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Quantitation of Aging Products Formed in Biodiesel during the Rancimat Accelerated Oxidation Test

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ABSTRACT: Biodiesel (rapeseed oil methyl ester) was aged in a Rancimat device at a temperature of 110 °C and an air flow of 10 L/h. Time-resolved analyses applying gas chromatography−flame ionization detection, gas chromatography−mass spectrometry, and ion-exchange chromatography on the formation of aging products were performed. Formic and acetic acid, fatty acids with chain lengths from 5 to 18 carbon atoms, fatty acid methyl esters, and epoxides were quantified. After 12 h of aging, the concentrations of formic and acetic acid were 5600 ± 80 and 1360 ± 80 mg/kg, respectively. Fatty acid concentrations were in the range of <18−4200 mg/kg after 18 h of aging. Linoleic acid methyl ester and linolenic acid methyl ester (19 and 9.1 mass % of the non-aged fuel) were shown to be fully decomposed after 24 and 18 h of aging, respectively. After 51 h of aging, the concentration of oleic acid methyl ester (63 mass % of the non-aged fuel) decreased to 2.2 mass % and *trans*-epoxy stearic acid methyl ester and *cis*-epoxy stearic acid methyl ester reached concetrations of 5.9 and 0.7 mass %, respectively. The fuel composition shows only minor changes in early stages of aging, and a strong timely correlation of the formation of aging products with the end of the induction period of fuel was observed.

INTRODUCTION

Biodiesel is a renewable diesel fuel that mainly consists of fatty acid methyl esters (FAMEs) and is derived from vegetable oils, animal fats, or waste oils. The production processes for FAMEs are well-established, and their usage in blends with petrodiesel is regulated in European standards (EN 590[1]). One reason, among others, for the maximum blending ratio of 7 vol % (B7) defined in EN 590 is the relatively low oxidation stability of FAMEs.

In vehicle fuel tanks oxygen occurs on the one hand dissolved in the fuel and on the other hand as part of the vapor phase and can lead to fuel aging. Because of fluctuations in the ambient temperature, a significant amount of air is exchanged with the environment if the fuel tank is permanently vented, an effect commonly referred to as tank breathing. Ullmann et al. report that the amount of air exchanged per day equals approximately 2 L/day in a 70 L tank filled with 10 L of fuel, assuming a change in temperature of 10 K.[2] A high fuel-filling level and the usage of venting valves can substantially reduce the amount of exchanged air. It was shown that fuel aging is directly connected to the presence of oxygen in the environment of the fuel.[2] In modern diesel engines, a common rail fuel injection system is used. There, all fuel injectors are supplied by one common fuel rail. Elevated temperatures of approximately 110−130 °C and pressures of more than 2000 bar lead to stressing of the fuel. While the major portion of the fuel is injected into the combustion chamber, a smaller portion is transferred back to the tank and can undergo the stressing process again. With ongoing engine development, pressures in fuel injection systems further increase. Fuel stability is therefore becoming an issue of increasing importance.

In contrast to petrodiesel, which consists of paraffinic and aromatic hydrocarbons, FAMEs show sites of unsaturation. The number of double bonds found in biodiesel depends upon its fatty acid composition, i.e., the feedstock used for its production. Allylic hydrogen atoms are susceptible to the attack of radicals, which leads to the formation of hydroperoxides. The mechanism is displayed in Figure 1. While, in monounsaturated compounds, the four possible hydroper-

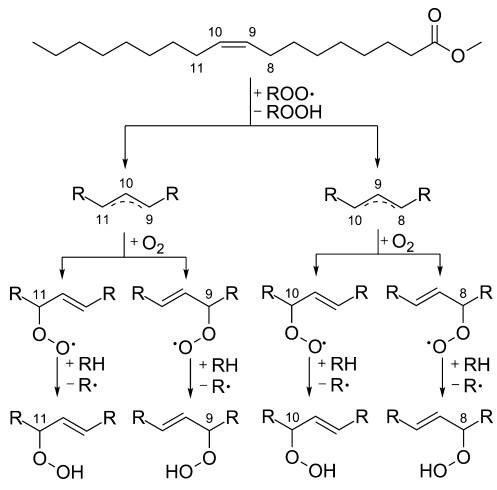

Figure 1. Mechanism of the formation of hydroperoxides from a monounsaturated FAME (C18:1), the first step of biodiesel aging.[3]

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oxides occur at similar ratios, the reactivity increases for bis-allylic hydrogen atoms, which can be found in polyunsaturated FAMEs. Relative rates of oxidation for methyl and ethyl esters of oleic, linoleic and linolenic acid are reported with 1:41:98.[3] Thus, degradation processes are not proportional to the number of double bonds in the molecule but to its number of bis-allylic sites.[4] Two common examples for polyunsaturated FAMEs are shown in Figure 2. The usage of oils containing

