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Chemical Changes in Fossil and Biogenic Heating Oils on Long-Term Storage

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Supporting Information

ABSTRACT: The formation of sediments in biogenic and fossil heating oils as well as in their blends is a well-known problem. These deposits can plug filters and nozzles in heating systems and, consequently, cause economic losses. Polymerization and the formation of corrosive acids are possible explanations for these incidents. To study the influence of long-term storage on different heating oils (biogenic, fossil, and a 10% blend) and to investigate the changes in their composition, the oils were stored for a period of 12−24 months at nearly ambient (40 °C) and analyzed with different techniques every 6 weeks. The formation of several kinds of oxidation products was demonstrated, including ketones, epoxides, aldehydes, carboxylic acids, and furans. Size-exclusion chromatography was used to demonstrate the formation of oligomeric products of the fatty acid methyl esters (FAMEs) (up to pentamers). Short-chain (C_1−C_6) carboxylic acids were quantified with ion chromatography, and larger carboxylic acids were indicated by mass spectrometry. The first recorded experimental evidence for a coupling reaction between a FAME and components of the fossil oil, namely, such containing the nitrogen heterocycle indols, is described. Cross-coupling products between biogenic and fossil compounds were detected using Orbitrap ultrahigh-resolution electrospray ionization mass spectrometry.

1. INTRODUCTION

In recent years, many countries have mandated that fossil fuels and heating oils are blended with biologically derived compounds, primarily fatty acid methyl esters (FAMEs) derived from plant oils. Thus, in the European Community, blends containing 7% are required (DIN EN 590). However, the use of FAMEs is not without problems of a chemical nature.

An important criterion for practical use is stability of the fuel. Just as vegetable oils are oxidized upon storage, especially the unsaturated FAMEs in blends are reactive with atmospheric oxygen to produce oxidized FAMEs,[1] but naturally occurring compounds, such as phenols, can increase the stability toward oxidation.[2] In subsequent reactions, these products can undergo chain scission, forming short-chain aldehydes and carboxylic acids.[3,4] A further oxidation pathway leads to dimers and oligomers of the FAMEs via radicals.[5] All such reactions reduce the quality of the blend because acidic and, thus, corrosive products are formed. Besides that, the viscosity and polarity of the blends increase. Because of the poor solubility of highly polar compounds in the nonpolar fuel matrix, those reaction products aggregate and can form sediments that can lead to clogging of tubing and nozzles with economic losses as a consequence.[6]

It is obvious that a thorough understanding of the reactions between oxygen and FAMEs in blends is of paramount importance for any attempt to reduce their impact. Such reactions have been studied in great detail for vegetable oils because of their immense economic importance as food stuff,[7] and many of these reactions and reaction products should be equally applicable to FAMEs. However, in blends, there may be an additional influence of the fossil components that in many cases are present at a higher concentration than the methyl esters. The possibility of interactions between the FAMEs and fossil components has often been postulated[8] but not well-documented and should present a fruitful field of research; only one example of such a reaction has been experimentally demonstrated.[9] Rational measures can be undertaken to reduce the influence of oxidative processes on the quality of the blends only if the details of these processes are understood.

As part of a project on the aging processes of blends, we undertook a long-term storage experiment that intentionally was carried out at only slightly above ambient, 40 °C. Very often, aging experiments are run at an elevated temperature to accelerate the process, but it has been noted that, among other things, the final viscosity can be considerably increased if higher temperatures are used.[10] Because our goal was to investigate processes that occur on normal storage of heating oil, we preferred as low as possible a temperature compatible with the goal that changes should be clearly visible within a 2-year period. Here, we report on the chemical characterization of blends aged in this way for up to 2 years. Gas chromatography, size-exclusion chromatography, ion chromatography, infrared spectrometry, elemental analysis, and mass spectrometry provided details on the functional groups in the aged material and allowed for the characterization of individual compounds. A sediment was also investigated using Orbitrap high-resolution mass spectrometry.

2. EXPERIMENTAL SECTION

2.1. Materials and Standard Compounds. Solvents were purchased from Acros Organics (Niederrau, Germany). The polyethylene glycol standard kit was supplied by Agilent (Böblingen,

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Germany). Methyl oleate (purity ≥ 99%) and standard compounds for gas chromatography/mass spectrometry (GC/MS) experiments were obtained from Sigma-Aldrich (Munich, Germany).

2.2. Long-Term Storage of the Heating Oils. Two heating oils extra light (sulfur < 50 ppm) and two FAME qualities were stored either pure or in blends for a period of 1 year in the case of FAMEs and 2 years in the case of the blends [containing 10% (w/w) FAME] and heating oils, as listed in Table 1. The aromatic contents of the heating oils are listed in Table S1 of the Supporting Information, and the distribution of the FAMEs are listed in Table S2 of the Supporting Information. The six fuels were stored in open glass bottles in a heating cabinet at 40 °C in a sufficient number of bottles to allow for withdrawal of one bottle of each fuel every 6 weeks for analysis of changes in fuel composition. The sediment and the liquid phase were separated by decantation.

Table 1. Heating Oil and Blends Used for Long-Term Storage Tests[a]

designation	material
B1	heating oil A
B2	heating oil B
B3	heating oil A + 10% (w/w) FAME 2
B4	heating oil B + 10% (w/w) FAME 2
B5	FAME 2 (70% RME + 30% SME)
B6	FAME 1 (100% RME)

[a]RME, FAMEs from rapeseed oil; SME, FAMEs from soybean oil.

2.3. Gas Chromatography with Flame Ionization Detection (GC/FID). The samples were diluted in a mixture of cyclohexane and dichloromethane (1:1, v/v) and analyzed using a Hewlett-Packard 5890 series II gas chromatograph with a FID and a SLB-5 ms Supelco capillary column (30 m × 0.25 mm × 0.25 μm). The oven temperature was held at 60 °C for 1 min, then programmed at 5 °C min^{-1} to 300 °C, and held for 5 min. The injection volume was 1 μL, and the flow rate of the hydrogen carrier gas was 40 cm/s.

