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FAME OXIDATION AND THERMAL STABILITY

Key-words

Fatty acids methyl esters, biodiesel, antioxidant, induction period.

Summary

The paper presents the results of determination of FAME oxidation stability untreated and treated with antioxidant additives. The results show that PN-EN 14112 (Rancimat method) which is required for produces of FAME applied as engine fuel does not allow to distinguish the additives effectiveness a concentration level of 500 mg/kg selected by the authors. Differential results were received when the same samples were tested according to ASTM D 525 (oxidative bomb method), which is based, as is the Rancimat method, on the calculation of induction period. These results were proved by changes of peroxides and acid numbers of FAME after the ASTM D 525 test. 2,6-Di–tert.butyl-4-methylphenol was the most effective of all the tested additives.

Introduction

Fatty acids methyl esters (FAME) play an important role in displacing Diesel fuel of crude oil origin and reducing emission of global warming gases. The production of each litre of FAME (biodiesel) avoids the emission of 3.253 kg of CO_2 (e.g. calculated as the emission of greenhouse gases) [1]. The other advantages of FAME to fossil Diesel fuel include the reduction of hydrocarbons, carbon oxide, smoke, and particulate emissions [2].

Because of its chemical structure, FAME can be very sensitive to oxidative and thermal degradation. When FAME are exposed to high temperatures and the oxygen in air, they can undergo chemical changes that form deposits and sediments and cause an odour and colour changes, and an increase in acid number, peroxide number and viscosity. The oxidation process leads to a variety of primary and secondary oxidation products such as hydroperoxides and peroxides [3] and then aldehydes, aliphatic alcohols, formic acid ester, formic acid, and short chain fatty acids [4]. The acetic acid, the propionic acid and high molecular organic acids are also the products of the oxidation process [5]. These products can attack many vehicle components, drastically reducing their service life. Ageing products can cause corrosion of fuel injection equipment, fuel leakage, filter plugging, and lacquer formation in hot areas of an engine. Some seal elastomers undergo softening, swelling or hardening and cracking. Solid impurities and particles can block nozzles and cause nozzle seat wear [5].

The stability of biodiesel can be improved by adding of antioxidant additives.

Several standard methods are established or adapted to determine the oxidative and thermal stability. Most important standard methods are based on a quantity of sediment formation in tested materials e.g.:

PN-ISO 12205 – Petroleum products is a determination of the oxidation stability of middle distillate fuels. This test method covers the measurement of inherent stability of distillate petroleum fuel under accelerated oxidising condition. The sample of fuel is aged at 95^{o}C for 16 hours while oxygen is bubbled through the sample. After ageing, the sample is cooled to room temperature and filtered to obtain the quantity of insolubles.

ASTM D 4625 – Standard Method for Distillate Fuel Storage Stability at 110^{o}F (43^{o}C) is a gravimetric measurement of filterable and adherent insolubles. It is a method of evaluating the storage stability of distillate fuels having flash points above 38^{o}C. The sample of fuel is aged at 43^{o}C for periods of 4 to 24 weeks. After ageing, the sample is cooled to room temperature and analysed for filterable and adherent insolubles.

The other methods used to determine the rate at which the oxidation process advances are related to the measurement of the concentration of primary and secondary oxidation products. The rate of the oxygen consumed during this process also can be used as an indicator for oxidation level.

Among other tests are the Schall oven, active oxygen method (AOM), thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) and methods in which induction time is the indicator for product oxidative stability: Rancimat method **PN-EN 14112** Fat and oil derivatives – Fatty acid methyl esters (FAME) is a determination of oxidation stability (accelerated oxidation test)] which is adopted from the fat and oil industry and conventional bomb method which is applied for gasoline **ASTM D 525 / ISO 7536 -** Standard Test Method for Oxidation Stability of Gasoline (Induction Period Method).

In the Rancimat method, the induction period is expressed as the time that passes between the moment when the measurement is started and the moment when the formation of oxidation products at 110°C rapidly begins to increase. The change of water solution conductivity in which the acid products of oxidative reaction are dissolved is the effect of this formation.

In the conventional bomb method, ASTM D 525, the induction period is expressed as the time elapsed between the placing of the pressure vessel in the bath and the break point at 100°C.

The sample is oxidised in a pressure vessel initially filled at 15°C to 25°C with oxygen pressure at 690–705 kPa and heated at a temperature between 98 and 102°C. The pressure is recorded continuously or read at started intervals until the breakpoint is reached.

