Fuel 232 (2018) 108–113

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Rancimat and PetroOxy oxidation stability measurements of rapeseed oil methyl ester stabilized with hydrazides and antioxidants

Ferdinand Bär[a,*], Henning Hopf[b], Markus Knorr[a], Jürgen Krahl[c,d]

[a] Coburg University of Applied Sciences and Arts, Coburg, Germany
[b] Technical University of Braunschweig, Germany
[c] OWL University of Applied Sciences, Lemgo, Germany
[d] Fuels Joint Research Group, Germany

ARTICLE INFO

Keywords:
Biodiesel
Additives
Antioxidants
Oxidation stability
Hydrazides

ABSTRACT

Fossil fuels are still one of the world's major sources of energy. Because of their reduced availability in the future, however, renewable resources like biodiesel provide an attractive substitute to meet the growing demand for energy supply. Significant problems associated with the use of biodiesel are low its oxidation stability and a higher NO_x emission tendency. It was shown by Bär et al. (2017) [1] that 2,4,6-tris-isopropylbenzoic acid hydrazide and benzoic hydrazide can act as antioxidants in distilled biodiesel. Simultaneously, hydrazides showed the potential to lower NO_x emissions [2]. In this context, 14 additional hydrazides and four phenolic antioxidants were tested for their antioxidant properties by using the Rancimat method (DIN EN 15751) and PetroOxy method (DIN EN 16091). All hydrazides were employed at a concentration of 7.26 mmol/kg, which corresponds to approximately 1000 ppm of benzoic hydrazide. It is shown that all hydrazides increase the oxidation stability. The Rancimat tests verified that *m*-anisic hydrazide was most effective and extended the induction period by 16.0 h, whereas isonicotinic hydrazide showed a maximum induction period extension of 24.47 min in the PetroOxy tests. Differences in measurement principles, temperatures and oxygen partial pressures of both methods might explain the varying result. However, the phenolic antioxidant 2,2′-methylenebis(6-*tert*-butyl-4-methyl-phenol) increased the induction period from 3.7 h for neat RME to a maximum of 21.2 h in the Rancimat test and from 16.18 min to a maximum of 71.91 min in the PetroOxy test.

1. Introduction

Despite many advantages of biodiesel like renewability, high lubricity and reduced emissions of carbon monoxide (CO), unburned hydrocarbons (HC) and particulate matter (PM) compared to fossil diesel fuel, biodiesel tends to increase NO_x emissions and has a poor oxidation stability.

A common theory for the higher NO_x emissions of biodiesel in pump-line-nozzle fuel injection systems contributes with speed of sound and bulk modulus of compressibility of biodiesel and fossil diesel fuel. Biodiesel is less compressible than fossil fuel, which leads to premature fuel injection. This results in a higher peak in-cylinder temperature and increasing thermal NO_x formation [3–5]. However, Cheng et al. [6] showed that a fixed start of combustion timing leads to a load-averaged NO_x increase of about 10% for soy-based biodiesel relative to fossil diesel fuel.

Due to the fact that bulk-modulus effect cannot occur in common rail injection systems, a number of other theories were developed. It is known that biodiesel combustion produces less soot than the combustion of fossil diesel fuel. Mueller et al. [7] and Cheng et al. [6] investigated the radiative heat transfer of soot particles within the combustion chamber and found evidence that higher soot emissions from fossil diesel fuel combustion lower the combustion temperature by radiative heat transfer and therefore produces less thermal NO_x compared to the combustion of biodiesel. Another theory presented by Hoekman and Robbins [8] postulate that the higher cetane number of biodiesel causes a shorter ignition delay and therefore a longer residence time at elevated temperature. However, this theory is in contrast to results of McCormick et al. [9], who reduced NO_x emissions by cetane number enhancers. They concluded that a higher cetane number leads to less premixed air/fuel-mixture at the moment of combustion and that this could lead to a lower peak in-cylinder temperature.

Various studies showed that additives can mitigate NO_x emissions from biodiesel and biodiesel blends [9–14]. Krahl et al. [2]

---

[*] Corresponding author.
E-mail address: ferdinand.baer@tac-coburg.de (F. Bär).
URL: https://www.fuels-jrg.de (J. Krahl).

https://doi.org/10.1016/j.fuel.2018.05.095
Received 8 January 2018; Received in revised form 30 April 2018; Accepted 18 May 2018

demonstrated that 2000 ppm of *cis*-9-octadecenoic hydrazide in combination with a solubilizer reduces NO_x emissions from biodiesel combusted in an ignition bomb to ca. 45%. Bär and Krahl [15,16] showed that under optimized pressure and temperature conditions a slight decrease of NO_x emissions from ignition bomb tests can be found by adding 1000 ppm benzoic hydrazide into rapeseed oil methyl ester.

The poor oxidation stability of biodiesel is caused by unsaturated and polyunsaturated compounds like oleic acid methyl ester (C18:1), linoleic acid methyl ester (C18:2) and linolenic acid methyl ester (C18:3). Those compounds tend to abstract allylic and bis-allylic hydrogen radicals, initiating a classical free radical chain reaction mechanism (autoxidation) [17]:

$$RH \rightarrow R^{\cdot} + H^{\cdot}$$

$$R^{\cdot} + O_2 \rightarrow ROO^{\cdot}$$

$$ROO^{\cdot} + RH \rightarrow ROOG + R^{\cdot}$$

$$R^{\cdot}\ R^{\cdot} \rightarrow RR$$

$$ROO^{\cdot}\ R^{\cdot} \rightarrow \text{stable products}$$

The formation of reaction products is a multi-step process where primary oxidation products like hydroperoxides and epoxides decompose, interact with each other and form stable secondary oxidation products such as aldehydes, aliphatic alcohols, formic acid, formate esters, shorter chain fatty acids and oligomers with molecular weights up to 1600 g/mol [17,18]. The resulting oxidation products can lead to higher emissions, a higher corrosiveness, fuel filter blocking, clogging of fuel injectors, the formation of deposits in the fuel system and a decreasing lubricity [19].