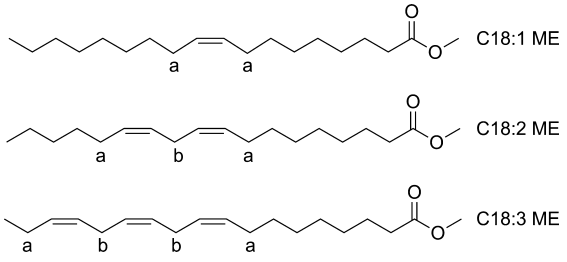

Figure 2. Common unsaturated C18 methyl esters in biodiesel: C18:1 ME, oleic acid methyl ester; C18:2 ME, linoleic acid methyl ester; and C18:3 ME, linolenic acid methyl ester, with (a) allylic positions and (b) bis-allylic positions.

high amounts of linoleic acid (C18:2) or linolenic acid (C18:3) is therefore limited, even though these feedstocks provide advantages, such as their excellent cold flow properties.

The hydroperoxides formed are rather unstable. They can undergo several different secondary reactions, which occur simultaneously and lead to a wide range of aging products. One of the most important of these reactions is β-cleavage (Figure 3). This fragmentation leads to the formation of aldehydes and

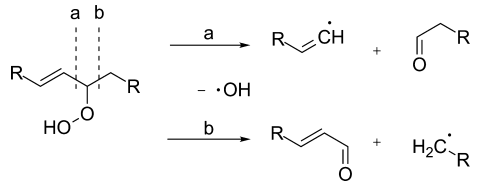

Figure 3. β-Cleavage can occur at two positions, leading to different aldehydes and radicals.

radicals. The former can be further oxidized to acids, while the latter react to form olefins or aldehydes. Other possible reactions of hydroperoxides are epoxidations, dehydrations, and oligomerizations, leading to the formation of epoxides, allylic ketones, and dimers and higher oligomers, respectively. These reactions were investigated in literature because of their importance in biological systems and food science. The book by Frankel offers an extensive overview of this matter.[3]

Several different methods for the determination of diesel fuel stability have been established. The most widely used methods can be devided into two measuring principles. In ASTM D2274[5] and EN ISO 12205,[6] the stability of diesel fuels is determined by the amount of sludge formed after several hours of heating the sample to 95 °C and purging it with oxygen. These methods are not suitable for biodiesel or petrodiesel/biodiesel blends. Because of the higher polarity of these fuels, a significant amount of sludge stays dissolved and is not accounted for in the analysis.[7] A second parameter for describing the stability of a fuel is the induction period (IP), also referred to as oil stability index (OSI). The IP gives information on the aging reserve that a fuel possesses under defined conditions. At the end of the IP, all natural and synthetical antioxidants are consumed and the actual fuel aging begins.

For the analysis of biodiesel and petrodiesel/biodiesel blends, the method to determine the IP is the accelerated oxidation test using a commercially available Rancimat device. The fuel sample is heated to 110 °C and purged with dry air. Volatile aging products, such as formic and acetic acid, are transferred to a measuring vessel, containing distilled water and a conductivity measuring cell. This oxidation test is in accordance with the European standards EN 14112[8] for pure biodiesel (B100) and EN 15751[9] for B100 and blends with a minimum of 2 vol % biodiesel. An alternative method is using an oxidation chamber pressurized with oxygen, in which the fuel sample is heated. A oxygen pressure decrease of 10%, caused by the reaction of the tested fuel with the oxygen, indicates the IP. A commercially available instrument fulfilling the corresponding standards ASTM D7545[10] and EN 16091[11] is the PetroOxy apparatus. The method is valid for biodiesel, petrodiesel, and blends of these in all ratios.

Jain and Sharma have extensively reviewed studies on the stabilities of biodiesel and its blends, investigating correlations of parameters, such as iodine value, peroxide value, and viscosity.[12] Investigations on the oxidative behavior of the precursors of biodiesel, mainly vegetable oils, have been carried out applying different strategies for the acceleration of the aging process. In the early studies by Frankel, oleic acid methyl ester and linoleic acid methyl ester were investigated as model compounds for the oxidation of fats and oils. Aging was performed by stirring samples under an oxygen atmosphere at temperatures ranging from 25 to 80 °C, and numerous aging products were identified.[13,14] In other studies, a Rancimat device was used to simulate the process of frying. Vegetable oils were heated to 180 °C, and the reaction vessels were left open and exposed to air. After transmethylation of the aged samples, various aging products, such as epoxy acids, keto acids, and hydroxy acids,[15] aldehydes, alcohols, and ketones,[16] were quantified. A recent study investigated the oxidation of soybean oil and biodiesel derived from soybean oil heated to 110 °C in a Rancimat. Losses in the tocopherol content, the development of oligomeric compounds, and sum parameters, such as acid value, peroxide value, and viscosity, were correlated to the IP.[17] Strömberg et al. investigated the formation of short-chain fatty acids (formic, acetic, and propionic acid) during accelerated aging of biodiesel and B7 at 80 °C under reflux in two studies. It was shown that, in biodiesel samples aged under these conditions for 14 days, formic acid is responsible for more than 40% of the total acid number and acetic and propionic acid are responsible for more than 7 and 3%, respectively.[18] Possible catalytic effects of aging products on freshly added fuel were investigated in a second study, but no direct influence of aging products on the degradation rate of freshly added fuel was found.[19]