Table 1 summarises conditions, advantages and limitations as well as application of the Rancimat and bomb methods.

The Rancimat test is required by the European specification for FAME used as fuel for Diesel engines (PN EN 14214). The requirement is min. 6 hours in 110°C. The test is quick and simple to run. Although it provides a repeatable measure of the antioxidant capacity of the biodiesel, the correlation between these measurements and field tests has not been established [6].

Published data shows that the Rancimat induction period is well correlated to other biodiesel quality parameters such as peroxide and acid value, kinematic viscosity, ester and polymer content [7].

Table 1. Comparison of Rancimat and bomb methods

Test method	PN-EN 14112 Rancimat method	ASTM D 525 Bomb method
Temperature Sample Size	110°C 3 g	100°C 50 mL
Test Condition	Borosilicate glass vessel. Oxygen flow 10 l/h	Borosilicate glass container in pressure vessel. Oxygen pressure 690-705 kPa
Advantages	Simple test employing conductivity drop for break point	Simple test employing pressure drop definition for break point
Limitations	The end of the induction period corresponds to the appearance of the secondary oxidation products volatile organic acids (formic acid)	Important method for gasoline in which soluble gum is a function of autooxidation break point
Application	FAME specification	Gasoline specification

1. Methods and materials of the experimental studies

In this study, the Rancimat method (PN-EN 14112) and the bomb method (ASTM D 525), both based on induction periods, were used to determine oxidation stability of samples and results were compared. The model 743 Rancimat (Metrohm AG, Herisau, Switzerland) and the model W-30-60 (Seta, UK) for bomb method were used for measurements of oxidation stability.

Peroxide values (ISO 3960) and acid numbers (ASTM D 664) were measured before and after the bomb method test. The results display the FAME degradation process in which oxidised acidic compounds are formed.

The characteristic of FAME derived from rapeseed oil is reported in Table 2.

Table 2. The main FAME properties in relation to European standard PN EN 14214 requirements

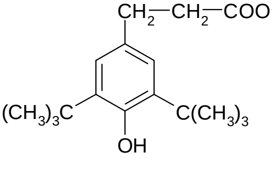
Property Unit	**Biofuel no 1**	**Limits**	**Testing method**
Fatty acids methyl esters content, *%(m/m)*	96.5± 2.2	min. 96.5	PN EN 14103
Density at 15°C, kg/m^3	883.3± 0.4	860 - 900	PN EN ISO 12185
Kinematic viscosity at 40 °C, mm^2/s	4.643± 0.061	3.50 - 5.00	PN EN ISO 3104
Flash point, °C	178 ± 8.8	min. 120	PN EN ISO 3679
Cetane number	56.3 ± 3.6	min. 51.0	PN EN ISO 5165
Water content, mg/kg	500 ± 99	max. 500	PN EN ISO 12937
Oxidation stability at 110 °C, h	7.2 ± 1.5	min. 6.0	PN EN 14112
Acid value, mg KOH/g	0.24 ± 0.04	max. 0.50	PN EN 14104
Group I metals (Na+K), mg/kg	0.8 ± 0.6	max. 5.0	PN EN 14108 PN EN 14109
Group II metals (Ca+Mg), mg/kg	<1.0	max. 5.0	PN EN 14538
Phosphorus content, mg/kg	<0.3	max. 10.0	PN EN 14107

Five antioxidants were evaluated for their potential for improving the stability of FAME.

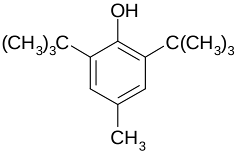
The following antioxidant additives were established:

Additive 1

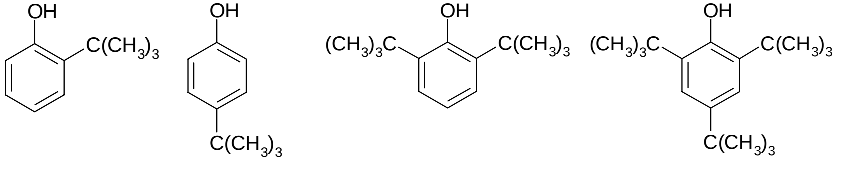
Octadecyl 3-(3,5-Di-tert.butyl-4-hydroxyphenyl)propionate.



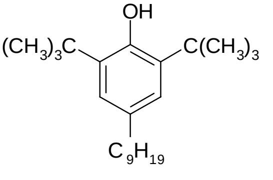
Additive 2
2,6-Di –tert.butyl-4-methylphenol.



