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Development of a novel multifunctional succinic-type detergent-dispersant additive for diesel fuel

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Out of numerous additive types the detergent-dispersant (DD) additives have the most important role; their consumption is more than 50 % of the total amount of applied additives. Their function is to clean and keep clean the fuel supply system and the combustion chamber, thus the removal of deposits and the prevention of their formation. High DD efficiency of succinic-type additives is commonly known. The aim of our research work was the modification of the additive structure by the incorporation of a fatty acid methyl ester molecule into the succinic-type additive. Beside the objective to keep the advantageous properties of the conventional succinic-type additive structure, further advantageous effects were expected to be assured by the new structure of the additive. During the several steps of product design we determined the advantageous process parameters of the synthesis; we investigated the effect of the different feedstocks on the quality of the final products. Detergent-dispersant, additional antiwear and corrosion inhibiting effects of the novel additive were verified by analytical and laboratory performance tests, and by Peugeot XUD-9 engine tests. Infrared spectroscopy (IR) and magnetic nuclear resonance (NMR) tests were carried out to determine how the fatty acid methyl ester compound connects to form the novel structure of the additive.

1. Introduction

Modern fuels consist of environmental friendly blending components and high performance additives. Among the additives applied in engine gasoline and/or diesel fuel the detergent-dispersant (DD) additives have very important role. Their function is to clean and keep clean the fuel supply system and the combustion chamber, thus the removal of deposits and the prevention of their formation. Many kind of compounds have been developed in order to carry out this task, however they only have this function even if they have high DD efficiency.
World-wide the additive industry has a turnover of about 7000-8000 €/year of which the European market is its one third. The petroleum additive industry in Europe is a major exporter. Diesel fuel consumption shows increasing tendency world-wide, thus the quality and quantity demand for their additives is also increasing. The tightening

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environmental legislations can only be satisfied by high performance detergent-dispersant additives. In a long period these additives are not only responsible for the cleaning of the engine, but they also decrease fuel consumption. The DD additives have about 40-50% share of the additive market (Haycock and Thatcher, 2004). The detergent-dispersant additives are usually long chain hydrocarbons with polar group. By the introduction of low sulphur diesel (≤10mgS/kg) the demand for lubricity improving additives has also increased due to the removal of those sulphur compounds which are originally responsible for the lubricity of diesel fuel. Based on the foregoing the aim of our research work was to develop such an additive having novel structure which not only has high DD efficiency, but also additional lubricity improving and other effects.

2. Experimental

Based on our previous experiments during the product design of the novel multifunctional additive radically initiated synthesis was applied (Kocsis et al., 2003), because researchers (Quesada, 2003, Candy et al., 2005) reported the formation of gum like by products during the use of the conventional thermal reaction of maleic anhydride and fatty acid methyl ester.

2.1 Materials and synthesis of the additive

Synthesis of the novel additive was carried out in two steps. In the first step the so called intermediate product was synthesized by the use of fatty acid methyl ester (FAME), polyisobutylene (PIB) (number average molecular weight: 1000; BASF Chemical Company; Glissopal 1000), maleic anhydride (MA), aromatic solvent and radical initiator. In the second step the intermediate product was diluted with base oil (SN-150, API Group I., viscosity index: 96), then different polyethylene-polyamines (PEPA) were acylated.

To characterize the performance properties of the additive in diesel fuel and diesel fuel containing biodiesel unadditized gas oil – satisfying the regulations of the EN 590:2004 except the lubricity properties – and biodiesel – satisfying the regulations of the EN 14214:2003 – were used.

2.2 Methods

Table 1. Applied methods

Properties	Methods
Kinematic viscosity	EN ISO 3104
Acid number	ISO 6618
Saponification number	ISO 6293
Active material content	local standard (column chromatography)
Molecular weight and distribution	GPC (PIB standards)
Washing efficiency	local standard (thin layer chromatography)
Detergent index	local standard (photometric)
Copper strip corrosion	EN ISO 2160
Steel drift corrosion	EN 2388
Lubricity	ASTM D-4172
	EN ISO 12156-1

The product properties were investigated according to international standards and in-house methods of the Department of Hydrocarbon and Coal Processing of the University of Pannonia (Hancsók et al., 2008) (Table 1).

3. Results and discussion

3.1 Synthesis of the intermediate product and the additive

Production of succinic type additives is a two step process. The reaction parameter range of the synthesis of the so called intermediate product (polyisobutylene-succinic anhydride containing fatty acid methyl ester molecule in its structures: PSF) was selected according to the results of our previous experiments applied for the synthesis of succinic type additives (Hancsók et al., 1999). The effect of temperature (120-160°C), reaction time (4-7h), the PIB:FAME:MA molar ratio, the amount of solvent (<30%), the amount of initiator (<15% based on the amount of MA), the number and sequence of the feed of the reactants on the product yield and quality was investigated. Removal of the solvent and unreacted maleic anhydride was carried out in vacuum at 200°C in 1h. Number average molecular weight of the intermediate products varied between 1530 and 2200 (Table 2). Number average molecular weight of the polyisobutylene feedstock was about 1000, while that of the fatty acid methyl ester was about 300. According to these results probably one or two fatty acid methyl ester molecule linked into the succinic structure formed by polyisobutylene and maleic anhydride. Active material content and acid number changed in a relatively high region in case of the intermediate products shown in Table 2, it is due to the different feedstock affecting the quality.

