Full Length Article

Oxidation products of biodiesel in diesel fuel generated by artificial alteration and identified by mass spectrometry

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ABSTRACT

The aim of the present study is the storage stability evaluation of diesel fuel and various blends of diesel with fatty acid methyl esters (FAME, biodiesel), derived from rapeseed and soybean oil, by means of artificial fuel alteration. In this case, this is a lab-based procedure to effect accelerated changing of fuel properties under defined and reproducible conditions via oxidative stress. All oxidation products – volatile, liquid or solid – were captured thus enabling in-depth characterisation of the oxidised fuels obtained by conventional analytical methods as well as gas chromatography coupled with mass spectrometry (GC–MS). Special focus was laid on the identification of oxidation products in the oxidised fuels at various stages of the experiments. It could be demonstrated that especially neutralisation number and water content behaved proportionally to the oxygen consumption. They showed only marginal changes during the induction period, while increasing dramatically with the rapid onset of oxygen consumption as soon as the induction period was passed. The investigated fuels were ranked according to their storage stability in the order of neat diesel fuel > B7 blends > B20 blends > neat FAME. FAME content decreased rapidly in the stage characterised by rapid oxygen pressure break down, corresponding to 60% FAME loss in B20 RME. As main oxidation products in B20 RME, azelaic acid mono-ME, 9-oxo-nonanoic acid ME and hexanoic acid were identified. Moreover, carboxylic acids with chain lengths from C1 up to C9 as well as hydroxycarboxylic acids, dicarboxylic acids, and carboxylic acids with an epoxy group were formed. In B20 SME, main oxidation products were the same as detected for B20 RME. However, a distinctly broader variety of oxidation products was determined, e.g., carboxylic acid methyl esters from C8 to C18, unsaturated carboxylic acids up to C8, alcohols, and aldehydes. The main oxidation products detected in all samples are identical with those evolving during alteration of model mixtures containing linoleic acid methyl ester and linolenic acid methyl ester, respectively.

1. Introduction

A growing awareness concerning limited fossil fuel availability and the impact of greenhouse gases on global warming, in conjunction with legislative issues, provoked intense efforts into replacing fossil fuels fully or partially by fuel components from renewable resources [1–6]. For the admixture in diesel fuels, biodiesel based on fatty acid methyl esters (FAME) is employed. Rapeseed oil methyl ester (RME) represents the main biodiesel in Europe followed by soybean oil methyl ester (SME) and sunflower oil methyl ester [7].

However, the application of biodiesel is not free of concerns. One important issue turned out to be its storage stability. Biodiesel is highly prone to oxidation due to its elevated content of unsaturated fatty acid methyl esters. These have proven highly sensitive to storage conditions such as temperature, and exposure to air and light [8–11]. Thus, oxidation products in the form of precipitates and, subsequently, deposits are built up which consequently may harm engines and fuel supply systems [10–12]. In this context, a variety of studies were performed [8,10,13–17], which often used the induction period (IP) as determined by the Rancimat method according to DIN EN 14112 [18] for neat diesel fuel, or

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DIN EN 15751 [19] for biodiesel blends, as criterion for the storage stability [8,10,20]. The IP is defined as the period of time from the beginning of the experiment until the maximum rate change for the build-up of oxidation products [18,19]. Various antioxidants extend the oxidative stability of biodiesel significantly [9,20,21]. Examples of such compounds are hindered phenols, e.g., butylated hydroxyanisole, butylated hydroxytoluene, 2,5-di-*tert*-butylhydroquinone, propyl gallate, amines, e.g., *N,N′*-di-*sec*-butyl-*p*-phenylenediamine, or tocopherol.

For the characterisation of biodiesels, conventional analytical parameters such as acid number, peroxide number, iodine number, water content, or viscometric data are examined to determine fuel condition. On the other hand, hyphenated molecular analytical methods, such as gas chromatography coupled with mass spectrometry (GC–MS) or with flame ionisation detection (FID), as well as high resolution mass spectrometry using electrospray ionisation (ESI), are gaining more and more importance for the elucidation of oxidation reaction mechanisms of biodiesel [8,13–16].