2.4. Gas Chromatography with Mass Spectrometry (GC/MS). The gas chromatograph was a Finnigan MAT GCQ coupled with a Finnigan MAT GCQ Polaris MS mass spectrometer. The same column and temperature program as in the GC/FID analysis were used. The carrier gas was helium at 40 cm/s. Databases used were those from the National Institute of Advanced Industrial Science and Technology (AIST, Japan) and Wiley Subscription Services (WSS, Inc., Hoboken, NJ).

2.5. Solid-Phase Extraction (SPE) of FAME Oxidation Products. A total of 200 μL of the biodiesel B5 was added to a silica gel cartridge (SampliQ, 200 mg, 3 mL, from Agilent) and eluted with 3 mL of cyclohexane, 3 mL of cyclohexane/dichloromethane (1:1), and 3 mL of dichloromethane. The fractions were collected separately and analyzed by GC/FID and GC/MS.

2.6. Size-Exclusion Chromatography (SEC). About 100 mg of the samples was weighed and dissolved in 1 mL of tetrahydrofuran (THF). The solutions were analyzed using a PSS SECurity GPC system coupled with a refractive index detector (Agilent Infinity 1260 RID). A combination of four columns of the same type were used (PSS SDV, 100 Å, 5 μm) with a guard column of 5 cm length and three columns of 30 cm length each. THF was used as the mobile phase at a flow rate of 0.7 mL/min. The correlation of molar mass with the elution volume was made with the help of a calibration with polyethylene glycols (194−16 100 Da).

2.7. Infrared (IR) Spectrometry. Undiluted samples were filled into a sample holder with a barium fluoride window and measured with a Bruker Vector 22 spectrometer.

2.8. Elemental Analysis. The elements C, H, and N were determined in-house with a VARIO EL III (Elementar Analysensysteme GmbH, Hanau, Germany). The oxygen data were obtained by subtracting the numbers thus determined from 100%. This is a good approximation because no other elements, except C, H, N, and O, should be present in noticeable amounts in the samples. The data in Table 2 were determined by Hekatech GmbH (Wegberg, Germany).

2.9. Ion Chromatography (IC). A total of 1 mL of the sample, 1 mL of heptane, and 5.5 mL of carbonate buffer (pH 10.33) were successively filled into a syringe (10 mL). The syringe was turned upside down to dispel the air. Then, the syringe was shaken slowly for 1 min and placed in a test tube rack for phase separation. After 1 h, the aqueous phase was separated from the organic phase and analyzed using IC. Samples of B6 after 0 and 6 months of storage and a blank without sample were investigated.

The system used was a Metrohm 882 Compact IC plus a Metrosep Organic Acids column (250 × 7.8 mm) with conductivity detection. The eluent was a 95:5 (v/v) mixture of acetonitrile and sulfuric acid (0.05 mol/L) at a flow rate of 0.5 mL/min.

2.10. Mass Spectrometric Analysis. The samples were analyzed using electrospray ionization (ESI) and high-resolution mass spectrometry (Thermo Fisher, Orbitrap LTQ XL) in the positive or negative mode. The measurements were performed in the Institute of Organic Chemistry, University of Münster, Münster, Germany.

3. RESULTS AND DISCUSSION

3.1. Long-Term Storage. Two low-sulfur heating oils (sulfur content < 50 ppm) and two FAME qualities were stored either pure or in blends for a period of up to 24 months, as listed in Table 1.

The storage temperature was 40 °C to accelerate the aging somewhat. Samples were taken at 6-week intervals and extensively analyzed for changes using GC, SEC, IC, IR spectrometry, MS, and elemental analysis. GC, IC, and MS give information on changes of individual compounds, while the other techniques are rather bulk-dependent.

Table 2. Elemental Analysis Data (%, w/w)[a]

sample	storage time (months)	C (%, w/w)	H (%, w/w)	O (%, w/w)
heating oil B2	0.0	86.26 ± 0.14	13.52 ± 0.02	0.33 ± 0.03
	24.0	86.75 ± 0.03	13.50 ± 0.01	0.21 ± 0.02
blend B3	0.0	85.69 ± 0.09	13.24 ± 0.03	1.28 ± 0.02
	18.0	85.21 ± 0.01	13.10 ± 0.03	2.09 ± 0.00
	24.0	85.04 ± 0.05	13.10 ± 0.02	2.20 ± 0.01
sediment of B3	19.5	69.73 ± 0.01	9.09 ± 0.01	20.96 ± 0.06
blend B4	0.0	85.29 ± 0.05	13.38 ± 0.09	1.21 ± 0.04
	18.0	85.33 ± 0.12	13.34 ± 0.01	1.51 ± 0.03
	24.0	85.35 ± 0.04	13.30 ± 0.04	1.56 ± 0.02
biodiesel B6	0.0	77.30 ± 0.05	12.18 ± 0.01	10.80 ± 0.03
	12.0	75.44 ± 0.09	11.89 ± 0.03	12.85 ± 0.01

[a]Average results of two determinations are shown.

