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Impact of detergent-dispersant additives on B20 fuel oxidation stability

The impact of detergent-dispersant additives prepared by INiG – PIB and the commercial oxidation inhibitor on the oxidation stability of diesel fuel containing 20% (*V*/*V*) FAME is presented. Oxidation stability was monitored during a six-month testing at room temperature. Two method of oxidation stability were used (PN-EN 15751 and PN-EN 16091). Additionally Dynamic Light Scattering technique was used to estimate the subtle stability changes in time. Good antioxidant properties of the polyisobutylene-succinimide-amide detergent-dispersant additive in diesel fuel containing 20% (*V*/*V*) FAME have been confirmed for up to five months fuel stored at room temperature. The application of the same substances as effective detergent-dispersant and antioxidant additives in fuel results in significant cost reductions, compared to the application necessity of both detergent-dispersant additives and additionally other substances as antioxidant additives.

Key words: oxidation inhibitor, B20 fuel, oxidation stability, detergent-dispersant additive.

Wpływ dodatku detergentowo-dyspergującego na stabilność paliwa B20

W artykule przedstawiono wyniki badania wpływu dodatku detergentowo-dyspergującego opracowanego w INiG – PIB oraz handlowego inhibitora utleniania, na odporność na utlenianie oleju napędowego zawierającego 20% (*V*/*V*) FAME. Odporność na utlenianie monitorowano w trakcie sześciomiesięcznego testu przechowywania próbek w temperaturze pokojowej. Do badań wykorzystano dwie metody oznaczania stabilności oksydacyjnej (PN-EN 15751 oraz PN-EN 16091). Dodatkowo w celu oszacowania subtelnych zmian stabilności badanych próbek w czasie wykorzystano technikę dynamicznego rozpraszania laserowego. Potwierdzono dobre właściwości przeciwutleniające dodatku detergentowo-dyspergującego o strukturze poliizobutylenobursztynoimido-amidu w oleju napędowym zawierającym 20% (*V*/*V*) FAME do pięciu miesięcy przechowywania paliwa w temperaturze pokojowej. Stosowanie w paliwach tych samych substancji jako skutecznych dodatków detergentowo-dyspergujących oraz przeciwutleniających powoduje znaczne obniżenia kosztów w stosunku do konieczności stosowania zarówno dodatków detergentowo-dyspergujących, jak również dodatkowo innych substancji jako dodatków przeciwutleniających.

Słowa kluczowe: inhibitor utleniania, paliwo B20, stabilność oksydacyjna, dodatek detergentowo-dyspergujący.

Introduction

Biocomponents currently used in diesel fuels are almost exclusively fatty acid methyl esters (FAMEs) produced by catalytic transesterification of natural triglycerides [1–3, 5, 6, 10, 23]. The standard [26] permits the introduction of FAMEs which meet the requirements of the standard [25] in the amount of up to 7% (*V*/*V*) in diesel fuel. Due to the global trends concerning the growth of biofuel consumption in transport, research is being conducted ref. to fuels with higher content of biocomponents.

The use of FAMEs can cause many operational problems, including deteriorated low-temperature properties, higher viscosity, higher susceptibility to corrosion, poor thermal stability and oxidation resistance, storage problems and low energy value [4, 9, 10, 14–19].

The process of fuel oxidation leads to the formation of various types of deposits from resins and acids. Oxidation deposits can damage fuel pumps, block filters and fuel lines and can disturb the fuel injection process by settling on the injector tips. Acid oxidation products contribute to the degradation of engine parts by causing increased corrosion and rapid degradation of seals [7, 10–12, 19–22, 24].

The most effective method of preventing FAME oxidation is the use of antioxidant additives. The most commonly used synthetic antioxidants include: BHT, a mixture of 3-tert-butyl-

4-hydroxyanisole and 2-tert-butyl-4-hydroxyanisole (BHA), 2-(1,1-dimethylethyl)-1,4-benzenediol (TBHQ), 1,2,3-trihydroxybenzoate (PY) and propyl ester of 3,4,5-trihydroxybenzoic acid (PG) [22].

Experimental part

Feedstocks

BHT

An oxidation inhibitor with a structure of 2,6-ditert-butyl-4-methylphenol with a broad spectrum of applications. The manufacturer of the additive used in the testing and available under a commercial name of Ionol CP is Degussa Sant Celoni S.A.

DETS

Polyisobutylene-succinimide-amide, as a detergent-dispersant additive synthesised in INIG – PIB, has antioxidant properties too. The technology of its production is protected by the Polish Patent Office (patent applications: P.413867 and P.419859). The dosage of this additive for testing in a quantity that ensures the appropriate detergent-dispersive properties is 100 mg of active substance per 1 kilogram of fuel.