To prevent those effects, diesel fuel contains oxidation inhibitors (antioxidants). Beside natural antioxidants a number of highly effective synthetic antioxidants have been developed. In general, antioxidants can be classified as hydroperoxide decomposers or radical scavengers, which break the chain reaction of autoxidation. However, antioxidants are consumed in this process, resulting in partial loss of their efficiency against oxidative stress during an induction period.

Phenolic and aminic antioxidants break the chain reaction by abstracting hydrogen radicals. These hydrogen radicals react with radicals from autoxidation and form stable products. The resulting antioxidant radical is either stable or further engages in a reaction to form stable molecules. Hydroperoxide decomposers, convert hydroperoxides into non-radical, non-reactive, and thermally stable products.

Since oxidative stability significantly affects fuel quality, a number of oxidation stability determination methods have been developed. The standardized accelerated oxidation stability test method accepted in DIN EN 590 and DIN EN 14214 is the Rancimat test (DIN EN 15751 and DIN EN 14112). A more rapid test to determine oxidation stability of fuels called PetroOxy test was reported by Neumann et al. [20] (DIN EN 16091). Both methods determine a so-called induction time, which can be correlated to the oxidation stability.

The European standard DIN EN 14214 sets a lower limit of 8 h for neat biodiesel as the minimum induction period determined by the Rancimat method. DIN EN 590 defines a limit of 20 h for fuel blends with up to 7% (V/V) biodiesel content. Minimum values for induction periods determined by PetroOxy have yet to be defined for European standards.

Bär et al. [1] reported that 2,4,6-tris-isopropylbenzoic acid hydrazide and benzoic hydrazide can act as antioxidants in biodiesel. Timmins and Deretic [21] reported that hydrazides can abstract hydrogen atoms from the hydrazide group breaking the chain reaction of autoxidation (Fig. 1). Simultaneously, hydrazides showed the potential for NO_x emission reduction [2,15,16].

In this context, the main goal of this paper is to compare the oxidation behavior of biodiesel treated with various hydrazides and common antioxidants. Oxidation stabilities were measured by the Rancimat and the PetroOxy method.

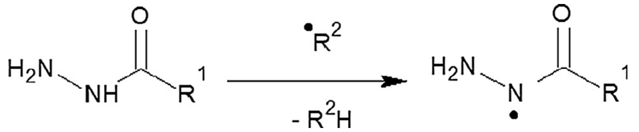

Fig. 1. Antioxidative action of hydrazides.

2. Experimental details

2.1. Additives

The additives used in the present study are shown in Table 1. Pivalic hydrazide was synthesized according to Bär et al. [22]. 2,4,6-tris-isopropylbenzoic hydrazide was synthesized according to Bär et al. [1]. All other additives were either purchased by Alfa Aesar, Merck, Lanxess or Sigma Aldrich (for synthesis).

The additives were compared either in constant mass concentration or constant molar concentration. A comparison of mass concentrations is the more technical approach, whereas a comparison of molar concentrations gives a better scientific understanding of the effectiveness of the additives. BHT is a commonly used antioxidant in biodiesel and therefore it was used as a reference.

2.2. Fuels

Following the common nomenclature, the amount of biodiesel added to conventional fossil diesel fuel determines the blend name (e.g. 7% biodiesel = B7)

The B100 used was made of rapeseed oil, which gives rapeseed oil methyl ester (RME) purchased from ASG – Analytik Service Gesellschaft.

Distilled rapeseed oil methyl ester contains no natural antioxidants and therefore it was used to prevent interactions between natural and synthetic antioxidants. The distilled RME was obtained from ASG – Analytik Service Gesellschaft.

The fossil diesel fuel was delivered from remaining stock of the Thünen Institut Braunschweig.

2.3. Methods

The oxidation stability tests with benzoic hydrazide, 2,4,6-tris-isopropylbenzoic hydrazide and BHT in distilled RME were done in triplicate. Results are presented as mean values and standard deviations of three replicates.

All other oxidation stability tests were performed as single determination.

A statistically different significance was accepted for a 95% confidence interval which reflects a significance level of $P < .05$.

Oxidation stability was determined by the Rancimat method (Metrohm Biodiesel Rancimat 873) according to DIN EN 15751 and by the PetroOxy method (Petrotest PetroOxy) according to DIN EN 16091.

The Rancimat method was first proposed by Hadorn and Zurcher [23]. The accelerated oxidation test is carried out by heating a sample to 110 °C in a sealed test tube while passing an air flow through it. Volatile oxidation products such as acetic acid and formic acid are dragged by the air flow into a vessel filled with distilled water. The conductivity of the aqueous phase is monitored and due to the appearance of the oxidation products in the water a significant change of conductivity can be detected when the aging process has started. The oxidation stability can be correlated to the so-called induction time elapsed from the start of the test until secondary oxidation products increase the conductivity in the water cell.

The PetroOxy method was originally presented by Neumann et al.