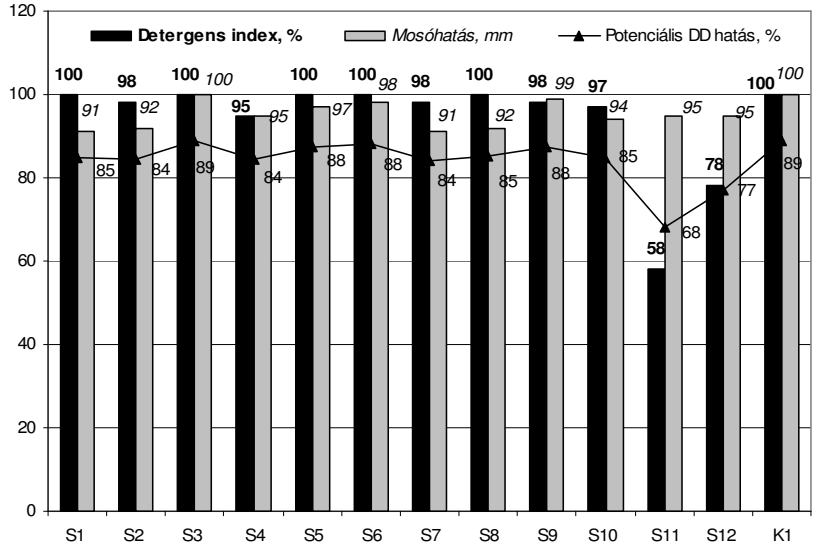

Figure 1. Washing efficiency and PDDE of the prepared additives.

Based on the laboratory tests the best additives were chosen and investigated by Peugeot XUD-9 test. As it is shown on figure 2. the test result confirmed the result of PDDH test; all the samples had better DD efficiency than the reference.

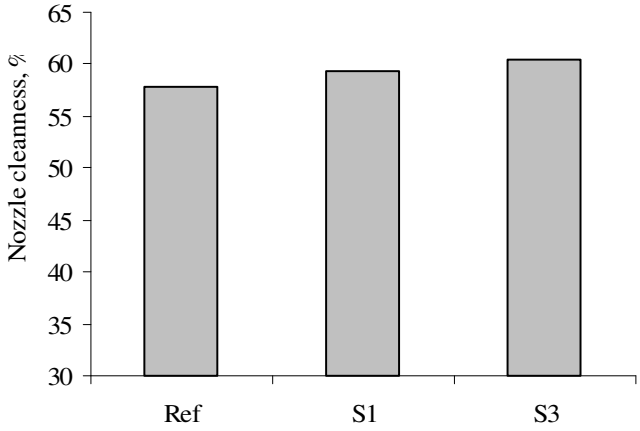

Figure 2. The results of Peugeot XUD-9 test

Based on the copper strip corrosion tests it was found that the additives had also excellent corrosion inhibiting properties. The result of copper strip test conducted with unadditized gas oil was 1B so the colour of the strip changed to dark orange. The additives applied in 10-30 ppm concentration inhibit the corrosion completely, thus the classification of the strip after the test was 1A. The results of stricter rust prevention in ferrous parts confirmed the previous effects in copper strip test.

Dark coating and black spots appeared on the surface of the test-piece after a short time (ca. 1 hour) during the steel strip corrosion test conducted with the unadditized base gas oil (Figure 3.). The area of spots increased with the contact time, thus the corrosion was classified as 3. However, no sign of corrosion on the steel strip was observed when our synthesized additives were blended into gas oil in 5, 10, or 20 ppm concentration. Consequently, the corrosion class of the additized gas oil was 0. We concluded that the synthesized additives provide excellent corrosion inhibiting property for the investigated diesel fuel

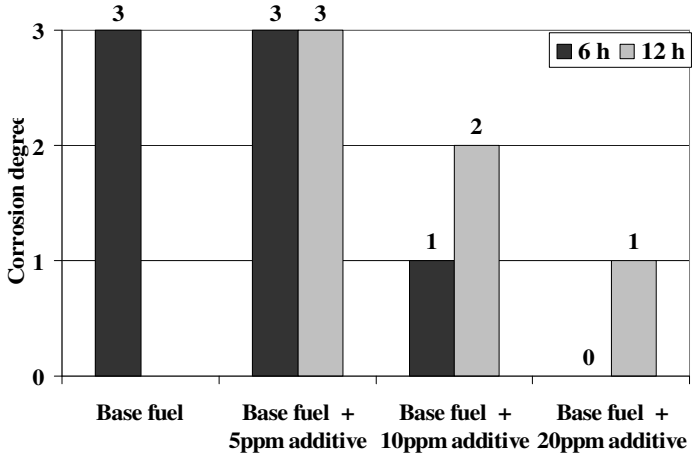

Figure 3. Corrosion degree of the prepared additive

The lubricity improving efficiency of the additives was investigated in the range of 50-400 ppm in gas oil. The wear scar of the unadditized gas oil used as a reference was 530 µm. According to the performance tests, the lubricity of all gas oils was enhanced significantly. These results showed that the additives based on vegetable oil had significant lubricity improving effect at 100 ppm amount of additive (Figure 4.).

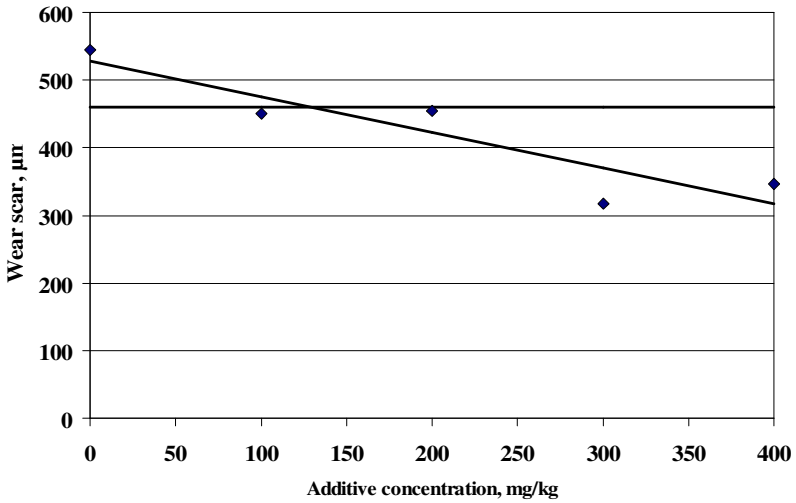

Figure 4. The lubricity properties of the additives

3. Summary

The aim of this work was to produce multifunctional additives on vegetable oil basis that provide not only detergent-dispersant effect in a fuel but also other advantageous properties. Beside, the goal was to use raw materials of partly renewable origin in order to meet biodegradability requirements. Intermediates were produced from polyisobutylene maleic anhydride and rapeseed oil methyl ester by radically initiated

method. These intermediates were used to acylate polyethylene polyamines. The analytical and efficiency tests of the final products showed similar or even better DD properties compared to traditional PIB-succinimides.
The new additives showed detergent dispersant-, corrosion inhibiting- and lubricity improving effects in both gas oil and gas oil containing biodiesel component.

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