In the present study, we report a detailed investigation of selected aging products formed during the accelerated aging of biodiesel. The accelerated aging was performed using a Rancimat device, which is widely established as a testing instrument for the oxidation stability of commercial biodiesel. The Rancimat offers exact temperature control, reproducible aging conditions, and the comparability of the results to the IP determined according to EN 14112. Analyses were focused on low- and medium-molecular-mass aging products that occur in

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high amounts, have a major influence on the characteristics of the fuel, or are attributed to malfunctions of engine parts.

EXPERIMENTAL SECTION

Sample Material. The biodiesel used in all experiments was rapeseed oil methyl ester (RME), obtained from ADM, Hamburg, Germany, and characterized according to EN 14214[20] using various standard methods.[8,21−35]

Equipment. A Metrohm 743 Rancimat device was used for biodiesel aging. For sample preparation, an Eppendorf Centrifuge 5702 was used. The gas chromatography−flame ionization detection (GC−FID) used for the analysis of FAMEs and epoxides was an Agilent 7890A system with a CTC Analytics autosampler and a DB-WAX (30 m, 0.25 mm, and 0.15 μm) column. The GC−FID used for the analysis of fatty acids was a Hewlett-Packard 5890 Series II system with a HP 7673 injector and a HP-5 (30 m, 0.32 mm, and 0.25 μm) column. Peak identification was carried out using a HP 6890 GC system with a HP 5973 MS, a HP 7683 injector, and a DB-5MS UI (30 m, 0.25 mm, and 0.25 μm) column. For ion-exchange chromatography (IEC), an Agilent 1260 LC system, a Bio-Rad Aminex HPX-87H (300 mm, 7.8 mm, and 9 μm) column, and a multiple wavelength detector were used.

Accelerated Aging of Biodiesel. Biodiesel was aged in a Rancimat device (Figure 4), following the parameters described in EN 14112.[8] In brief, 3.0 g of the fuel was weighed in a reaction vessel. The temperature was set to 110 °C, and the sample was purged with a constant stream of air of 10 L/h. After a defined reaction time, the aging procedure was stopped and fuel samples were stored under nitrogen at −20 °C until further analysis. Conductivity measuring vessels were filled with 50 mL of distilled water. The water was exchanged after every full hour to prevent large losses of water volume because of the stream of air. All water samples were kept and stored under nitrogen at +4 °C until further analysis.

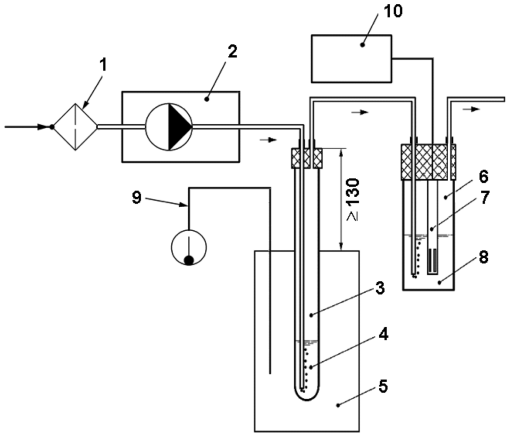

Figure 4. Scheme of the Rancimat device: (1) air filter, (2) gas membrane pump with a flow rate controller, (3) reaction vessel, (4) sample, (5) heating block, (6) measurement/conductivity cell, (7) electrode, (8) distilled/demineralized water, (9) thyristor and contact thermometer, and (10) personal computer (PC) for measuring and recording.

Quantification of Formic and Acetic Acid (IEC). The volatile acids formic and acetic acid were determined in both the aged sample and the Rancimat water vessel. Rancimat water samples were directly analyzed without further purification. Aged fuel samples were extracted with water, and the extract was purified using solid-phase extraction (SPE). The extraction was carried out by extracting a defined volume of sample (2−3 mL) with the same volume of distilled water by vigorous shaking in 10 mL screw-cap vials. To ensure optimal phase separation, the samples were centrifuged for 5 min at 4400 rpm. The organic layer was removed, and 0.9 mL of the aqueous phase was applied to a SPE cartridge (IST Isolute, C18-EC, 1 g, 6 mL). The analytes were eluted with 2.7 mL of distilled water. The aqueous eluate was used for analysis. Each sample preparation was performed at least in double. For IEC analysis, 10 μL of sample were injected (50 μL for samples with low concentrations of analytes). H_2SO_4 (5 mM) was used as an eluent with a flow rate of 0.6 mL/min. The column temperature was 75 °C, and a wavelength of 210 nm was used for detection. Quantification was carried out by external standard calibration with concentrations of 5, 10, 25, and 100 mg/L for formic acid and 5, 10, 25, 100, and 200 mg/L for acetic acid in distilled water.

