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Use of fatty acid methyl esters as Biocomponents for diesel fuels and for preparation of Cetane number improvers

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Abstract: Up to 15% of fatty acid methyl esters (FAMEs) have been used as biocomponents for the manufacture of biodiesel fuels corresponding to the requirements of EN 590-09. Applying nitration with various agents has been obtained additives reducing the time delay of self-ignition (TDSI) of diesel fuels containing 20% light catalytic gas oil. The nitro products thus obtained increase also the resistance of the diesel fuel towards oxidation.

Keywords: Methyl Esters, Biodiesel, Nitration, Additives, Oxidation Stability

1. Introduction

Although the world-wide petroleum reserves are in front of future depletion fuel consumption increases. Simultaneously the exhaust emissions from conventional fuels deteriorate the environment and face us before an ecological disaster. As an urgent measure to combat environmental and energy crisis, the European Union adopted on 8 May 2003, Directive 30, which promotes the use and production of renewable fuels for transport - biofuels, according to which the share of biofuels compared to petroleum-based fuels should reach 20% in 2020.

Vegetable oils hold promise as alternative fuels for diesel engines. But their high viscosities, low volatilities and poor cold flow properties have led to the investigation of various derivatives. Fatty acid methyl esters known as Biodiesel, derived from triglycerides by transesterification with methanol have received the most attention [1].

Alternative diesel fuels are made from natural, renewable sources such as vegetable oil and fats [1]. The most commonly used oils for the production of Biodiesel are soybean [2], sunflower [3], palm [4], rapeseed [5], canola [6], cotton seed [7] and jatropha [8].

The use of additive allows reducing TDSI [9]. Moreover, additives that increase the cetane number not only provide better engine performance but also facilitate its start-up at lower temperatures and contribute to more complete fuel combustion [9, 10].

The scientific literature provides numerous organic compounds which in one way or another increase the self-ignition of diesel fuel. Among them, compounds containing nitrogen and oxygen [9, 10] have been most widely used.

The aims of the present work were

- To study of the possibility for use of FAMEs as a component in the production of biodiesel fuel.
- Synthesis of additives by nitration of FAMEs with various agents with the purpose of reducing the TDSI of diesel fuel containing 20% light catalytic gas oil.

2. Materials and Methods

Fatty acids (FAs) obtained as waste product in production of sunflower oil were used as feedstock. In order to remove the undesirable impurities, the same were subjected in advance to vacuum distillation in the temperature range from 95 to 250°C and at a residual pressure of 15 hPa. The mixture of FAs was analyzed by chromatograph using the methodology of Cert [11]. The

chromatographic analysis of the FAs mixture demonstrated in Table 1 shows that the sunflower oil contains mainly unsaturated carboxylic acids, namely Linoleic and Oleic acids, with a total content of 85.3%.

The saturated carboxylic acids are represented mainly by Palmitic acid - 8.9% and Stearic acid - 5.1%, while the total content of Arachidic and Myristic acid is less than 1%.

Table 1. *Chromatographic analysis of the mixture of fatty acids*

Acids	Content, %
Linoleic acid (9Z,12Z-octadecadienoic acid)	64,8
Oleic acid (9Z-octadecenoic acid)	20,5
Palmitic acid (hexadecanoic acid)	8,9
Stearic acid (octadecanoic acid)	5,1
Arachidic acid (eicosanoic acid)	-
Myristic acid (tetradecanoic acid)	0,7

The esterification of the FAs mixture was carried out according to the method of Aluyor [12] and the characteristics of the feedstock and of the obtained FAMEs is pointed in Table 2. As it is seen from the data in Table 2, the acid number of the mixture decreases from 195.73 to 0,46 mg KOH/g, and the kinematic viscosity measured at 50 and 100°C decreases from 10.24 and 3.41 to 2.52 and 1.04 mm^2/s, respectively which is an evidence of the successful performance of the esterification process.