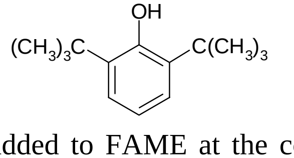
Additive 3:
2,6-Di-tert.butylphenol (>50%) + 2,4,6-tri-tert.butyl phenol (<20%) + 2-tert.butylphenol (<10%) + 4-tert.butylphenol (<10%):



Additive 4
2,6-Di-tert.butyl-4-nonylphenol



Additive 5:
2,6-Di-tert.butylphenol



Each antioxidant was added to FAME at the concentration of 500 mg/kg (Table 3).

Table 3. Biofuel sample numbers and biofuel compositions

Biofuel sample number	Biofuel composition
1	FAME
2	FAME + 500 mg/kg Additive 1
3	FAME + 500 mg/kg Additive 2
4	FAME + 500 mg/kg Additive 3
5	FAME + 500 mg/kg Additive 4
6	FAME + 500 mg/kg Additive 5

2. Results

Samples of FAME and FAME treated with additives (1-5) were tested for oxidation stability using the Rancimat and bomb methods. Peroxide values and acid numbers were determined before and after bomb tests.

Results of the Rancimat tests are shown in Table 4; whereas, bomb method tests, peroxide values and acid number results are shown in Table 5.

In the Rancimat method, the induction time for the break point of conductivity is reported (Fig.1).

In the bomb method, the oxygen pressure after 10 h of test is reported (Fig.2). Additionally, pressure was recorded continuously during the tests and the results are shown in Fig 3.

Peroxide values and acid numbers before and after bomb test are shown in Fig. 4 and 5.

Table 4. Rancimat test results

Biofuel sample number	Rancimat method Oxidation stability at 110°C, [h]
1	7.2 (0.81*)
2	7.2 (0.81*)
3	7.8 (0.86*)
4	7.1 (0.80*)
5	6.6 (0.75*)
6	7.2 (0.81*)

* PN-EN 14112 repeatability. Repeatability of the method is r = 0.09x + 0.16, where x is the average value of the test result.

Table 5. The bomb test results and the peroxide value and the acid number after bomb tests

Biofuel sample number	1	2	3	4	5	6
Bomb method. Oxygen pressure after 10h [psi]	59 (3*)	109 (5.5*)	118.5 (6*)	105 (5*)	80.5 (4*)	113 (5.5*)
Peroxide value before test [milieq O_2/ kg]	38.73	34.78	35.14	35.64	35.40	35.73
Peroxide value after test, 10h [milieqO_2/kg]	652.39	295.14	145.54	346.60	619.00	231.6
Acid number before test [mg KOH/g]	0.28	0.30	0.30	0.30	0.28	0.28
Acid number after test, 10h [mg KOH/g]	5.87	1.29	0.73	1.56	4.06	1.00

* ASTM D 525 repeatability. Repeatability of the test method is 5% of average value.

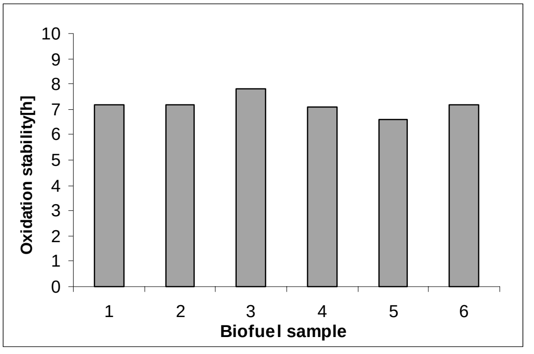


Fig.1. Rancimat method. Oxidation stability of untreated FAME (biofuel sample No. 1) and treated with additives (biofuel samples No. 2-6)

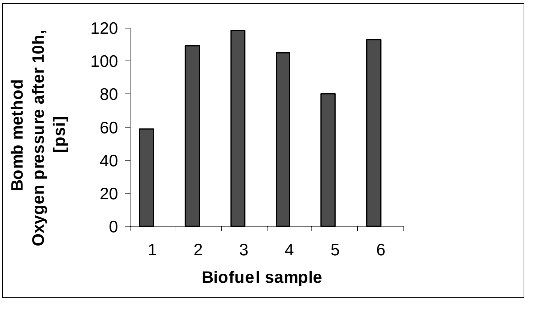


Fig 2. Bomb method. Oxygen pressure after 10h of bomb test of untreated FAME (biofuel sample No. 1) and treated with additives (biofuel samples No. 2-6)