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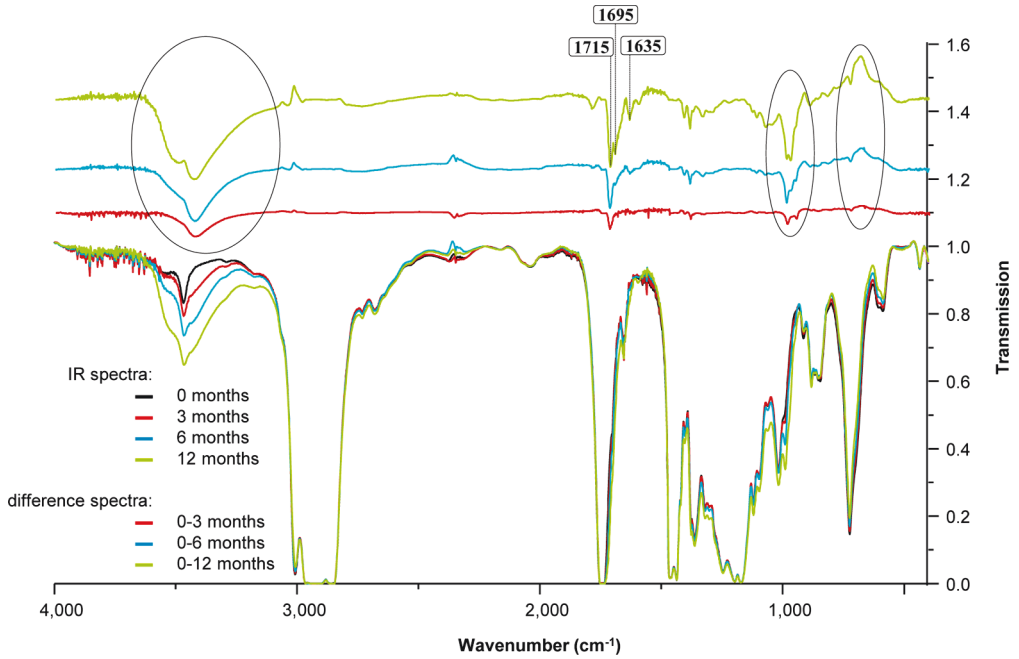

Figure 1. IR spectra of sample B6 (100% FAME) taken at 0 months (black), 3 months (red), 6 months (blue), and 12 months (green). The differential spectra of 0−3 months (red), 0−6 months (blue), and 0−12 months (green) of storage are shown at the top of the figure. The indicated areas are discussed in the text.

3.2. Elemental Analysis. The elemental analyses of three samples at the start and after several months of storage are listed in Table 2.

There are no noticeable changes in the element composition for the fossil oil. Blend B3, which formed a sediment during the storage, shows a larger increase in the oxygen content than blend B4, which did not form a sediment, as well as FAME sample B6, which showed a clear increase in the oxygen content throughout the storage period. In B3, an increase of the oxygen content of 70% was observed. To start from the premise that oxygen reacted with the unsaturated FAME part of the blend, 1.5 oxygen atoms were taken up on average per FAME molecule after 24 months of storage. In this blend, a sediment was formed after 18 months. The sediment continued to separate after 6 more weeks of storage and could be separated from the liquid phase. Unsurprisingly, the oxygen content is very high in the sediment, with an average of 2.2 oxygen atoms taken up per unsaturated FAME molecule, and shows that polar species must have been formed that are insoluble in the rather nonpolar matrix and, thus, aggregate and separate as a gum from the liquid matrix. No sediment was formed in blend B4. The oxygen content increased by approximately 30%, which reflects an uptake of 0.7 oxygen atoms per unsaturated FAME molecule. In the biodiesel B6, the amount of oxygen increased by 20% after storing for 12 months. This means an uptake of oxygen of 0.4 oxygen atoms per unsaturated molecule. No sediment was formed in the biodiesel samples. This may be due to the fact that its matrix consists only of FAME, making the matrix more polar than that of the fossil matrix in the blends, with the consequence that the products of oxidation are soluble.

3.3. IR Spectrometry. IR indicates functional groups and has been extensively used to follow oxidative changes in FAME blends.[11−14] Subtracting the IR spectrum of the non-aged material from that of the aged material gives a differential spectrum that highlights any changes. In Figure 1, the IR spectrum of a FAME mixture is reproduced at times 0 and after 6 and 12 months of storage together with the differential spectra between these and the non-aged sample (top). There are clear increases in signals for hydroxy groups (3495 cm^{-1}), as evidenced by the signal in this region in the differential spectrum. The OH band can, in principle, be derived from water, a product of the oxidation of FAMEs, but thorough drying of the sample to remove water did not change the spectrum, so that the band in this region is ascribed to organic compounds containing the OH function, such as alcohols, hydroperoxides, and carboxylic acids. Even at the start of the storage, there are small signals that point to oxidation products. These must have arisen either through oxidation during the transport and storage in tanks before the biodiesel was used for these experiments or because of residual glycerol in the FAME mixture. The presence of glycerol in biodiesel cannot be excluded. In DIN EN 14214, a maximum content of 200 ppm of free glycerol and 7000 ppm of monoglycerides is allowed, so that this may explain (part of) the band at 3495 cm^{-1}.

The region of carbonyl groups (ca. 1715 cm^{-1}) also shows enhanced absorption in the differential spectra. Ketones as well as aldehydes, formed after chain scission, are well-known products in the oxidation of FAMEs.[15] After 12 months of storage, a further absorption band at ca. 1695 cm^{-1} emerged, which is attributed to carbonyl groups as well.[16] The positions of the bands do not allow for a distinction to be made between the different possible functionalities because of overlapping wavelengths of their absorption.

A weaker increase at 1635 cm^{-1} points toward a double bond that is conjugated with another double bond or a carbonyl group. In the natural FAMEs, the double bonds are isolated; therefore, an isomerization to a conjugated system is indicated by this IR band,[17] as is known to happen upon aging.[7] In the fingerprint region, an increase for the *trans* double bonds (980 cm^{-1}) and a decrease for the *cis* double bonds (685 cm^{-1}) is easily visible. FAMEs are known to react with oxygen to allylic