Table 2. *Characteristics of the raw material, of fatty acids mixture after vacuum distillation and of the obtained methyl esters*

Indices	**Raw material**	**Mixture of Fas**	**FAMEs**
Density at 20°C, kg/m^3	904.4	890.8	874.7
Kinematic viscosity, mm^2/s			
- at 50°C	13.31	10.24	2.52
- at 100°C	3.92	3.41	1.04
Refractive index, n_D^{20}	1.4727	1.4680	1.4582
Iodine number, g I_2/100g	130.57	134.92	132.03
Acid number, mg KOH/g	196.16	195.73	0.46
Element composition, %			
- carbon	-	76.84	77.28
- hydrogen	-	11.68	11.87
- oxygen	-	11.48	10.85

In order to prove the character of the proceeding processes during esterification the IR spectra of the purified FAs and of the obtained FAMEs were recorded Fig. 1.

The spectral analysis was performed in the range within 600-3600 cm^{-1}. In the IR-the spectrum of the feedstock are observed bands for the characteristic oscillations of aliphatic carboxylic acids – a wide plateau is observed at 3600-2400 cm^{-1} corresponding to the their dimeric structure. Fig. 1 also shows that this plateau in the spectrum of the mixture of FAMEs narrows, which is an indication of loss of the carboxyl group. The valence vibrations of hydroxyl group bonded in the carboxyl at 900-1000 cm^{-1} disappear and at 1720 cm^{-1} is observed an intense peak, characteristic of valence oscillation of the bond ν (C = O) in the ester group.

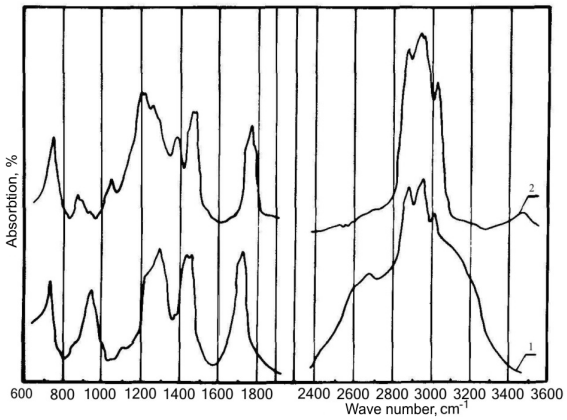

Fig 1. *IR spectra of fatty acid (1) and fatty acid methyl ester (2)*

In order to accomplish the second task we have carried a modification of the obtained FAMEs using different nitrating agents - dilute nitric acid, aluminum nitrate nanohydrate and nitrogen oxides. The conditions under which the modification of FAMEs was conducted are indicated in Table 4. Experiments were carried out with diesel fuel containing 20% catalytic gas oil.

3. Results and Discussion

For the purpose of the first object of the research, namely the use of FAMEs as biocomponents in the production of diesel fuel we have prepared and investigated samples containing 5, 10 and 15 vol. % esters. The study on the physicochemical characteristics of the base petroleum-derived diesel fuel and of the obtained samples was performed according to the regulations of EN 590-09.

The results reported in Table 3 show that fuels containing up to 15% vol. FAMEs meet the requirements of EN 590-09 for diesel fuels.

Cetane number and cetane index increase, indicating that the resulting fuels have better self-ignition characteristics. FAMEs exert also positive effect on lubricity.

Increase in the quantity of FAMEs, however, deteriorates the low-temperature properties of the base diesel fuel - increasing the percentage of FAMEs increases the cold-filter plugging point of the fuel. However, samples containing 10 and 15% vol. FAMEs could be attributed to Class "D" and "E". It is also observed a substantial increase in the temperature at which 95% of the fuel distilled, while for the fuel containing 15% of esters this indicator is on the limit of the requirements of the standard. All three samples do not show increased corrosion aggressiveness.

The studies show that FAMEs affect negatively those indicators which characterize the chemical stability of the fuel and its tendency to soot formation. The amounts of coke residue of the 10% distillation residue and of the insoluble products of oxidation are near to the limits of the standard requirements Table 3. These results are related to the fact that the majority of FAs are unsaturated. Therefore our further our studies will continue on the basis of hydrogenation of the resulting mixture of FAMEs.