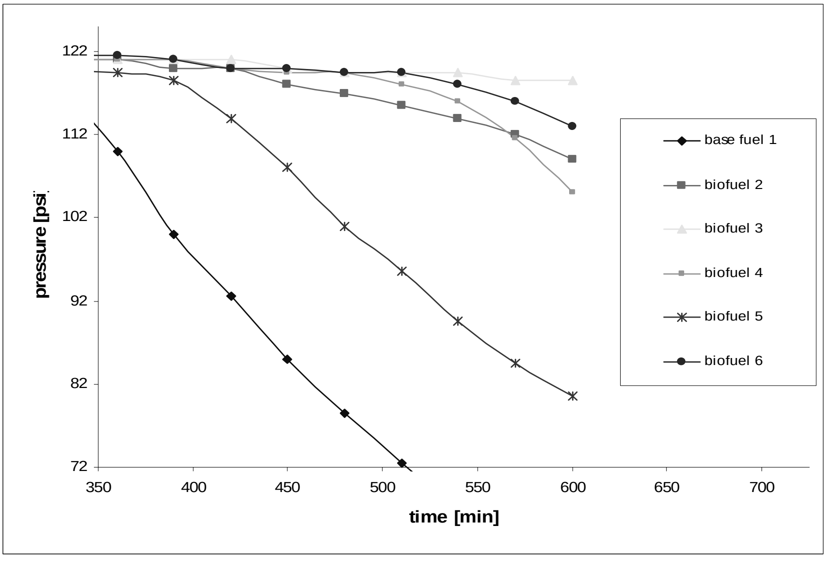


Fig. 3. Bomb method. The pressure recorded during the bomb test for of untreated FAME (biofuel sample No. 1) and treated with additives (biofuel samples No. 2-6)

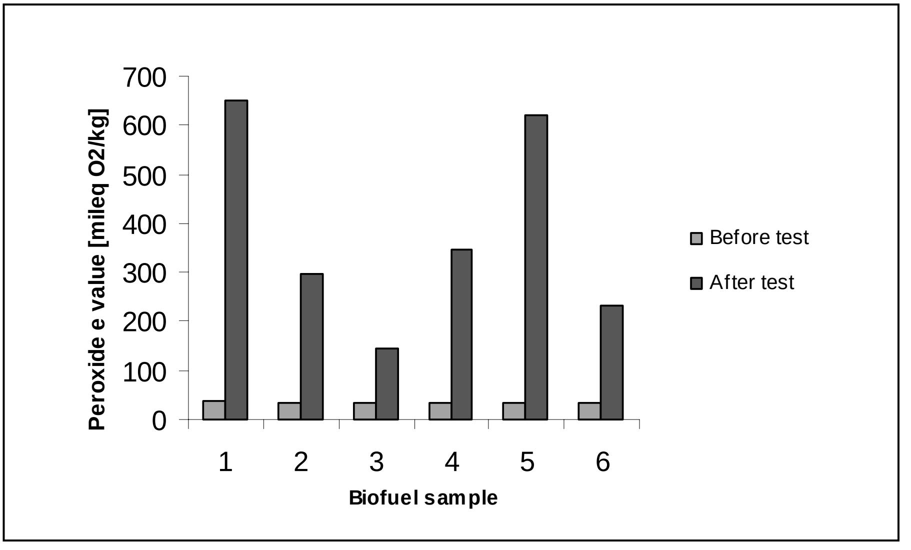


Fig 4. Peroxide values of untreated FAME (biofuel sample No. 1) and treated with additives (biofuel samples No. 2-6) before and after bomb test