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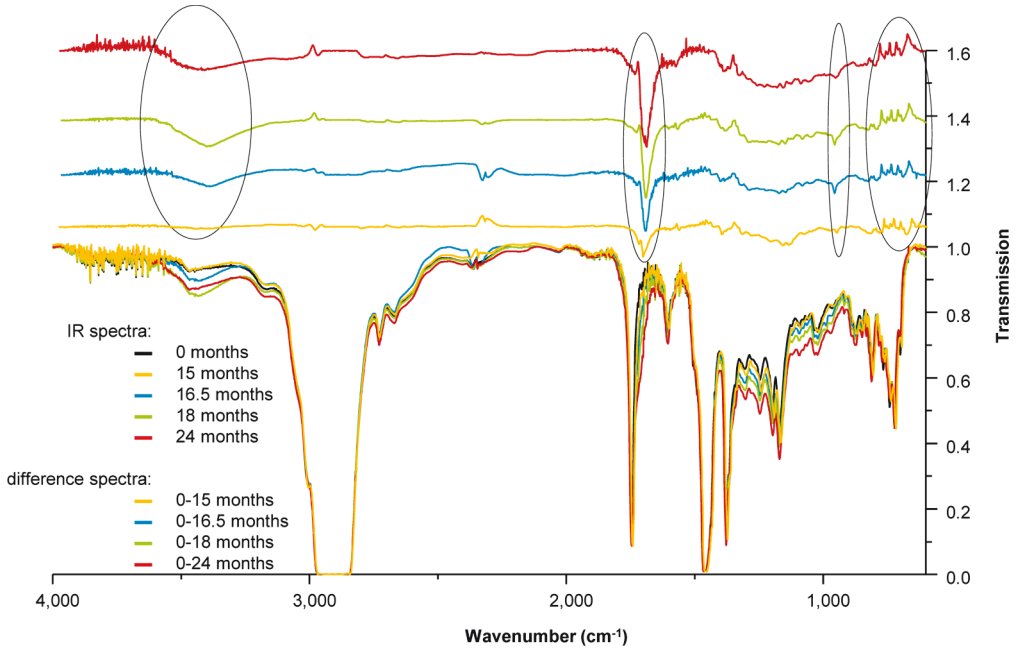

Figure 2. IR spectrum of sample B3 (10% FAME) taken at 0 months (black), 16.5 months (blue), 18 months (green), and 24 months (red) at 40 °C. (Top) Differential spectra of 0−16.5 months (blue), 0−18 months (green), and 0−24 months (red) of storage. The indicated areas are discussed in the text.

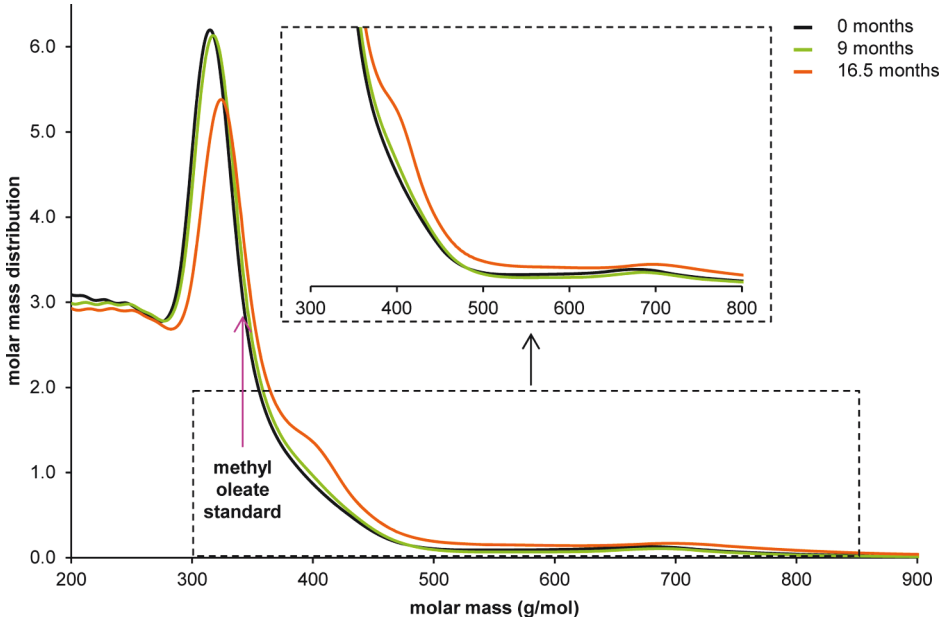

Figure 3. SEC of blend B3 at 0, 9, and 16.5 months of storage. The elution volume axis has been labeled with the corresponding molar mass. The calibration of the *x* axis was performed using polyethylene glycols and may not be accurate for FAMEs. Methyl oleate has a molar mass of 296 g/mol.

radicals that may isomerize to the more stable *trans* isomer.[15] Furthermore, the *cis* double bonds can form epoxides and, thus, are removed from the mixture.[18]

The spectra of the two FAMEs (B5 and B6) are identical. This may be explained by nearly the same content of unsaturated compounds (see Table S2 of the Supporting Information). In the two fossil heating oils (B1 and B2), there were only small differences in the fingerprint region between the spectra before aging and after storage for 18 months. They are a result of the loss of rather volatile compounds, such as low-molecular-weight aromatics (880−680 cm^{-1}). When the fossil heating oil B1 was stored for 9 months with copper to accelerate the aging process, a sediment was formed and a large number of aromatic ketones were indicated by MS, among them indanones, naphthyl ketones, and 9-fluorenones.[19]

The loss of volatile compounds was also present in the two blends (B3 and B4), and in addition, there are some other differences in the IR spectra (Figure 2). The FAMEs in both blends were stable for more than 1 year, but in B3, there were first signs of changes in the composition after 15 months. New signals appeared at wavenumbers of 3420 cm^{-1} (hydroxyl), 1738 cm^{-1} (carbonyl), and 990 cm^{-1} (*trans* double bonds) and a decrease of the signals at 800−670 cm^{-1} (*cis* double bonds) until 18 months. Both of the blends consist of the same FAME