The calculation of the concentrations in the aged fuel samples was obtained by applying eq 1, where $c(X,an)$ is the concentration of the respective acid detected by IEC and f is the dilution factor of 4 because of the SPE purification step.

$$c(X) = c(X,an)f \tag{1}$$

The amount of acids evaporated from the fuel samples was calculated from the acid concentrations in the water vessels. The volume of water (V_W) of 50 mL and the sample mass (m_S) of 3.0 g were taken into account, applying eq 2.

$$c(X) = \frac{c(XX,an)V_W}{m_S} \tag{2}$$

Because the water vessels were exchanged hourly, the concentrations of acids detected in the individual vessels were summed up to give the total amounts of acids produced during the aging process.

The efficiency of the extraction step was determined by extracting standard solutions of different concentrations of formic and acetic acid in unaged biodiesel, following the procedure described above. The recovery rate of the SPE purification step was determined by applying the purification procedure to standard solutions of different concentrations of formic and acetic acid in distilled water.

Quantification of Fatty Acids (GC−FID). A total of 10 fatty acids (see Table 1) were quantified in aged biodiesel. Samples were diluted in pyridine by a factor of 100 to a final concentration of approximately 10 mg/mL. Heptadecanoic acid (diluted in pyridine to a final concentration of approximately 0.1 mg/mL) was added as an internal standard (IS). A total of 100 μL of *N*-methyl-*N*-(trimethylsilyl)-trifluoroacetamide (MSTFA) (97%, Acros Organics) was added as a silylating agent directly to the sample solution into the 2 mL crimp top vial used for GC analysis. The sample was injected (1 μL) via a split injection system with a split ratio of 1:50. The starting temperature of 100 °C was held for 4 min, and then a temperature gradient of 10 °C/min was applied until a temperature of 300 °C was reached and held for 5 min. Fuel aging was carried out in triplicate, and each sample was analyzed in triplicate.

For external calibration, standard solutions of the analyzed acids in different concentrations and heptadecanoic acid as IS were silylated with MSTFA and analyzed applying the same GC parameters as described for the sample solutions. For all acids, five calibration points in the range of approximately 0.4−20 mg/L were analyzed. For nonanoic acid, the calibration range was extended to 60 mg/L.

Table 1. Quantified Fatty Acids

	systematic name	common name
C5	pentanoic acid	valeric acid
C6	hexanoic acid	caproic acid
C7	heptanoic acid	enanthic acid
C8	octanoic acid	caprylic acid
C9	nonanoic acid	pelargonic acid
C9di	nonanedioic acid	azelaic acid
C14:0	tetradecanoic acid	myristic acid
C16:0	hexadecanoic acid	palmitic acid
C18:0	octadecanoic acid	stearic acid
C18:1	*cis*-9-octadecenoic acid	oleic acid

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Table 2. Determined Fuel Properties of the Biodiesel Used in All Experiments

property	unit	test method	limit	result
ester content	mass %	EN 14103	≥96.5	99.6
density at 15 °C	kg/m^3	EN ISO 3675	860−900	882.8
viscosity at 40 °C	mm^2/s	EN ISO 3104	3.5−5.0	4.4833
flash point	°C	EN ISO 3679	≥101	179.5
sulfur content	mg/kg	EN ISO 20846	≤10	3
carbon residue remnant	mass %	EN ISO 10370	≤0.3	0.06
sulfated ash content	mass %	ISO 3987	≤0.02	<0.01
water content	mg/kg	EN ISO 12937	≤500	175.5
total contamination	mg/kg	EN 12662	≤24	6
oxidation stability at 110 °C	h	EN 14112	≥8	7.2
acid value	mg of KOH/g	EN 14104	≤0.5	0.16
iodine value	g/100 g	EN 14111	≤120	111.6
linolenic acid methyl ester	mass %	EN 14103	≤12	9.1
polyunsaturated methyl esters (≥4 db)	mass %	EN 14103	≤1	<0.1
methanol content	mass %	EN 14110	≤0.2	0.03
monoglyceride content	mass %	EN 14105	≤0.7	0.63
diglyceride content	mass %	EN 14105	≤0.2	0.08
triglyceride content	mass %	EN 14105	≤0.2	<0.01
free glycerine	mass %	EN 14105	≤0.02	0.007
total glycerine	mass %	EN 14105	≤0.25	0.18
Group I metals (Na + K)	mg/kg	EN 14538	≤5	<0.2/<0.2
Group II metals (Ca + Mg)	mg/kg	EN 14538	≤5	<0.2/<0.2
phosphorus content	mg/kg	EN 14107	≤4	<0.2

Quantification was obtained by comparing the peak areas of the analytes in the samples (after IS correction) to the obtained calibration curves.