The present study comprises the determination of oxidative stability of various diesel-FAME blends from commercial components, as well as the in-depth analytical characterisation of biodiesel oxidation products at various stages of accelerated oxidation. Therefore, the first task was the adaptation of currently used standard methods for stability assessment, in order to fulfill the desired requirements. The most important requirement was the capturing of all oxidation products for a comprehensive monitoring of fuel oxidation. Subsequently, systematically altered fuel samples were analysed by the joint use of conventional as well as hyphenated molecular analytical methods with special focus on the detection and characterisation of oxidation products.

In order to account for the unknown impact of the oxidation process on fuel performance, the term 'alteration' is proposed and used in this publication, as opposed to conventional terms such as 'ageing' and 'maturation'. In contrast to those terms, 'alteration' remains strictly neutral. In accordance, 'artificial alteration' means lab-based procedures to effect accelerated changing of fuel in properties under defined and reproducible conditions, here caused by oxidative stress.

The paper in hand focuses on the set-up of the modified artificial alteration procedure, and presents the results of in-depth chemical analysis of the artificially altered fuel samples, thereby offering a deeper insight into the oxidation products formed in diesel fuel and FAME blends.

2. Experimental

2.1. Examined fuels, fuel blends and model mixtures

For experimental work, the following commercial fuels and fuel components were employed: 1) diesel fuel (B0), without additives, 2) rapeseed oil methyl ester, without additives, as well as 3) soybean oil methyl ester, without additives. 1) to 3) were all supplied by OMV Refining & Marketing GmbH. Both FAME correspond to requirements according to DIN EN 14214 [22].

The two biodiesels were blended to diesel fuel in different ratios, i.e., 7 Vol% (B7) representing the currently used commercial fuel quality in the market, and the elevated concentration of 20 Vol% (B20).

In addition to these conventional fuel blends, model mixtures of B0 with linoleic acid methyl ester (C18:2 ME) and linolenic acid methyl ester (C18:3 ME) as single components, respectively, were investigated in order to determine their role in the initiation of the oxidation process. They were dosed at the level of their natural occurrence in B7 RME formulation, i.e., 1.6 wt% in the case of C18:2 ME and 0.7 wt% in the case of C18:3 ME. Both chemical substances were obtained from Sigma Aldrich, Missouri, USA in GC grade ($\geq$99%).

2.2. Development and execution of the artificial alteration method

For the development of an artificial alteration method tailor-made for the present task, a survey on standards for stability assessment of diesel fuels as well as FAME was carried out. Four standards were found to be currently valid:

1. DIN EN ISO 12205 [23] referring to oxidation stability of middle-distillate fuels
2. DIN EN 14112 [18] referring to oxidation stability of FAME (Rancimat test)
3. DIN EN 15751 [19] referring to oxidation stability of diesel-FAME blends (Rancimat test)
4. DIN EN 16091 [24] referring to oxidation stability of diesel-FAME blends (Petroxy test)

All these standards, except for DIN EN 16091, describe an open device, which may significantly impact the composition of the (oxidised) fuel sample and also possible reaction pathways due to the evaporation of volatile oxidation products by gas flow as well as by elevated temperatures. These would remain in the fuel during natural oxidation (e.g., storage in the fuel tank). Consequently, the samples obtained by those methods are not representative enough to be investigated by comprehensive analysis. On the other hand, DIN EN 16091 has the disadvantage of a very small sample volume of only 5 mL, making a comprehensive analytical investigation impossible. Therefore, all standard methods were found inappropriate for application in the present study.

For this reason, standard ASTM D 2272 (Rotary Pressure Vessel Oxidation Test, RPVOT) [25] was used as basis for the modified artificial alteration method. Originally, this standard is used for steam turbine oils, and it describes an accelerated oxidation procedure in a closed pressure vessel. This standard was adapted according to parameters of DIN EN 12205 with regard to the application on fuel samples.

Table 1 shows a comparison of the standards DIN EN 12205 and ASTM D 2272 with the resulting modified RPVOT method. In the

Table 1
Comparison of standardised methods for stability assessments with the modified RPVOT method.

Parameter	DIN EN 12205	ASTM D 2272 (RPVOT)	Modified RPVOT
Application	Diesel fuel	Lubricants	Diesel fuel
System	Open glass device	Closed pressure vessel	Closed pressure vessel
Sample Amount	350 mL	50 g	50 g
Temperature	95 °C	150 °C	95 °C
Oxygen Flow	3 L/h	–	–
Oxygen pressure	–	6.2 bar	6.2 bar
Contamination	–	Cu-spindle (for catalysis) Water (for hydrolysis)	–
Alteration duration	16 h		Variable