FUEL

The subject matter of the research was a diesel fuel containing 20% (*V*/*V*) of higher fatty acid methyl esters. The fuel was composed on the basis of a diesel fuel purchased from Grupa Lotos S.A. and FAMEs manufactured in ORLEN Południe S.A. and treated by the BHT additive (1000 mg/kg) as an antioxidant. The diesel fuel properties estimated in physicochemical tests are given in Table 1 and the FAME test results are given in Table 2.

Table 1. Physicochemical properties of Lotos S.A. diesel fuel

Test type	Unit	Test results
Cetane number	–	51.4
Density at 15°C	kg/m^3	822.0
Sulphur content	mg/kg	below 5.0
Ignition temperature	°C	61.0
Fatty acid methyl esters	% (*V*/*V*)	0
Viscosity at 40°C	mm^2/s	2.384
Fractional composition: – distils to 250°C – distils to 350°C – 95% (*V*/*V*) distils to temperature	 % (*V*/*V*) % (*V*/*V*) °C	 45.5 92.9 357.8
Oxidation resistance	min	67

Table 2. Physicochemical properties of FAME

Property	Unit	Test results
FAME content	% (*m*/*m*)	98.0
Density at 15ºC	kg/m^3	882.8
Viscosity at 40ºC	mm^2/s	4.433
Ignition temperature	ºC	181.5
Copper corrosive effect test (3 h at a temperature of 50ºC)	corrosion degree	1a
Oxidation stability (at a temperature of 110ºC)	h	6.9
Acid number	mg KOH/g	0.20
Iodine number	g I_2/100 g	111.8
Content of linolenic acid methyl ester	% (*m*/*m*)	8.7
Content of poly-unsaturated fatty acid methyl esters (≥ 4 double bonds)	% (*m*/*m*)	below 0.6
Content of methyl alcohol	% (*m*/*m*)	0.01
Content of monoacylglycerols	% (*m*/*m*)	0.68
Content of diacylglycerols	% (*m*/*m*)	below 0.10
Content of triacylglycerols	% (*m*/*m*)	below 0.10
Free glycerol content	% (*m*/*m*)	0.006
Total glycerol content	% (*m*/*m*)	0.19
Water content	mg/kg	145
Total impurity content	mg/kg	9.2
Sulphate ash content	% (*m*/*m*)	below 0.005

Test methodology

The samples of B20 fuel used for tests contained: (1) a BHT additive in an amount of 150 mg/kg of fuel, (2) a DETS detergent-dispersant additive in an amount of 143 mg/kg of fuel (100 mg/kg of active substance), and (3) a reference sample without additives. The fuel samples were placed in borosilicate glass bottles closed with a cap with a tube which allowed the air access and prevented the contamination of the sample. One sample of each fuel type was prepared and then poured into separate bottles for each tested incubation period. The containers were stored in a drying oven (at a temperature of 25 ±0.5°C) without an access to light for a period of 6 months. The following tests were conducted at monthly intervals:

- the determination of oxidation stability by accelerated oxidation method according to PN-EN 15751,
- the determination of oxidation stability by rapid small-scale oxidation method according to PN-EN 16091,
- the determination of particle size distribution using the Zetasizer Nano S analyser.

Discussion of results

Table 3. Oxidation stability test results determined according to PN-EN 15751 and PN-EN 16091

Name	Storage time at 25°C, number of months	Oxidation stability according to PN-EN 15751 [h]			Oxidation stability according to PN-EN 16091 [min]		
		without an additive	with BHT	with DETS	without an additive	with BHT	with DETS
R0	0	37.50	47.70	42.70	92	113	94
R1	1	40.00	51.10	47.90	91	103	85
R2	2	36.22	45.93	46.42	97	118	102
R3	3	37.38	50.57	48.00	91	114	98
R4	4	34.05	45.95	45.00	81	106	97
R5	5	38.39	41.83	41.54	80	106	98
R6	6	24.20	44.16	29.40	60	108	69

Table 3 shows the results of the oxidation stability tests of the tested B20 fuel samples according to PN-EN 15751 and PN-EN 16091.

The oxidation stability determined according to the PN-EN 15751 standard did not show significant changes for all tested B20 fuel samples up to the fifth month of storage in 25°C. The sixth month of the test showed a sharp decrease in oxidation stability of the sample containing the DETS additive and the sample without additives. The fuels treated by the DETS and BHT additives were more stable than the untreated B20 fuel. The results obtained in individual test periods for both samples containing additives were within the measurement uncertainty.