Quantification of FAMEs and Epoxides (GC−FID). The standard method for determining the ester content of biodiesel, EN 14103,[21] was applied with two modifications. The amount of IS was reduced to improve the comparability of the peak areas of interest. For the analysis of epoxides, the GC temperature program was modified to avoid coelution with other compounds. Approximately 100 mg of sample and 50 mg of nonadecanoic acid methyl ester (≥99%, Sigma-Aldrich) as an IS were accurately weighed in a 10 mL tube and diluted with 10 mL of toluene. A total of 1 μL of the solution was injected via a split injection system with a split ratio of 1:100 and a constant flow of helium of 0.7 mL/min. For FAMEs, the starting temperature of 60 °C was held for 2 min and then a temperature gradient of 10 °C/min was applied until a temperature of 200 °C was reached. A temperature gradient of 5 °C/min was applied until a temperature of 240 °C was reached and held for 7 min. For epoxides, the starting temperature was 150 °C. A temperature gradient of 5 °C/min was applied until a temperature of 220 °C was reached and held for 15 min. Quantification was carried out by comparing the peak areas of the analytes to those of the IS, assuming the same detector response for all analytes of interest, applying eq 3. The mass percentage of the analyte of interest [mass % (X)] is determined by the peak areas of the analyte (A_X) and the IS (A_{IS}), respectively. m_{IS} is the mass of the IS added to a defined mass of sample (m_S).

$$\text{mass \% } (X) = \frac{A_X}{A_{IS}} \frac{m_{IS}}{m_S} \times 100 \tag{3}$$

Accelerated Aging of FAME Standards. Approximately 200 mg of oleic acid methyl ester (≥99%, Fluka), linoleic acid methyl ester (≥99%, Merck), and linolenic acid methyl ester (≥98%, Merck) were accurately weighed into a Rancimat reaction vessel. Approximately 1.5 g of stearic acid methyl ester (≥99%, Merck) was added to enable a sufficient sample amount for the Rancimat aging procedure. Temperature and stream of air were applied as described above. Samples of approximately 20−50 mg were taken with a Pasteur pipet and accurately weighed into 2 mL crimp top vials. Nonadecanoic acid methyl ester (≥99%, Sigma-Aldrich) was added as an IS in 1 mL of a solution in toluene (1 mg/mL). Analysis of the FAME composition was performed via GC−FID with the conditions described above.

RESULTS AND DISCUSSION

Characterization of Sample Material. The determined fuel properties are shown in Table 2, and the FAME composition is shown in Table 3. All parameters, except for oxidation stability, are within the specifications of EN 14214, and the FAME composition is typical for RME.

Quantification of Formic and Acetic Acid. To obtain a complete picture of volatile acid formation, the concentrations of formic and acetic acid were determined in the aged fuel samples in the heating block as well as in the distilled water of the Rancimat water vessel. Table 4 shows the amount of acids found in the aged fuel samples and the amount evaporated and

Table 3. FAME Composition of the Biodiesel Used in All Experiments

FAME	mass %
C10:0	<0.1
C12:0	<0.1
C14:0	<0.1
C16:0	4.5
C16:1	0.2
C18:0	1.8
C18:1	63
C18:2	19
C18:3	9.1
C20:0	0.6
C20:1	1.1
C20:2	0.1
C22:0	0.2
C22:1	<0.1
C24:0	<0.1
C24:1	<0.1

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Table 4. Concentrations of Formic and Acetic Acid Developed during the Aging Process of Biodiesel, Measured in Aged Biodiesel and Rancimat Water

	concentration of formic acid (mg/kg)		concentration of acetic acid (mg/kg)	
aging time (h)	water vessel	fuel sample	water vessel	fuel sample
0	nd[a]	nd	nd	nd
2	nd	nd	nd	nd
3	nd	nd	nd	nd
4	nd	nd	nd	4.9 ± 2.7
5	nd	nd	nd	nd
6	nd	5.1 ± 0.5	60 ± 30	26 ± 4
7	34 ± 2	13 ± 2	60 ± 30	84 ± 7
8	290 ± 10	110 ± 20	60 ± 30	230 ± 40
9	1300 ± 40	130 ± 2	160 ± 30	350 ± 50
10	2700 ± 60	200 ± 50	310 ± 40	520 ± 70
11	4100 ± 70	200 ± 30	480 ± 40	660 ± 70
12	5400 ± 80	190 ± 10	670 ± 50	690 ± 30

[a]nd = not detected.

transferred to the water vessels. The concentrations determined in the distilled water of the measuring vessel, which was exchanged every hour during the aging process, were summed up and referred to the mass of the aged sample.

