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Elucidation of oxidation and degradation products of oxygen containing fuel components by combined use of a stable isotopic tracer and mass spectrometry

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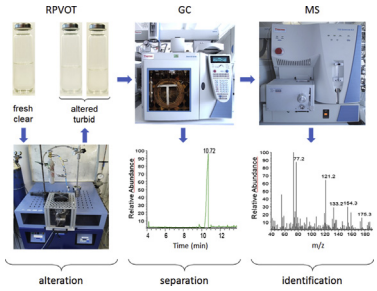
HIGHLIGHTS

- An approach combining artificial alteration, isotopic tracer and MS is presented.
- It is appropriate to monitor the build-up of oxidation products.
- Thermo-oxidative stability of oxygen-containing components is determined.
- Their role in oxidative degradation mechanisms on the molecular level is enabled.

GRAPHICAL ABSTRACT



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ABSTRACT

In order to reveal the degradation products of oxygen-containing fuel components, in particular fatty acid methyl esters, a novel approach was developed to characterize the oxidation behaviour. Combination of artificial alteration under pressurized oxygen atmosphere, a stable isotopic tracer, and gas chromatography electron impact mass spectrometry (GC-EI-MS) was used to obtain detailed information on the formation of oxidation products of (9Z), (12Z)-octadecadienoic acid methyl ester (C18:2 ME). Thereby, biodiesel simulating model compound C18:2 ME was oxidized in a rotating pressurized vessel standardized for lubricant oxidation tests (RPVOT), i.e., artificially altered, under $^{16}O_2$ as well as $^{18}O_2$ atmosphere. Identification of the formed degradation products, mainly carboxylic acids of various chain lengths, alcohols, ketones, and esters, was performed by means of GC-EI-MS. Comparison of mass spectra of compounds under both atmospheres revealed not only the degree of oxidation and the origin of oxygen atoms, but also the sites of oxidative attack and bond cleavage. Hence, the developed and outlined strategy based on a gas-phase stable isotopic tracer and mass spectrometry provides insight into the degradation of oxygen-containing fuels and fuel components by means of the accurate differentiation of oxygen origin in a degradation product.

1. Introduction

Influenced by the decline of natural resources and global warming, mainly caused by release of greenhouse gases by burning of fossil fuels, restrictions in gas emission regarding transportation

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and notable governmental support for alternative fuels have increased over the last decade. According to the United Nations Framework Convention on Climate Change at the 21st Conference of the Parties (COP 21), mobility should be possible without fossil fuels by 2050 at the latest. Norway even intends to prohibit gasoline and diesel vehicles from 2025 on [1]. Influenced by these developments, diesel blending with distinct amounts of biodiesel has gained more and more importance over the last decades [2–5]. Europe is among the world leaders in biofuel production, regarding biodiesel even the world's largest producer. For the year 2014 a production amount of 13,341 million (mio.) liters (L) biodiesel and renewable diesel was achieved. An estimated amounts for 2017 of 14,155 mio. L should be produced within Europe. Feedstock used for the production in 2014 is given with 11.21 kilo tons (kt), whereof 6,1 kt were from rapeseed oil, which corresponds to 55 percent (%) [6].

Biodiesel produced from rapeseed oil shows a distinct fatty acid methyl ester (FAME) pattern affected by the feedstock. The FAME composition of rapeseed oil methyl ester (RME) is mainly based on C18:1 (60.7 (w/w) %), C18:2 (19.6 (w/w) %), C18:3 (9.8 (w/w) %), C16:1 (4.4 (w/w) %) and C18:0 (1.8 (w/w) %) fatty acids [7].

In the past, the free radical oxidation of unsaturated lipids was investigated mainly due to medical interests [8–10]. Especially linoleate and its autoxidation mechanisms were of special research interest [11,12]. In previous work including RME-based FAME, focus was put on one of the most important issues of biodiesel, the storage stability [13]. Due to a high content of unsaturated fatty acids, FAME fractions are highly prone to oxidation, which is affected by storage conditions such as temperature, air exposure, or impact of sun light. Formed deposits are one consequence of oxidation reactions, which may cause damage to the engine or the fuel supply [14,15]. In order to determine the storage stability of biodiesel fuel blends, studies typically applying the Rancimat method according to DIN EN 15751 [16] are executed. Moreover, oxidative stability can be influenced and improved by addition of antioxidants, mainly hindered phenols or amines as well as combinations [17].