Table 2.Main process parameters and properties of some intermediate products

Properties	PSF-1	PSF-2	PSF-3	PSF-4
Main process parameters of the synthesis				
PIB:FAME:MA molar ratio	1.0:1.3:1.2	1.0:1.1:1.2	1.0:1.1:1.2	1.0:1.1:1.4
Reaction temperature, °C	140	140	140	140
Properties of the intermediate product				
Appearance	bright	bright	bright	cloudy
Active material content, %	55.8	72.3	59.6	63.0
Kinematic viscosity at 100°C, mm^2/s	94.0	141.2	195.8	163.4
Acid number, mg KOH/g	70.8	73.9	80.4	83.7
MA content, mg/g	0.9	1.6	3.6	1.9
$\overline{M}_n$ (number average molecular weigth)	1530	2000	2200	1700

Before the second step the intermediate product was diluted with SN-150 base oil and then different polyethylene-polyamines (PEPA, e.g.: triethylene-tetraamine, tetraethylene-pentaamine, pentaethylene-hexaamine, etc.) were acylated. The advantageous PEPA/PSF molar ratio (1.0:0.8 – 1.0:1.2) was determined by numerous reactions during the product design. The advantageous parameters of the acylating reactions were also determined: 165-185°C, 4-5h, mild vacuum, nitrogen atmosphere.

The water formed during the reaction and unreacted PEPA was removed in vacuum at 200°C in 1h. The process parameters and main properties of some products are summarized in Table 3.

The method for measuring the detergent index, washing efficiency and potential detergent-dispersant efficiency (PDDE) of the additives is well detailed in one of our previous article: Hancsók et al., 2008. Detergent index of all additives reached the maximum value. Washing efficiency of the additives increased with the acid number of the intermediate, because the higher the acid number of the intermediate was the higher amount of PEPA could react with the intermediate, resulting in more polar molecules, thus higher DD efficiency. These results were confirmed by the nitrogen content of the additives. Nearly all additives reached or some of them exceeded the potential detergent-dispersant efficiency (PDDE=80) of the reference commercial DD additive.

Table 3.Main process parameters and properties of some additives

Properties	PSF-IM 1	PSF-IM 2	PSF-IM 3	PSF-IM 4	PSF-IM 5
Applied intermediate product	PSF-1	PSF-1	PSF-2	PSF-4	PSF-4
PEPA/PSF molar ratio*	1.0:1.0	1.0:1.2	1.0:1.0	1.0:1.0	1.0:1.2
Nitrogen content, %	3.5	3.8	1.8	3.6	3.8
1,5% (based on the active material content) additive in base oil (viscosity of base oil at 40°C: 34,5 mm^2/s)					
Kinematic viscosity at 40°C, mm^2/s	35.6	35.3	34.6	34.7	34.9
Detergent index, %	100	100	100	100	100
Washing efficiency, mm	86	94	84	85	90
Potential DD efficiency, %	82	88	82	82	84
Application of the additive in gas oil					
Copper strip test classification	1A	1A	1A	1A	1A
Steel drift test classification	0	0	0	0	0
Lubricity improving effect: wear scar diameter					
fourball tester, μm**	835	786	841	825	806
HFRR, μm***	452	413	478	482	425

In these reactions tetraethylene-pentaamine was applied as PEPA, Base gas oil without additive: 854 μm** and 524 μm***, HFRR: High Frequency Reciprocating Rig

Based on the results of the copper strip corrosion test we established that the additives (20 mg/kg) provided corrosion inhibiting properties for the gas oil: the classification of the gas oil without additive was 1B, with additive it was 1A.

The stricter steel drift corrosion test has confirmed the previous results. In case of the base gas oil without additive dark spots could be observed after a short contact time, the area of spots increased with the contact time, corrosion classification was 3. However, the corrosion class of the gas oil containing 20 mg/kg of the novel additive was only 1. In case of all additives after the 12h test period, only a couple of dark spots could be observed on the steel drift. Thus, the synthesized additives provide corrosion inhibiting effect when applied in gas oil.

According to the results, lubricity of the gas oil was enhanced by all additives (200 mg/kg) and some satisfied the requirements of the EN 590:2004 standard: HFRR maximum 460 µm. Thus, the novel additive has lubricity improving effect, too.