Because of the applied stream of air and the elevated aging temperature, a major portion of both acids of interest (ca. 97% of formic acid and ca. 51% of acetic acid after 12 h of aging) was transferred to the water vessel.

In Figure 5, the development of the total concentration of formic and acetic acid formed during the aging process, calculated from Table 4, is shown.

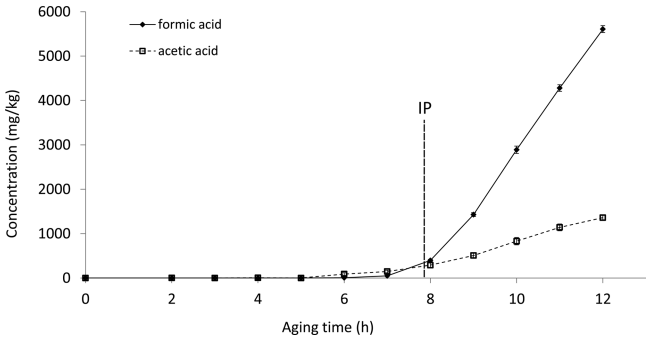

Figure 5. Total concentration of formic and acetic acid per kilogram of sample, measured in aged biodiesel and Rancimat water collected during the aging process. Error bars = standard deviation (SD).

The curves obtained for both examined acids show a slow increase 1−2 h before the end of the IP is reached. Then, a strong increase in acid formation was observed. This principle is used to determine the IP with the Rancimat device. The increase of conductivity measured in the water vessel is induced by the formation of formic acid, and, to a lower extent, acetic acid.

The amount of formic acid formed after 8 h, shortly after the end of the IP of the fuel, is 400 ± 20 mg/kg, and after 12 h of aging in the Rancimat, 5600 ± 80 mg/kg of formic acid is formed. This corresponds to concentrations of 7.6 ± 0.5 and 107 ± 2 mmol/L, respectively. These are amounts that are not negligible considering the corrosive effects that formic acid can have on fuel carrying and engine parts.

The amount of acetic acid formed after 8 h of aging is 290 ± 50 mg/kg, after 12 h, 1360 ± 60 mg/kg was observed. The corresponding concentrations of 4.3 ± 0.7 and 19 ± 1 mmol/L are significantly lower than for formic acid.

The efficiency of the extraction from biodiesel to water found for formic and acetic acid was above 98 and 99%, respectively. The recovery rate of the SPE purification was above 99% for formic acid and 82% for acetic acid, with relative standard deviations lower than 3%. These values were accounted for in the calculations.

The samples were also analyzed for propionic and butyric acid, with no results above the limit of quantification of 5 mg/kg.

A direct comparison of the present results to the study by Strömberg et al.[19] is not possible because of the different aging conditions applied. In the present study, the applied temperature was 110 °C and the sample was continuously purged with air, while in the study by Strömberg et al., the aging conditions were significantly milder. The fuel was aged at 80 °C in a reflux system, with contact to air only via a drying tube. This explains the differences in the concentrations of formic and acetic acid found in the two studies. For formic acid, Strömberg et al. report approximately 600 mg/kg after 14 days of aging, and for acetic acid, Strömberg et al. report approximately 160 mg/kg, with both values being about an order of magnitude smaller than the results after 12 h of aging in the present study.

Quantification of Fatty Acids. The linearity of the system is shown in Table 5. For all analytes, coefficients of determination after linear regression (R^2) of 0.9998 or higher were obtained. Limits of detection (LOD), defined as a signal/noise ratio of 3:1, were in the range of 8−18 mg/kg.

Table 5. Concentration Range and R^2 for the Determination of Linearity

analyte	concentration range in fuel (mg/kg)	concentration range after dilution (mg/L)	R^2
C5	40−2000	0.4−20	>0.9999
C6	40−2000	0.4−20	0.9999
C7	40−2000	0.4−20	0.9998
C8	40−2000	0.4−20	0.9999
C9	40−6000	0.4−60	>0.9999
C9di	40−2000	0.4−20	>0.9999
C14	40−2000	0.4−20	>0.9999
C16:0	40−2000	0.4−20	>0.9999
C18:0	40−2000	0.4−20	>0.9999
C18:1	40−2000	0.4−20	>0.9999

The analyzed fatty acids can roughly be divided into two groups, acids formed after fragmentation reactions and acids formed after hydrolysis of the corresponding methyl esters. In Figure 6, the results for fatty acids with a chain length of five to nine carbon atoms (C5−C9) and nonanedioic acid (C9di) are shown. Neither these acids nor their corresponding methyl esters are present in the unaged fuel. They are formed during the aging process, following the mechanisms described in Figures 1 and 3. Nonanoic acid (after 5 h of aging) and hexanoic acid (after 6 h) are the first acids to be detected. They are oxidation products of nonanal and hexanal, compounds derived from oleic acid methyl ester and linoleic acid methyl ester via β-cleavage. Nonanoic acid, originating from the major component (C18:1 ME) of the investigated fuel, is the carboxylic acid that reaches the highest concentration during

