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Investigating the Oxidation of Biodiesel From Used Vegetable Oil by FTIR Spectroscopy: Used Vegetable Oil Biodiesel Oxidation Study by FTIR

Ping Y. Furlan^a; Palmer Wetzel^a; Samuel Johnson^a; Jessica Wedin^a; Andrew Och^a

^a Chemistry Department, University of Pittsburgh at Titusville, Pittsburgh, PA

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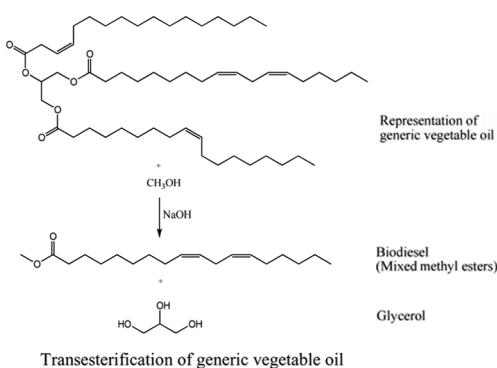
Chemistry Department,
University of Pittsburgh at
Titusville, Pittsburgh, PA

ABSTRACT The thermal oxidation of a biodiesel prepared from used vegetable oil was investigated using Fourier transform infrared (FTIR) spectroscopy. Spectral changes were observed in the hydroxyl, carbonyl, and *cis/trans* double bond regions for the control and Vitamin E-added samples. These spectral changes, increasing with increasing oxidation, were attributed to common oxidation products. IR results also suggested an oxidation-induced breakage of methyl ester linkages and agreed with those from selected physical property measurements. This preliminary study demonstrated the feasibility and potential of FTIR spectroscopy, a fast and reagent-free method, in assessing the oxidation state of biodiesel and providing understanding of its oxidative degradation.

KEYWORDS antioxidant, biodiesel, FTIR spectroscopy, thermal oxidation, used vegetable oil

INTRODUCTION

Biodiesel is a renewable, biodegradable, and environment-friendly fuel substitute for heating and transportation. It is compatible for combustion in diesel engines and can be easily made from transesterification of vegetable oils (fresh or used) or animal fats with methanol or ethanol:



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Address correspondence to Ping Y. Furlan, Chemistry Department, University of Pittsburgh at Titusville, 504 East Main Street, Titusville, PA 16354. E-mail: furlan@pitt.edu

As the cost and depletion of the petroleum-based oils continuously increase, the United States has set a mandatory fuel standard that requires 9.0 billion gallons of biofuels in 2008 and rises to 36 billion gallons by 2022.^[1] Unlike the petrodiesel, biodiesel has poor storage stability characteristics due to its content of unsaturated fatty acid chains that oxidize easily. The primary oxidation products are hydroperoxides, in which the original double bonds may have shifted or undergone *cis/trans* isomerization.^[2] Through various mechanisms, hydroperoxides subsequently form a variety of secondary products including aldehydes, ketones, alcohols, carboxylic acids, and higher molecular weight oligomers often called “polymers.”^[2–4] These degradation products clog up fuel lines or pumps and cause the fuel to deteriorate, compromising fuel quality and engine performance. Characterizing biodiesels and investigating oxidative changes under different conditions are important to the prevention of fuel deterioration caused by oxidation and the successful development and viability of these alternative fuels.

Numerous test procedures have been developed or adapted to indicate the oxidative status of bio-diesel.^[2,3,5] The common ones are the peroxide value (PV) for hydroperoxides, the acid value (AV) for carboxylic acids, the iodine value (IV) for degree of unsaturation, and the viscosity (v) for more polar, higher *trans*-content, and higher molecular weight products. A composite of these values is often used to best indicate the state of biodiesel oxidation, yet no oxidized system has been very well characterized due to the complexities of this oxidation process. Compared to most common methods, Fourier transform infrared (FTIR) spectroscopy is fast, is less expensive, and does not require the use of solvents and toxic reagents. It is a green method that provides rich structural information on the characteristics, composition, and chemical changes taking place in biodiesels and can complement or replace the conventional procedures. Yet, the literature on applications of FTIR spectroscopy to oxidation studies of biodiesels, particularly used ones, is limited.^[2,4,6]

In this project, we explore the feasibility of investigating the oxidation of used vegetable oil (UVO) biodiesel using FTIR spectroscopy. Control samples and samples containing Vitamin E (VE; tocopherol) are oxidized via heat treatment. VE, a natural antioxidant, is expected to retard biodiesel oxidation.^[2] We

report here the preliminary results based on the IR spectral changes of these biodiesel samples.

MATERIALS AND METHODS

Transesterification

The UVO was obtained from a local McDonald's restaurant. Methanol (anhydrous, reagent grade) and sodium hydroxide (p.a. grade) were used as received from Aldrich (St. Louis, MO). One liter of UVO was converted to biodiesel according to published methodology.^[7] One (1.0) mL of UVO required 3.0 mL of 0.1% of NaOH solution to neutralize the free fatty acid in the sample.