Table 3. *Characteristics of the diesel fuels obtained by mixing of base diesel fuel with fatty acid methyl esters*

Index	Test methods	Results				Standard value
		Base diesel fuel	Amount of FAMEs 5%vol	10%vol	15%vol	
Cetane index	EN ISO 4264	50.5	51.0	51.4	52.0	min 40
PAH, % wt	EN ISO12916	6.43	6.10	5.78	5.46	max 11
Flash point, °C	EN ISO 22719	75	76	78	80	min 55
Carbon residue (on 10% distillation residue), % wt	EN ISO 10370	0.010	0.085	0.171	0.289	max 0.30
Ash content, % wt	EN ISO 6245	0.001	0.001	0.001	0.001	max 0.01
Copper strip corrosion (3h @ 50°C), class	EN ISO 2160	1	1	1	1	Class 1
Viscosity at 40 °C, mm^2/s	EN ISO 3104	2.55	3.28	3.72	4.39	2.0 – 4.5
Water content, mg/kg	EN ISO 12937	98.8	104.6	111.2	118.3	max 200
Distillation recovered, %V/V, at:	EN ISO 3405					
- 250°C		42.5	41.3	39.9	38.2	≥ 65
- 350°C		97.0	96.0	94.8	93.2	≥ 85
95%(V/V) recovered at, °C		340	346	351	355	360
Cold filter plugging point	EN 116					
- Class D, °C		-	-	-13	-10	
- Class E, °C		-19	-16	-	-	
Density at 15 °C, kg/m^3	EN ISO 3675	836.7	836.7	837.8	839.4	820 - 845
Sulphur content, ppm	EN, ISO 20846	8.9	8.9	8.6.	8.4	max 10
Total contamination, mg/kg	EN 12662	4.3	4.3	4.3	4.2	max 24
Lubricity, corrected WSD 1.4 at 60 °C, µm	ISO 12156-1	360	360	348	332	max 460
Cetane number	EN ISO 5165	52	52	53	54	min 51
Oxidation stability, g/m^3	EN ISO 12205	12	12	17	21	max 25

Bench tests of the obtained fuels were conducted on a fuel installation (ITD-69) and their cetane number was determined. The results showed that fuels containing up to 15% vol. FAMEs have good starting and operation properties. At the same time it is found that by increasing the quantity of the used methyl esters over 10% vol. appears noticeably increased deposits on valves and of resins on the sprayer nozzle, which require additional use of additives possessing antioxidant, dispersing and detergent properties.

For the purposes of the second task, i. e. synthesis of additives that reduce the TDSI, the obtained methyl esters were subjected to nitration. However, it was found that the use of the pointed above nitrating agents did not lead to the obtaining of products suitable for additives due to their poor solubility in diesel fuel. The most suitable conditions for the nitration of FAMEs - molar ratio of raw material and nitrating agent, temperature and time of the reaction are shown in Table 4.

At nitration with nitric acid, the optimum contact time was four hours since at shorter contact time the rates of nitration is very low, and for a longer contact time are obtained products which are partially or completely insoluble in middle distillate fuels, and the solubility decreases with increasing acid concentration. From the data in Table 4 it is seen that an increase in the acid concentration from 15 to 25% at the same time of contact are obtained products with a high content of bound nitrogen.

Table 4. *Conditions of fatty acid methyl esters modification*

Sample №	Nitrating agent	Nitration conditions		
		Molar ratio raw material: nitrating agent	Temperature, °C	Contact time, h
1	15% HNO_3	1:1.5	90	4
2	15% HNO_3	1:1.5	90	6
3	25% HNO_3	1:1.5	90	4
4	25% HNO_3	1:1.5	90	6
5	$Al(NO_3)_3.9H_2O$	1:1	95	4
6	$Al(NO_3)_3.9H_2O$	1:1	95	6
7	$Al(NO_3)_3.9H_2O$	1:2	95	4
8	$Al(NO_3)_3.9H_2O$	1:2	95	6
9	Nitrogen oxides	-	50	2
10	Nitrogen oxides	-	70	2

In the case of aluminum nitrate nanohydrate as nitrating agent, best results are obtained with a contact time of 6 hours and a molar ratio of the raw material: nitrating agent of 1:2. Products obtained under these conditions are with a high content of bound nitrogen and are completely soluble in middle distillate fractions, which make them appropriate to be investigated as additives for diesel fuels. The most efficient is the nitration with nitrogen oxides, and in this case are obtained products with the highest content of nitrogen and highest iodine number. Furthermore, all the products are completely soluble in diesel fuel.