3.2 Peugeot XUD-9 engine tests

In our previous article (Hancsók et al., 2008) we reported successful Peugeot XUD-9 engine test (CEC-PF-023) carried out with gas oil by the application of the novel additive: the novel additive showed better performance than the commercial additive. According to the new regulations application of transportation fuels containing biomass-derived components has emerged into focus in the last years. The main reason of this tendency is the energy policy of the European Union, declared in Directive 2003/30/EC of the European Council and Parliament. Thus, the additive having the best performance during the laboratory analytical and performance tests was selected and blended in different concentrations (Table 4) into 5v/v% biodiesel containing gas oil(the highest possible applied concentration of biodiesel according to EN 590:2004 standard). As a reference additive we selected a commercial additive having high performance. Based on the results of the Peugeot XUD-9 engine test carried out to determine the detergent-dispersant efficiency of the additive we found that nozzle cleanness increased by the application of our novel additive. We observed synergic effect during the application of our additive together with the reference additive which is probably due to the different molecular structure of the two additives resulting in different mechanism of cleaning action. By the application of these two additives significant decrease of the total concentration of the additives can be achieved, meanwhile the efficiency remains the same, resulting in significant economical benefits.

Table 4. Results of the Peugeot XUD-9 engine tests

PSF-IM, mg/kg	Reference additive, mg/kg	Nozzle cleanness	
		%	change, %
0	0	46,2	100,0
100	0	46,9	101,5
300	0	49,0	106,0
0	100	47,1	101,9
0	300	48,7	105,4
0	600	50,8	109,6
50	300	50,1	108,4

3.3 Investigation of the molecular structure

For the investigation of the incorporation of the FAME molecule into the molecular structure of the additive IR spectroscopy and GPC tests were carried out previously (Hancsók et al, 2008). ^{1}H and ^{13}C NMR tests were carried out to confirm the possible structure (Figure 1) of the intermediate product.

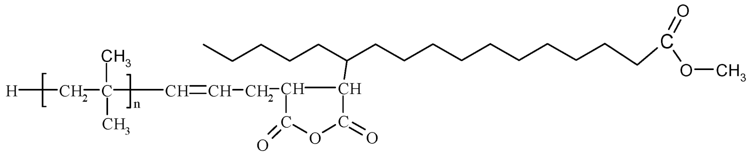

Figure 1. Possible structure of the intermediate product

Based on the results of the ^{1}H and ^{13}C NMR tests [^{13}C NMR (101 MHz, CDCl3) δ 174.33 (s, 1H), 130.41 – 129.62 (m, 4H), 77.31 (s, 43H), 77.00 (s, 42H), 76.68 (s, 42H), 59.80 – 59.01 (m, 30H), 58.82 (s, 3H), 58.40 – 57.75 (m, 4H), 51.43 (s, 2H), 38.64 – 37.36 (m, 36H), 34.10 (s, 2H), 32.74 – 32.10 (m, 12H), 31.70 (d, J = 37.9, 4H), 31.43 – 30.46 (m, 76H), 29.94 – 28.75 (m, 22H), 28.37 (s, 1H), 27.17 (d, J = 5.6, 4H), 26.61 (d, J = 15.9, 2H), 25.61 (t, J = 10.0, 1H), 24.93 (s, 2H), 22.61 (d, J = 10.9, 2H), 14.08 (d, J = 4.3, 2H)] it was found that in case of the intermediate product the succinic type molecule structure has formed and the methyl ester group was present, thus the original structure of the additive was confirmed. However, the wide molecule weight distribution of the polyisobutylene and the fatty acid methyl ester feedstock limits the proper description of the molecule structure of the intermediate product. In the near future NMR test with marked maleic anhydride are to be carried out.

4. Summary

Based on the results of our experiments, GPC, IR and NMR tests we concluded that an additive having a novel molecular structure and high performance could be produced with the incorporation of the fatty acid methyl ester molecule into the PIB-succinic type structure. The novel additive had the same or better detergent-dispersant efficiency as the commercial high performance additive, furthermore it provided other useful functional effect, such as corrosion inhibiting and lubricity improving effects. These results were confirmed by analytical and performance laboratory tests and Peugeot XUD-9 engine tests.

References

Candy, L., Vaca-Garcia, C. and Borredon, E., 2005, Eur. J. Lipid Sci. Technol., 107, 3–11.

Hancsók, J., Bartha, L., Baladincz, J. and Kocsis, Z., 1999, Lubrication Science, 11(3), 297-310.

Hancsók, J., Bubálik, M., Beck, Á. and Baladincz, J., 2008, Chemical Engineering Research & Design, 86, 793-799.

Haycock, R.F. and Thatcher, R.G.F., 2004, Fuel Additives and Environment, Technical Committee of Petroleum Additive Manufacturers in Europe

Kocsis, Z., Varga, G., Szirmai, L., Resofszki, G., Holló, A. and Hancsók, J., 2003, 4th International Colloquium on Fuels, Technische Akademie Esslingen, Germany, Ostfildern, ISBN 3 924813 51 5, 273-276.

Quesada, J., 2003, Eur. J. Lipid Sci. Technol., 105, 281–287.