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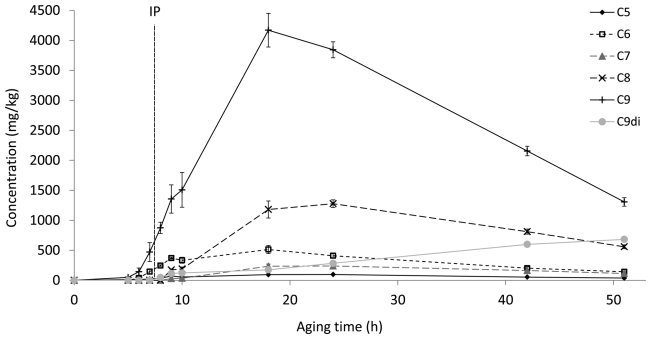

Figure 6. Concentrations of C5−C9 acids in aged biodiesel. Error bars = SD.

the aging process. Its concentration decreases at high aging times, when the content of C18:1 ME in the fuel decreases and nonanoic acid is further oxidized or decomposed.

In Figure 7, the results for free fatty acids with a chain length of 14−18 carbon atoms (C14−C18) are shown. Palmitic acid

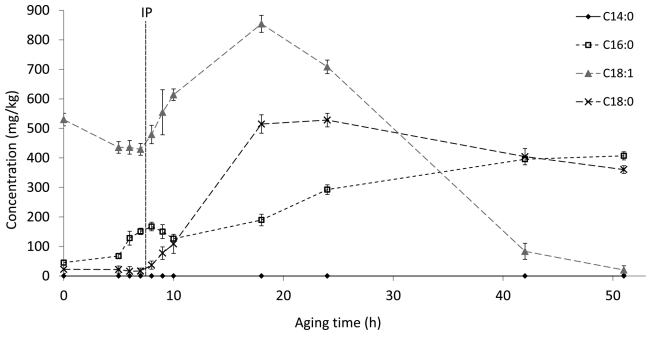

Figure 7. Concentrations of free C14−C18 acids in aged biodiesel. Error bars = SD.

(C16:0), stearic acid (C18:0, values below the limit of quantification of 40 mg/kg at 0, 5, 6, and 7 h of aging), and oleic acid (C18:1) are present as free fatty acids in the unaged fuel. After the end of the IP, the concentrations of these compounds increase. Hydrolysis of fatty acid methyl esters is catalyzed by acids, which are present in the fuel in significant amounts after this point. The concentrations of the saturated fatty acids C16:0 and C18:0 show only minor changes at higher aging times, but the monounsaturated fatty acid C18:1 undergoes decomposition because of fragmentation and epoxidation and is below the limit of quantification after 51 h of aging.

Myristic acid (C14:0) could not be detected in fresh or aged fuel samples.

Change in FAME Composition during Aging. The change in the FAME content and distribution is shown in Figure 8, using the different C18 methyl esters that are the main components of the investigated biodiesel as an example. Until the end of the induction period of the fuel is reached, the composition stays nearly constant. From 8 h on, there is a rapid decline for FAMEs with two or more double bonds. The concentration of the monounsaturated oleic acid methyl ester is declining as well, although with a slower rate. After 18 h of aging, C18:3 ME is not longer detectable in the samples, and after 24 h of aging, C18:2 ME is fully decomposed. The concentration of C18:0 ME stays roughly constant during the

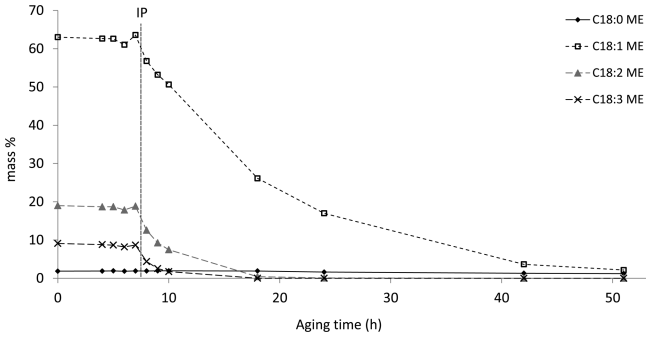

Figure 8. Change in C18 FAME composition of biodiesel during aging.

aging process, decreasing from 1.8 mass % in the unaged fuel to 1.2 mass % after 52 h of aging.

To show the different rates of aging reactions for unsaturated FAMEs more clearly, the aging process was also performed with a mixture of standard compounds of similar concentrations. The results are shown in Figure 9.