However, in order to improve oxidative stability of biodiesel formulations by well-directed measures, extensive analyses are necessary to understand the oxidation reactions taking place and to identify or characterize the degradation products built up during the oxidation process. For edible oils, the main pathway of oxidation is autoxidation, where hydroperoxides are formed as a first step. The steps of the following radical chain reaction were already described by Farmer et al. and Bolland in the years 1942 and 1949, respectively [18,19]. However, in the field of fuels, hydrocarbon-based lubricants, and their additives, there is still a lack of information about reactions taking place during the degradation process. Conventional analytical methods can provide information like acid number, viscosimetric data, peroxide number, degree of oxidation, or water content. In order to identify and/or characterize degradation products, mass spectrometry (MS) is the technique of choice. To mention some of the possible techniques, gas chromatography coupled with electron impact (EI) MS with analyzers such as quadrupole (Q), ion trap (IT), or quadrupole reflectron time-of-flight (QRTOF) is one of the first to be considered. However, high performance liquid chromatography (HPLC), on-line coupled or direct infusion with electrospray ionization (ESI) with a variety of analyzers, also seems to be suitable, as demonstrated in Refs. [7,20–22]. To give an example with direct infusion ESI-QRTOF-MS, Catharino et al. achieved fingerprint typification of biodiesel samples [22]. Moreover, information of the used alcohol, the state of degradation and the residual glycerol and glycerides was obtained.

As mentioned above, previous research work was focused on storage stability evaluation of diesel and various diesel-FAME blends by their analytical characterization in different degradation states. Therefore, standard artificial alteration methods currently in use had to be modified to fulfil the required tasks. The term artificial alteration is used to describe the accelerated, lab-based procedure to change the properties of the respective model fuels or generally applied fuels. Here, the defined and reproducible conditions play a crucial role. The online monitoring throughout the alteration as well as the complete collection of degradation products was of high interest, directing investigations towards the technique GC-MS. Subsequently, the sample aliquots (from different time points) were analyzed using GC-EI-MS to identify and characterize degradation products in the various blends [13].

Although the characterization of degradation products and the correlation with conventional fuel analysis showed insightful results, several questions were left unanswered by this conventional approach. Beside the origin of the degradation products, possible ways of degradation of the initial molecule was of high importance, but it is still unclear and should be explained on the molecular level. In order to reveal more and in particular detailed information concerning the path of degradation, i.e., obtaining mechanistic information, of FAME, the development of a new approach for the elucidation of oxidation reactions became necessary. In case of oxygen-containing lubricants and components, e.g. ethers and esters, a differentiation of oxygen origin in a degradation product, either from lubricant or via oxidation, is still difficult to determine. Hence, tracking of the reactions taking place while degradation is complicated. Therefore, we propose the novel approach using a ^{18}O stable isotopic tracer of the formed degradation products during artificial alteration with subsequent analysis by GC-EI-MS presented in this paper.

With 99.78% natural abundance, ^{16}O is the most common oxygen isotope followed by stable ^{18}O with 0.22% [23,24]. These different abundances can be used, e.g., to study atmospheric gas, marine carbonate deposits, or for stable isotopic tracer methods. This has been applied to improve methods for protein quantification and gain insight in their functions and dynamics [25]. Another highly interesting approach for use of isotopic tracer is the use of stable isotopic tracers to track chemical changes or reactions on the molecular level. Exemplarily, usage of ammonium-based ionic liquids (IL) was simulated by means of artificial accelerated alteration. Subsequent evaluation of degradation products by mass spectrometry showed that certain cation moieties are prone to degradation. However, a comprehensive proposal of degradation mechanisms were not obtained so far [26].

To gain the maximum degree of information during artificial alteration of molecules of interest, a novel approach was designed. Not the target molecule itself was labelled with an isotopic moiety, but the atmosphere involved in the oxidative degradation of these substances consists solely of ^{18}O isotopes to track the oxidation products derived from the gas-phase. The unique element of this approach is the application of a gas-phase stable isotopic tracer for the formation of degradation products to monitor this process instead of the more common labelling of the target molecule. Hence, a completely new approach in lubricant analysis was elaborated. In order to determine fuel component degradation on a molecular level, a combination of artificial alteration under oxygen pressure, a stable isotopic tracer, and GC-EI-MS was used to obtain detailed information on the oxidation products of oxygen-containing fuel components. This approach was applied to the fuel additive/replacement (9Z), (12Z)-octadecadienoic acid methyl ester (C18:2 ME) to develop the proof of concept. The elucidation of degradation process in case of oxygen-containing fuels and fuel components by means of the definite differentiation of oxygen origin in a degradation product proved to be feasible.

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