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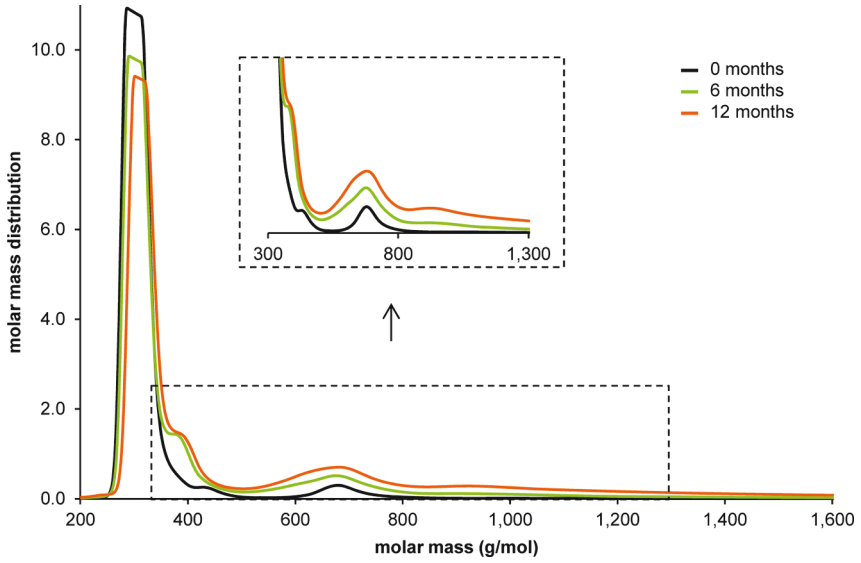

Figure 4. SEC of biodiesel B6 at 0, 6, and 12 months of storage. The elution volume axis has been labeled with the corresponding molar mass. The calibration of the *x* axis was performed using polyethylene glycols and may not be accurate for FAMEs.

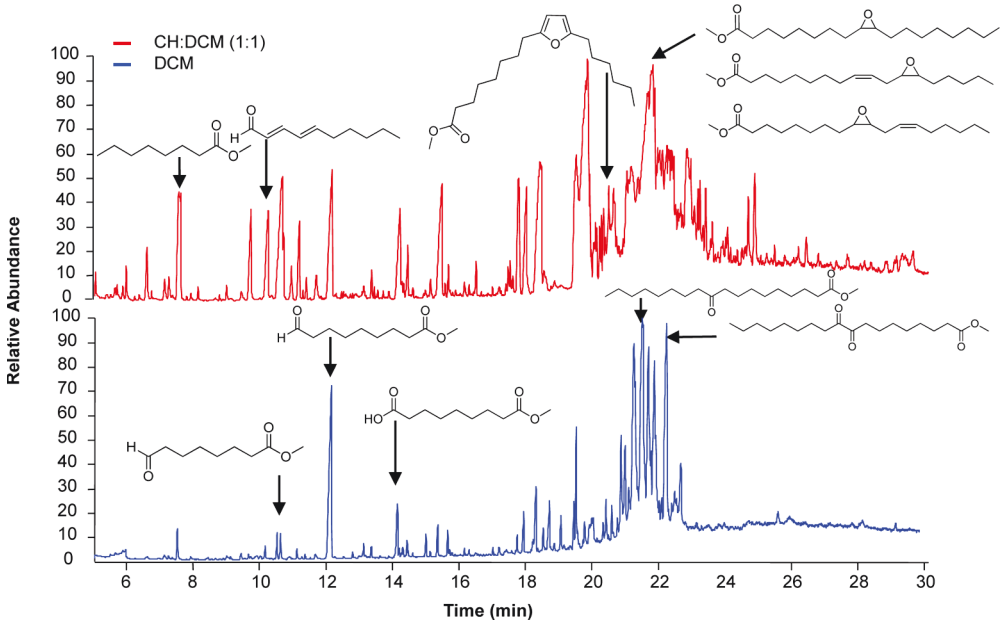

Figure 5. Gas chromatogram with mass spectrometric detection of FAME mixture B5 after 12 months of storage: fraction 1 (CH/DCM = 1:1, top, red) and fraction 2 (DCM, bottom, blue). Identified oxidation products are indicated with their chemical formulas.

but different heating oils; therefore, it seems evident that the heating oil used in B4 is able to stabilize the biogenic part better than the heating oil in B3 or the heating oil in B3 promotes the destabilization process of the biogenic part of the blend.

3.4. SEC. SEC was employed to gain information on the degree of oligomerization of the FAMEs. With the help of polyethylene glycol standards, it was possible to classify the chromatographic signals into groups of monomers, oxidized monomers, dimers, trimers, and oligomers of higher *n* (number of monomers in the oligomers). Because of the differing hydrodynamic volumes of polyethylene glycols and FAMEs, this correlation is not very exact. Methyl oleate as a substance of known molecular weight was used to calibrate the measured masses, enabling the assignment of a value of *n* to the different groups. The molar masses indicated by the polyethylene glycols are obviously overstated.

In the fossil heating oil B1 (see Figure S1 of the Supporting Information), there were no changes in the molar mass distribution, except for the substances of low molecular masses that showed a small decrease. These results matched those of the IR and GC/MS measurements and are attributed to the loss of volatile compounds during the storage in the open glass vessels. The same applies to B2.

Blend B3 exhibited a different pattern (Figure 3). As was the case for the fossil materials, there were no changes after 9 months of storage; however, a noticeable increase in the oxidized FAMEs (ca. 400 g/mol) set in after 16 months, and weak signs of dimers (600−800 g/mol) appeared. With longer storage time, the maximum of the dimers moved to higher masses. This points to a further uptake of oxygen into the dimers. In B4, there was only a very small indication of changes

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in composition; possibly a longer time of storage would be needed to reach the degree of transformation shown by B3.