The results in Table 5 show that the oxygen content and acid number in the obtained products are in direct dependence both on the contact time and on the type and amount of the nitrating agent.

Table 5. *Characteristics of the obtained products after fatty acid methyl esters nitration*

Sample №	Element composition				Acid number, mg KOH/g	Iodine number, $gI_2/100g$
	C	H	O	N		
1	68.72	10.30	19.15	1.83	6.72	40.32
2	59.00	9.10	28.10	3.80	22.60	35.06
3	65.50	9.70	22.40	2.40	8.75	35.13
4	54.70	8.40	32.60	4.30	26.21	29.07
5	73.45	12.29	13.46	0.80	3.36	72.89
6	64.41	11.06	20.39	4.14	6.42	20.83
7	73.21	11.48	14.11	1.20	6.73	67.31
8	60.22	9.58	24.84	5.36	10.84	13.22
9	70.66	9.20	16.40	3.72	5.42	15.23
10	62.28	8.95	22.25	6.57	8.20	9.61

Table 6. *Effect of additive on the cetane number and oxidation stability of the blended diesel fuel*

Sample number	Type and amount of the additive	Results for:	
		Cetane number	Oxidation stability, g/m^3
1	-	47	29.8
2	0.05%ECA-8478	50	23.9
3	0.15%ECA-8478	52	23.6
4	0.20%ECA-8478	53	23.2
5	0.05% sample.6	49	23.5
6	0.10% sample.6	50	22.4
7	0.20% sample.6	51	21.2
8	0.05% sample.8	50	23.1
9	0.10% sample.8	51	22.2
10	0.20% sample.8	52	21.1
11	0.05% sample.9	50	22.9
12	0.10% sample.9	52	21.8
13	0.20% sample.9	53	20.7
14	0.05% sample.10	51	22.3
15	0.10% sample.10	53	21.1
16	0.20% sample.10	54	20.1

At approximately the same nitrogen content the products obtained by nitration with nitric acid are with the highest oxygen content and acid value. Thus, in this case oxidation processes also take place.

The products resulting from the modification of FAMEs were tested as additives for diesel fuels in order to reduce the TDSI. The results of the research are presented in Table 6.

The efficiency of these products as additives for reducing the TDSI was studied and compared with commercial additive ECA-8478, which is based on aliphatic nitro derivatives.

Of the synthesized products samples 6, 8, 9 and 10 were used. As already mentioned, they contain the same functional groups, but are prepared by nitration with various nitrating agents and under different conditions and, therefore, have different content of bound nitrogen, acid and iodine number Table 5. The starting fuel and the samples containing additives were characterized according to the requirements of EN 590-09 and it has been found that the additives have a major impact only on the cetane number and oxidation stability. The fuel containing up to 0.2% of sample 10 is characterized by the highest oxidation stability.

The results in Table 6 reveal that the efficiency of the synthesized by us additives with respect to the cetane number of the diesel fuel with 20% light catalytic gas oil is identical to that of the stock additive. The value of the cetane number depends on the type of the additive, i.e. on the conditions of its preparation due to major importance of the amount of bound nitrogen. The highest increase in cetane number is demonstrated by the additive in sample 10, which in amount of 0.10% increases the cetane number by 6 points.

4. Conclusions

1. It was found that FAMEs improve the self-ignition and lubricating properties of the diesel fuel.

2. It was established that the fuels containing FAMEs have lower oxidation stability, greater tendency to deposits formation and poorer low-temperature properties.

3. It was found that diesel fuels containing up to 15% vol. FAMEs meet the requirements of the standard for diesel fuel.

4. It was found that at the nitration of FAMEs are obtained nitro products which reduce the TDSI, i.e. improve cetane number of diesel fuel.

5. It was shown that the highest efficiency is demonstrated by the product obtained at nitration at a temperature of 70°C and duration of 2 hours. This product in amount of 0.10 % increases cetane number by 6 points.

6. It was found that the obtained nitro products enhance the oxidation stability of the diesel fuel.

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