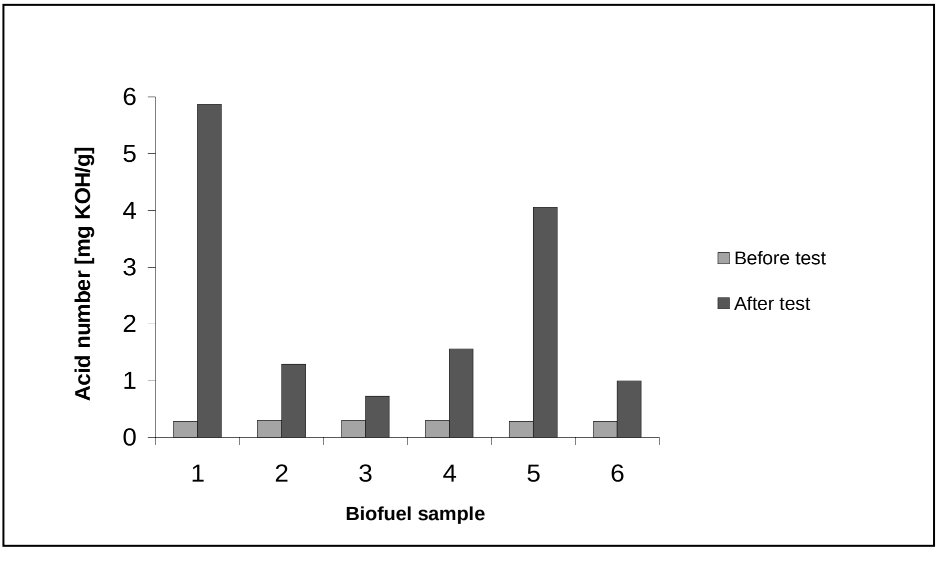


Fig 5. Acid number of untreated FAME (biofuel sample No. 1) and treated with additives (biofuel samples No. 2-6) before and after bomb test

Discussion

The Rancimat method (PN-EN 14112) is recommended by European specification PN-EN 14214 for testing the oxidation stability of FAME, but this study demonstrates that the Rancimat method does not allow to distinguish the additives effectiveness at the concentration level of 500 mg/kg (Table 4 and Figure 1) selected by the author, which is especially evident after taking into consideration the precision (the repeatability) of the method.

However, differential results were received when the same samples were tested according to ASTM D 525 method, which is based, as is the Rancimat method, on the calculation of induction period.

The faster oxidative degradation of untreated FAME (biofuel No. 1) (substantial drop in pressure) in comparison to FAME with additives (biofuels 2-6) was observed.

2,6-Di–tert.butyl-4-methylphenol (biofuel No. 3) was the most effective in increasing oxidation stability followed by 2,6-Di-tert.butylphenol (biofuel No. 6). 2,6-Di-tert.butyl-4-nonylphenol showed the lowest effectiveness (biofuel No. 5). This sequence of the oxidative effectiveness of the additives was proved by the results of peroxide value and acid number measurements after the duration of 10 hours of bomb tests (ASTM D 525).

Conclusion

1. FAME is a product that needs special protection against the oxidation process, especially at higher temperatures. The protection is provided by antioxidant additives. The selection of the type of antioxidants and treatment rate used for FAME is determined by PN-EN 14112 tests results (Rancimat method). The Rancimat test method is required for producers of FAME applied as engine fuel of quality, according to PN-EN 14 214 standard. This paper shows that the Rancimat method of testing FAME treated with different antioxidants does not differentiate their effectiveness at the concentration level of 500 mg/kg.
2. However, other methods such as the bomb method (ASTM D 525) used together with acid number and peroxide value measurement of samples after oxidising test allowed for the differentiation of the efficiency of antioxidants at the same concentration level of 500 mg/kg.
3. 2,6-Di–tert.butyl-4-methylphenol was the most effective and 2,6-Di-tert.butyl-4-nonylphenol showed the lowest effectiveness of all the tested additives.

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Reviewer:
Wiesław SZEJA

Stabilność termiczna i oksydacyjna FAME

Słowa kluczowe

Estry metylowe kwasów tłuszczowych, biodiesel, antyutleniacz, okres indukcyjny.

Streszczenie

W artykule przedstawiono wyniki badania stabilności oksydacyjnej estrów metylowych kwasów tłuszczowych, nieuszlachetnionych i z dodatkami przeciwutleniającymi. Wyniki badań wskazują, że metoda PN-EN 14112 (metoda Rancimat), która jest wymagana dla FAME jako paliwa silnikowego, nie pozwala na rozróżnienie efektywności działania zastosowanych dodatków przy wybranym przez autorów stężeniu 500 mg/kg. Natomiast metoda ASTM D 525 (metoda z bombą utleniającą), która tak jak metoda Rancimat również oparta jest na obliczeniu okresu indukcyjnego, pozwala na rozróżnienie efektywności tych samych dodatków przeciwutleniających, co zostało potwierdzone wynikami zmian liczb nadtlenkowych i kwasowych FAME po teście ASTM D 525. Spośród wszystkich badanych dodatków najbardziej skuteczny okazał się: 2,6-Di–tert.butyl-4-metylfenol.