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Full Length Article

Determination of oxidation stability and degradation degree of rapeseed oil methyl ester by fluorescence spectroscopy

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HIGHLIGHTS

- The oxidation stability of the rapeseed oil methyl ester (RME) is related to the oxidation products and natural antioxidants.
- Quick and direct determination of the degradation degree and the oxidation stability of RME are enabled by fluorescence spectroscopy.

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ABSTRACT

The degradation of rapeseed oil methyl ester (RME) under accelerated conditions was investigated by use of total fluorescence spectroscopy (TFS). This technique provides an easy and quick analysis of natural antioxidants (e.g. vitamin E, chlorophylls, etc.) and of oxidation products (e.g. hydroperoxides and oligomers) of RME at their characteristic excitation and emission wavelengths. In the result it was proven that similar to the specification related Rancimat-test (EN 14112) the oxidation stability of RME could be determined by fluorescence signals of the oxidation products. Additionally a quick and direct determination of the degradation degree and the oxidation stability of RME by fluorescence spectroscopy is enabled by use of the correlation between the Rancimat- and the fluorescence-measurement.

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1. Introduction

To fulfill the German law "Biokraftstoffquotengesetz" [1] the blending quota for biodiesel in fossil diesel can be up to 7%. A number of studies, however, presented that one of the main reasons for massive changes in fuel properties is the oxidative ageing of the fuel [2–5,37]. These changes of the fuel properties range from the increase in viscosity probably caused by the formation of oligomers, the deterioration of the lubricating properties caused by increase of acid value, to the formation of precipitates in blends. The ageing could be explained by autoxidation mechanism for hydrocarbon oxidation [3].

Damages caused by aged fuel can, for example, occur at fuel pumps, in the injection line and in the engine oil as well as in the exhaust gas aftertreatment systems. The fuel system reacts sensitively to an increase in viscosity. The high injection pressures of current diesel engines don't forgive viscosity any exceeding the fuel standard [6]. Moreover, the continuous entry of fuel into the engine oil during the regeneration cycle of diesel particle filters (DPF) leads to oil dilution and oil sludge formation through the ageing process of biodiesel. Conventional fossil diesel fuel can evaporate from the engine oil, while biodiesel, in which fatty acid methyl esters (FAME) are major constituents, remain in oil due to their higher boiling range. Also, biodiesel can form – forced by certain operating conditions – oligomers leading to oil sludge. Technically to shorter the oil change interval [4,7–9]. In addition, the problem of the aged biodiesel frequently appears in plug-in hybrid vehicles, an emergency generator, heating systems, due to the long storage-time of biodiesel.

The oxidation stability of fuel refers to the ability can withstand oxidative processes without drastic deterioration of its chemical properties. The oxidation stability is an important parameter of quality requirements of modern diesel fuels and biodiesel (EN 590, EN 14214). Rapid, accurate quantification of the oxidation stability of biofuels or biodiesel blends is therefore of enormous importance to ensure the fuel quality.

The so-called Rancimat-test is the typical test for determining the oxidative stability of biodiesel (EN 14214, EN 15751 and EN 14112). The Rancimat-test is an accelerated ageing test which is run at elevated temperatures (110 °C). The sample is passed through by a stream of ambient air (10 L/h). The volatile com-

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pounds (mainly acids formed as oxidation products) are transported by the air into a collection flask containing distilled water. The quantification is indirectly carried out by an electrical conductivity measurement. The oxidation stability is determined by the induction period. The induction period is the time between the start of the test and the sudden conductivity increase of the aqueous solution in a collection flask. After the induction period, the degradation of biodiesel accelerates [10].

Many studies have reported that the fluorophores of biodiesel are natural antioxidants, e.g. α-tocopherol (vitamin E), chlorophylls, pheophytins, phenolic compounds, vitamins (A, D and K) and hydroperoxides [11–14]. Meira et al. have determinated the oxidation stability of soy biodiesel and soy oil by spectrofluorimetry and multivariate calibration [15].

In this work aged RME was analyzed by total fluorescence spectroscopy. Additionally, a method based on fluorescence spectroscopy was developed to determine the oxidation stability and the degradation degree of rapeseed oil methyl ester measuring directly the increase of oxidation products and the decrease of antioxidants at their characteristic excitation and emission wavelengths. The results revealed that the new fluorescence-based method allows the direct determination of the oxidation stability without heating procedure by use of a multivariate calibration model.