The oxidation stability of all the tested B20 fuel samples determined according to PN-EN 16091 showed small fluctuations of the tested parameter up to the fifth month in storage at 25°C while in the sixth month, the oxidation stability were deteriorated for the fuel containing no additives and the fuel treated by the DETS additive.

The changes occurring in particle size distributions determined by DLS method are presented in Figures 1 to 3 (Fig. 1 – B20 fuel without additives, Fig. 2 – B20 fuel with BHT additive, Fig. 3 – B20 fuel with DETS additive).

During the storage of all the B20 fuel samples (without additives and containing BHT and DETS), a slow decrease in

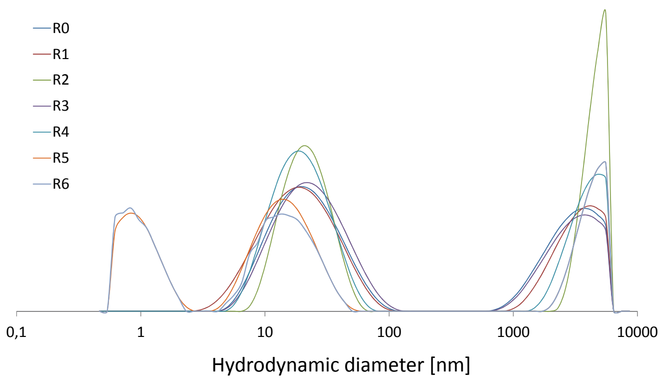

Fig. 1. Changes in particle size distributions in the B20 sample

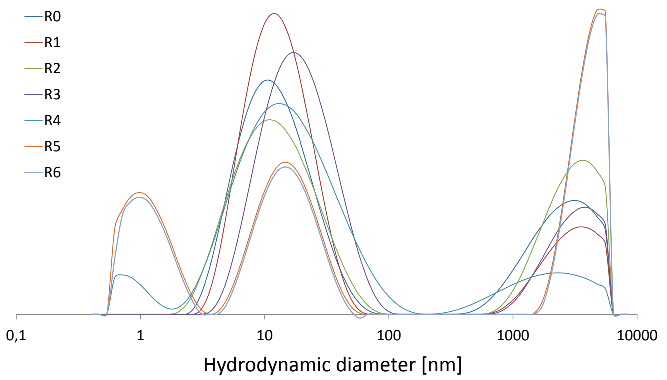

Fig. 2. Changes in particle size distributions in the B20-BHT sample

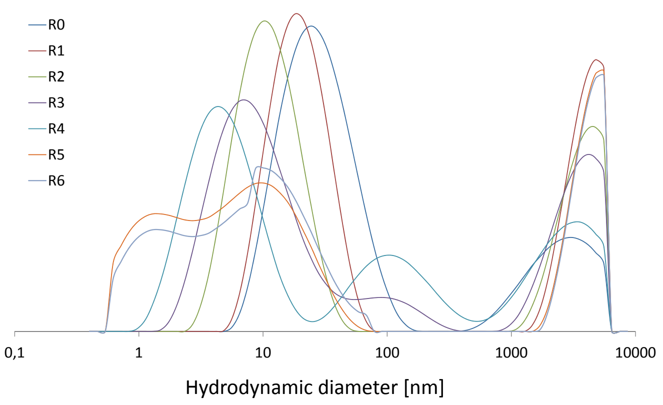

Fig. 3 Changes in particle size distributions in the B20-DETS sample

the intensity and widening of the most intensive peak width were observed. This course of changes in particle size distributions is characteristic for the samples that are unstable across time in which slow formation of macro-particles with larger hydrodynamic sizes occurs. However, it should be noted that these changes were not characterised by intensive dynamics.

Summary

As part of the conducted tests, the effectiveness of the detergent-dispersant antioxidant additive evaluated by INiG – PIB was compared to a commercial oxidation inhibitor. The tests confirmed good antioxidant properties of the detergent-dispersant additive with a structure of polyisobutylene-succinimide-amide in diesel fuel containing 20% (*V*/*V*) of FAMEs for up to five months during storage at a room temperature. Prolonging the fuel storage period up to six months reduced its effectiveness. The possibility to apply the one substance to treat fuels as effective detergent-dispersant and antioxidant additives significantly reduces costs compared to the need to use both detergent-dispersant additives and other additional substances as antioxidants.

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Legal and normative acts:

[25] PN-EN 14214+A1:2014-04 Ciekłe przetwory naftowe – Estry metylowe kwasów tłuszczowych (FAME) do *użytku w silnikach samochodowych o zapłonie samoczynnym (Diesla) i zastosowań grzewczych – Wymagania i metody badań.*
[26] PN-EN 590+A1:2017-06 *Paliwa do pojazdów samochodowych – Oleje napędowe – Wymagania i metody badań.*

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