The FAMEs decreased continuously in biodiesel B6 (Figure 4). At the same time, there was a parallel increase in oxidized FAMEs (around 400 Da in Figure 4) as well as in dimers, trimers, and higher oligomers. The same was true for B5. Although there were indications of higher oligomers (up to n = 5), no sediments were formed in either biogenic fuels. This may be attributed to the comparatively higher polarity of the biogenic fuel as opposed to the fossil fuel that makes the polar oxidation products better soluble in the matrix, and therefore, these do not precipitate as sediments as easily.

3.5. GC/FID. The two purely fossil materials B1 and B2 as well as the blends B3 and B4 did not show any changes in their gas chromatograms during the storage, except that the more volatile compounds had evaporated to some degree. The FAME mixtures B5 and B6 on the other hand displayed characteristic signals for shorter chains than the initial C_{18} esters (see Figure S2 of the Supporting Information). Besides this, there were some additional peaks for compounds eluting later than the FAMEs (see Figure S3 of the Supporting Information) that are probably derived from epoxides or similar oxidized products and with retention of the carbon chain.

3.6. GC/MS Analysis of Oxidation Products of B5. To obtain more information on the products formed during storage, GC/MS measurements were performed after a fractionation on a SPE column to separate the oxidation products from the FAMEs. The identification of several structures was made by comparing the mass spectra to those from databases and standard compounds.

Many substances were formed during 12 months of storage under slightly accelerated conditions. Chain scission led to aldehydes as well as carboxylic acids (see IC below), but several oxidation products containing the original carbon chain of the FAMEs were also discovered. Experiments with biodiesel at elevated temperatures (90 °C for 360 h) were described to lead to 10-oxooctadecanoate as one of the major decomposition products.[11] This substance was present in our dichloromethane fraction as well, although milder conditions were chosen. Many products of different chain lengths and with different functional groups were identified in a high-temperature degradation (180 °C for 15 h) of FAMEs.[18] Esters, such as methyl octanoate, methyl 9-oxononanoate, azelaic acid monomethyl ester, and methyl 8-(5-hexyl-2-furyl)-octanoate, were identified under such harsher conditions but were also identified in either the cyclohexane/dichloromethane fraction or the dichloromethane fraction in the present experiments (Figure 5).

3.7. IC of Short-Chain Carboxylic Acids in B6. IC revealed a series of short-chain free fatty acids in the oxidized mixtures. The acids were extracted from the sample using a carbonate buffer and, after acidification, separated in the ion-exclusion chromatography mode that separates acids according to their pK_a and hydrophobicity.[20] We found small amounts of isobutyric acid of unknown origin. Lactic acid was present in small amounts in the sample before the storage but, as shown in Figure 6, was clearly indicated after 12 months and supposed to arise through oxidation of residual glycerin.[20,21] For these compounds, IC was preferred instead of MS (see below) because it can more easily provide quantitative data and isomers (such as butyric and isobutyric acids) are resolved. Short-chain carboxylic acids are known products of FAME degradation.[20] Formic acid, for example, might be a product of hydroperoxy aldehydes.[22]

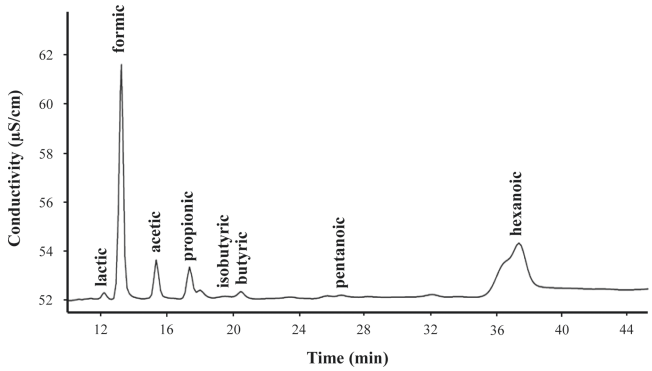

Figure 6. Ion chromatogram of the acids of the FAME mixture B6 after 6 months of storage.

The quantitative data are listed in Table S3 of the Supporting Information. The concentration of formic acid is 4.8 mM after 6 months and is by far the dominant acid after hexanoic acid, followed by acetic and propionic acids in about equal molar amounts. These acids are the most volatile acids, and therefore, losses through evaporation are probable because the aging of the blends was conducted in open vessels for a prolonged period of time at a somewhat elevated temperature. Small amounts of the acids were found at time 0, again showing that some oxidation had taken place from the moment of manufacture of the FAMEs until the start of the storage.

As indicated by small peaks in the chromatogram, some further acids that were not identified have also been formed. Obviously, a whole range of fatty acids are formed upon storage.

3.8. ESI−MS of Carboxylic Acids in B6. In a search for carboxylic acids of longer chains in the biodiesel that were outside the capability of the IC, the extracted aqueous phase was analyzed using a high-resolution mass spectrometer in the negative mode.

All identified compounds are tabulated in Table S4 of the Supporting Information. The relative ion abundance should not be taken as a measure for the concentration because ESI is known to inflate the recorded ion abundance of the more hydrophobic ions.[23] Signals for the substances identified by IC were detected here as well. The mass spectrum (Figure 7) of the analyzed sample shows clear signals for carboxylic acids. There exists a homologous series of saturated and unsaturated acids as well as monomethyl esters, starting at a chain length of nine carbon atoms.

Moreover, signals for acids with methyl ester functional groups can be observed. The most abundant signal at m/z 201.112 75 is the azelaic acid monomethyl ester, and the second most abundant signal with m/z 115.076 28 is caused by hexanoic acid (Figure 8). The high abundance of this acid is a result of the high amount of linoleic acid that is unsaturated in the 12,13 position and undergoes cleavage in this position.

3.9. MS of the B3 Sediment. The sediment formed in blend B3 was analyzed by high-resolution MS (see Figure S5 of the Supporting Information) to obtain information on its composition. The separated sediment was dissolved in a mixture of di- and trichloromethane and directly sprayed into the ion source. Both H^+ and Na^+ adducts were detected in the positive mode.