2. Experimental

2.1. Fuels

The fresh biodiesel rapeseed oil methyl ester (RME) was purchased from Analytik-Service Gesellschaft (ASG), Germany. The fuel specifications data are reported in Table 1.

2.2. Ageing procedure

The biodiesel sample (350 mL) was heated in a 500 mL three-neck round-bottom flask under a flow of 350 mL/min of air at 110 °C for 64 h. The ageing time (up to 64 h) using the same conditions as the highly accelerated Rancimat test revealed much more than the usual induction period of RME. Such extreme conditions may occur only under heavy degradation circumstances of biodiesel, for example long-term storage or the entry of biodiesel into hot engine oil, etc. A condenser reduced loss the decomposed products to the air. For the first 12 h, a sample of 2 mL of the aged product was taken every hour. Thereafter it was taken after every four hours.

A Rancimat machine was used as reference for clarification of oxidative stability relative to total fluorescence spectroscopy. Aged RME from the Rancimat-test was measured by fluorescence spectroscopy at different ageing times (0–12 h). These fluorescence spectra were used as reference spectra to determinate the degree of degradation of unknowingly aged RME.

2.3. Analytical method

The ageing samples were analyzed using a total fluorescence spectrometer (Hitachi F-4500) fluorophor to determine the concentration and degree of oxidation. For total fluorescence measurement the sample was continuously irradiated by a monochromatic light. Perpendicular to the direction of the excitation radiation, the intensity of the emitted fluorescence light are measured with wavelength dependent by a detector photomultiplier tube (PMT). A three-dimensional contour map (Excitation-Emission Matrix, EEM) of the fluorescence intensity (z-axis, abbreviation: I) as a function of the excitation and emission wavelengths (y- and x-axes, abbreviation: EX and EM) is usually presented from the measurement [16,17]. In the TFS-measurement the excitation range can be set from 200 to 600 nm and the emission range from 200 to 900 nm.

3. Results and discussion

3.1. Assignment of fluorophores

The fluorescence EEMs of the fresh and aged biodiesel at different ageing times are shown in Fig. 1. Fig. 2 shows fluorescence-

Table 1
Fuel data in accordance with DIN EN 14214 of the biodiesel fuels RME

Properties	Methods *DIN EN*	Units	Limit *Min.*	Limit *Max*	RME
Ester content	14103	% (m/m)	96.5	–	>99
Density (15 °C)	ISO 12185	kg/m^3	860	900	883.3
Kin. viscosity (40 °C)	ISO 3104	mm^2/s	3.5	5.0	4.463
Flashpoint	ISO 3679	°C	101	–	178.5
CFPP	116	°C	–	0/-10/-20	-17
Sulphur content	ISO 20884	mg/kg	–	10.0	<5(1.9)
Carbon residue	ISO 10370	% (m/m)	–	0.3	<0.10
Cetane number	15195		51		55.6
Ash content	ISO 3987	% (m/m)	–	0.02	<0.01
Water content	ISO 12937	mg/kg	–	500	74
Total contamination	12662	mg/kg	–	24	4
Copper strip corrosion (3 h–50 °C)	ISO 2160	degree	1	1	1
Oxidation stability	14112	h	6	–	7.1
Acid number	14104	mg KOH/g	–	0.5	0.391
Iodine number	14111	g iodine/100 gr	–	120	113
Linolenic acid content	14103	% (m/m)	–	12	9.8
ME ⩾ 4 double bonds	15779		–	1	<0.6
Methanol content	14110	% (m/m)	–	0.20	0.02
Free glycerol	14105	% (m/m)	–	0.02	0.02
Monoglycerides	14105	% (m/m)	–	0.80	0.43
Diglycerides	14105	% (m/m)	–	0.20	0.12
Triglycerides	14105	% (m/m)	–	0.20	0.11
Total glycerine content	14105	% (m/m)	–	0.25	0.15
Phosphorous content	14107	mg/kg	–	10	<4(<0.5)
Alkali content	14538	mg/kg	–	5	<1
Alkaline earth content	14538	mg/kg	–	5	<1

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