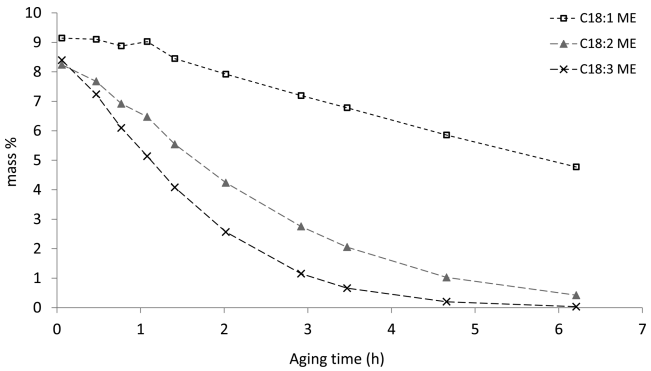

Figure 9. Change in the composition of a C18 methyl ester standard mixture during aging.

Because the mixture was composed only of standard materials of high purity, there are no natural or synthetic antioxidants present. Therefore, the mixture does not possess an aging reserve, and the aging process immediately begins. The decrease of C18:2 ME and C18:3 ME is already visible after half an hour, while the concentration of C18:1 ME stays constant for more than 1 h. The reactivity of the compounds examined is C18:3 ME > C18:2 ME ≫ C18:1 ME, which is in accordance with existing literature.[3]

Epoxide Formation during Aging. Two epoxides were identified as major aging products, *trans*-9,10-epoxy stearic acid methyl ester and *cis*-9,10-epoxy stearic methyl ester (Figure 10). Identification of the two isomers was obtained by comparison of the GC elution order with literature data.[36,37]

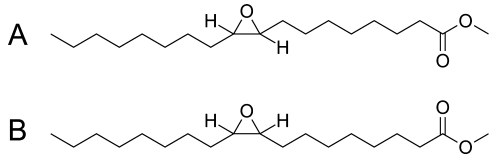

Figure 10. Structures of epoxides formed from oleic acid methyl ester during aging: (A) *trans*-epoxy stearic acid methyl ester and (B) *cis*-epoxy stearic acid methyl ester.

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On a polar capillary column, such as the DB-WAX column used in this study, the *trans* isomer elutes first.

The formation of these epoxides is visible after the end of the IP of the fuel, with the concentration of the *trans* isomer being higher than the concentration of the *cis* isomer (Figure 11).

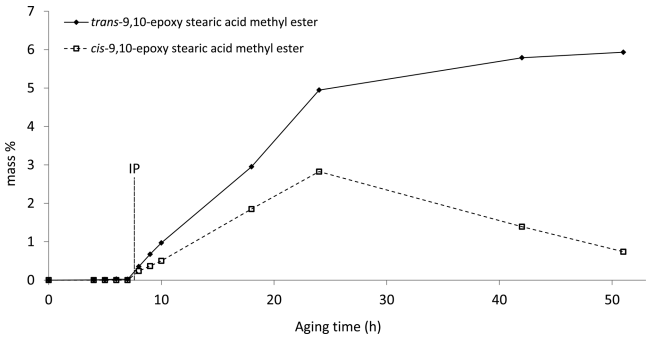

Figure 11. Concentration of epoxystearates in aged biodiesel.

After 24 h of aging time, there is a change in the curve shape for both epoxides. The increase in the concentration of the *trans* isomer slows down with higher aging time, while the concentration of the *cis* isomer decreases. Thermal isomerization, leading to the formation of the thermodynamically more stable *trans* isomer, is a possible explanation for this behavior.

Additionaly, four different epoxy oleic acid methyl esters, which result from the monoepoxidation of linoleic acid methyl ester, can be observed. Because of the lower initial content of C18:2 ME in the fuel and the higher affinity of C18:2 ME to form hydroperoxides and undergo β-cleavage, their content in the aged fuel is much lower and does not exceed 0.1 mass % after 24 h of aging. Because of the remaining double bond in the molecules, these epoxides can easily undergo further reactions.

CONCLUSION

The end of the IP of a biodiesel as determined by the Rancimat accelerated oxidation test is the starting point for major changes in fuel composition. Unsaturated FAMEs, which are the main components of biodiesel, are decomposed or oligomerized, and aging products, such as acids of various chain lengths, aldehydes, alcohols, and epoxides, begin to form. Some of these aging products can influence fuel carrying or engine parts and engine performance in a negative way. Quantification of individual aging products can give important information when evaluating the quality of a fuel. The IP is a substantial indicator for fuel stability and can be significantly increased by the addition of synthetic antioxidants, leading to a prolonged period with little or no aging product formation. On a large scale, biodiesel is mainly used as a blending compound for petrodiesel. The investigation of the aging behavior in these blends and the mutual influence that the blended fuels have on each other will be of great interest in the future.

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Notes

The authors declare no competing financial interest.

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