In the range of low mass-to-charge ratios (m/z 130−280; Figure 9), the most abundant substances are nitrogen-containing compounds that derive from the fossil part of the

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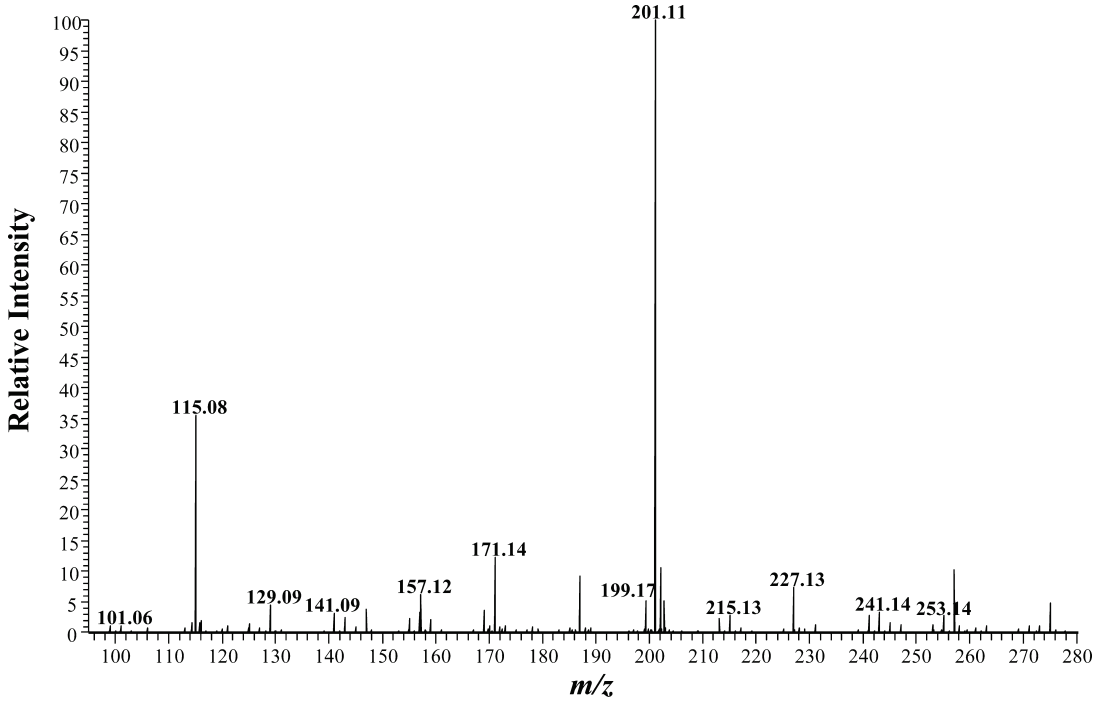

Figure 7. (−)ESI mass spectrum section of the aqueous phase of the acid extraction. For assignments of the masses, see Table S4 of the Supporting Information. *m/z* were rounded to the second decimal place.

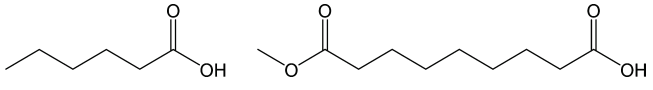

Figure 8. (Left) Structure of hexanoic acid, *m/z* 115.076 28 ([M − H]⁻), with a calculated mass of 115.076 45 and deviation of −1.50 ppm. (Right) Structure of azelaic acid monomethyl ester, *m/z* 201.112 75 ([M − H]⁻), with a calculated mass of 201.113 23 and deviation of −2.39 ppm.

blend as well as short-chain oxidation products resulting from the FAMEs. The fact that the nitrogen compounds appear in the positive mode indicates that they are basic compounds, probably alkylpyridines. Because of the high number of double bond equivalents, differently alkylated and hydrogenated quinolines are more likely products that may be formed during hydrodenitrogenation of the fossil material.[24] Furthermore, there are indications of alkylated acridines. Their elemental composition is given in Table S6 of the Supporting Information, and possible structures are shown in Figure 10.

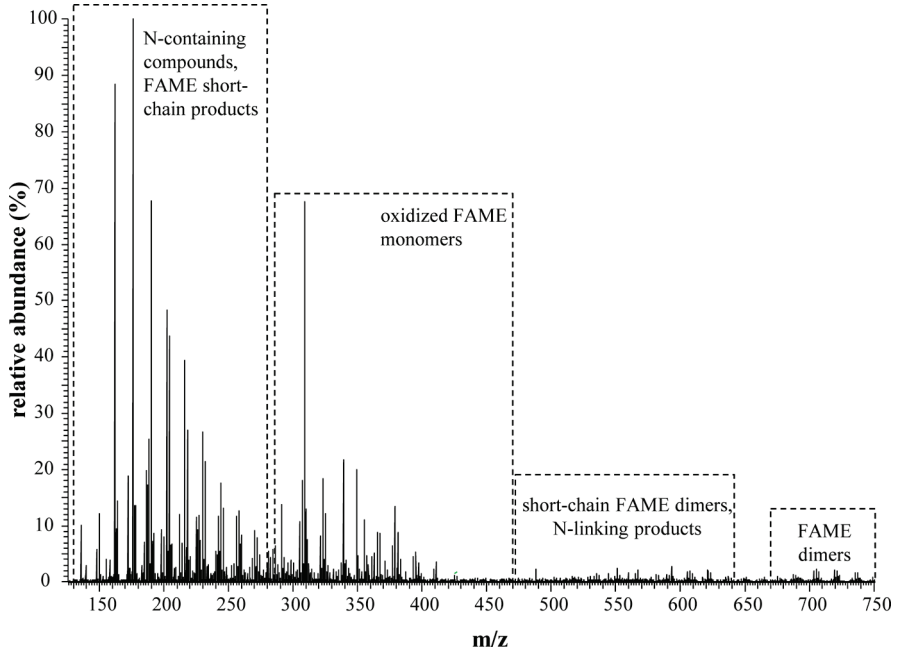

Figure 9. (+)ESI mass spectrum of the sediment of blend B3 after 19.5 months of storage.

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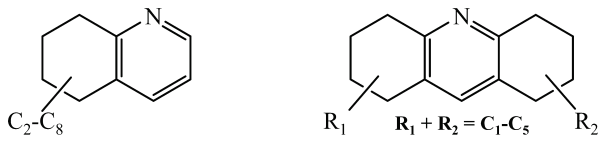

Figure 10. Putative structures of nitrogen-containing compounds in the sediment of blend B3 after 19.5 months of storage in (+)ESI mass spectrum.

Basic nitrogen heterocycles are expected to show up extremely well because of their facile ionization under the conditions of ESI.[25] In the negative ionization mode, there is evidence of the presence of oxidized indoles (see Table S7 of the Supporting Information). The next group (m/z 310−470; Figure 9) represents oxidized monomers of the FAMEs. Hardly any of the native FAMEs were found in the sediment. This finding supports the assumption that only highly polar compounds precipitate as sediments. However, it should be remembered that a much more facile ionization of these substances through cation adduct formation compared to that of the quite nonpolar FAMEs must be expected. In the m/z range from 500 to 650, the most abundant signals are those of oxidized dimeric FAMEs, in which a scission of one of the FAME chains, usually in position 9 or 10, has taken place. A list of substances is shown in Table S5 of the Supporting Information. Of particular interest is that, in this area, some ions are found that can only be explained as products of FAMEs with components of the fossil part. The nitrogen atom is a clear evidence of this.

A possible structure of one of the compounds might be similar to the indole coupling product shown in Figure 11. Indoles are well-known substances in fossil fuels, and 2-methylindol is known to couple easily with other species. Aging experiments have shown it to react with phenols.[26]

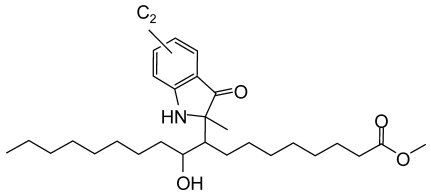

Figure 11. Putative structure of the compound with m/z 488.372 51 (H^+ adduct), with a calculated mass of 488.373 44 and deviation of −1.62 ppm.

In other experiments in our group,[9] it was shown that a reaction between 2-methylindole and FAMEs takes place when the indole is heated at 120 °C for 24 h in a FAME mixture under an air pressure of 4.5 bar. Without an identification of the products, it can only be speculated that these products are structurally similar to the product formed under quite different conditions here, but it is noteworthy that, under the relatively mild conditions in this work, such coupling products can be observed.

4. CONCLUSION

In this work, we demonstrate that the composition of biodiesels and their blends with fossil heating oil undergoes enormous changes during the long-term storage at 40 °C. The elemental analysis showed that, in pure fossil fuel, there is nearly no change in composition after 24 months of storage but, in biodiesel, a continuous rise in the oxygen content was observed, as expected. These results correspond with the IR data that demonstrate that, in the biodiesel, the absorption bands of carbonyl or alcohol groups, formed in oxidation processes, steadily increase with time. With the onset of sediment formation, changes in the composition of the blend were measurable. Ketones and epoxides as well as chain-shortened products from the FAMEs, such as aldehydes and carboxylic acids, are the result. The present experiments at only slightly above ambient, thus, confirm previous oxidation products that have frequently been obtained at considerably higher temperatures.

The composition of the pure biodiesel was changed to a larger extent than the composition of the blend, but no sediment was formed in the biodiesel. The sediment of the blend consisted of FAMEs that on average had taken up 2.5 oxygen atoms per molecule. The polar oxidation products, thus, seem to be soluble in the slightly polar matrix of the biodiesel; however, they aggregate in the less polar matrix of the blend, and as a result, sedimentation occurs.

SEC showed the formation of polymeric compounds. In the biodiesel, dissolved oligomeric structures containing up to five FAME monomers were indicated but were much less pronounced in the blend. However, here, a sediment was formed. Apparently, also the oxidized oligomeric structures are better soluble in the biodiesel than in the fossil diesel matrix.

Carboxylic acids were identified in the range from formic acid to hexadecenoic acid. They may have an influence on corrosion processes during storage.

ESI−MS showed the first examples of long postulated compounds derived from cross-coupling between biogenic and fossil components. This finding supports the assumption that interactions between the fossil and biogenic parts of fuel blends should be possible. The question why some blends are stable with respect to sediment formation and others are not remains to be answered, but the present results should help in the search for the answer.

■ ASSOCIATED CONTENT

Supporting Information

Distribution of the aromatic compounds in the two fossil heating oils A and B (Table S1), FAME distribution in the FAMEs 1 and 2 in percent on a mass basis, determined by GC/FID measurement with $C_{15:0}$ as the internal standard (Table S2), concentration of free fatty acids in FAME mixture B6 after 0 and 6 months of storage as determined by IC (Table S3), (−)ESI−MS measurement of fatty acids in the alkaline aqueous extract of FAME B6 after 12 months of storage (Table S4), signals from (+)ESI−MS spectrum of the sediment of blend B3 (Table S5), nitrogen-containing compounds in the sediment of blend B3 after 19.5 months of storage as found by (+)ESI−MS (Table S6), nitrogen-containing compounds in the sediment of blend B3 after 19.5 months of storage as found by (−)ESI−MS (Table S7), size-exclusion chromatogram showing the molar mass distribution of fossil heating oil B1 before and after storage for up to 18 months (Figure S1), gas chromatogram with FID of FAME mixture B5 after 0 and 12 months of storage (Figure S2), gas chromatogram with FID of FAME mixture B5 after 0 and 12 months of storage (Figure S3), and (+)ESI−MS of the sediment of blend B3 after 19.5 months of storage

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(Figure S4). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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