Thermal Oxidation

Forty (40.0) mL of biodiesel control samples and samples with VE (NOW brand Gamma E Complex) concentrations ranging from 0.15 g/kg to 2.00 g/kg were placed in 50-mL beakers and heated at 110–120°C in an oven (Isotemp Vacuum Oven, Model 281 A, Fisher Scientific, Pittsburgh, PA) for a period of 2 weeks. Small amounts of samples were collected using pipettes at different times during this heating period for FTIR measurements.

Characterization

IR spectra were recorded using a Genesis II FTIR Spectrometer (Mattson, Madison, WI) on polyethylene IR cards (Thermo Spectra-Tech ST-IR cards, Shelton, CT) as neat liquid. A total of 32 scans was used at a resolution of 4.0 cm^{-1} . Local baselines and relative peak heights were employed for quantitative analyses. Density was determined by measuring the mass of 10.0 mL of the sample in a 10-mL graduate cylinder using a top-loading balance (Denver Instrument XE-410D, Bohemia, NY). Cloud point was determined as the temperature at which the sample became opaque during cooling. Color and viscosity were inspected visually and qualitatively.

RESULTS

Figure 1 shows the FTIR spectra of used McDonald's vegetable oil and the resulting fatty acid methyl ester or biodiesel. The major differences between these spectra are the disappearance of the peaks associated with the O-CH₂ groups in

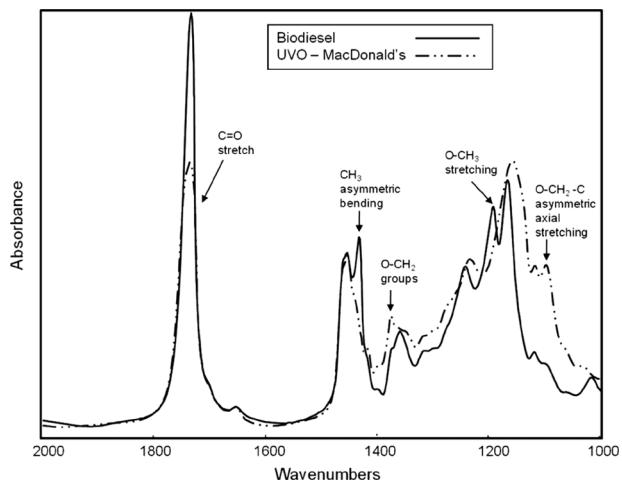


FIGURE 1 FTIR spectra of used McDonald's vegetable oil and biodiesel.

glycerol moiety at 1377 cm^{-1} and 1090 cm^{-1} and the appearance of the peaks associated with the methyl ester groups at 1377 cm^{-1} and 1196 cm^{-1} .^[8] These spectral changes suggest that the intended transesterification has taken place.

In order to detect small spectral differences between control and oxidized samples, subtractive IR spectroscopy is used in this study. The IR spectrum of a thermally treated sample is subtracted from that of the same sample before heat treatment (control). Figure 2 illustrates the subtractive spectra of UVO (McDonald's) biodiesel heated at $110\text{--}120^\circ\text{C}$ for 51, 96, and 190 hr. The negative peaks indicate the

formation of new molecular species or oxidation products, and the positive peaks indicate the loss of functional groups or other structural changes. As oxidation progresses, it can be seen from Fig. 2: (i) the appearance of a broad peak in the OH-stretching region ($3400\text{--}3600\text{ cm}^{-1}$), (ii) the appearance of peaks (1726 cm^{-1} and 1695 cm^{-1}) on the low frequency side of the triglyceride ester linkage absorption (1744 cm^{-1}),^[4] and (iii) sharp increase in peaks in the *trans* double bond region ($900\text{--}1000\text{ cm}^{-1}$) and decrease in the peaks associated with *cis* double bonds (710 cm^{-1} , 3009 cm^{-1}). Each of these regions is examined below:

i. *OH region.* The appearance of a broad peak in the OH-stretching region ($3400\text{--}3600\text{ cm}^{-1}$) indicates the formation of oxidative products containing OH groups. As biodiesel undergoes oxidation, the reaction involves the uptake of oxygen via the formation of hydroperoxides. Hydroperoxides exhibit characteristic absorptions in this region due to their $-\text{OO}-\text{H}$ vibrations. A careful inspection of the new broad peak reveals a new shoulder appearing at 3444 cm^{-1} . This shoulder peak may be due to the OH stretching of hydroperoxides, a peak assignment established by early work on oxidation of edible oils.^[9,10] The broad new peak, maximizing at 3546 cm^{-1} , may be attributed to the OH-stretching absorptions of

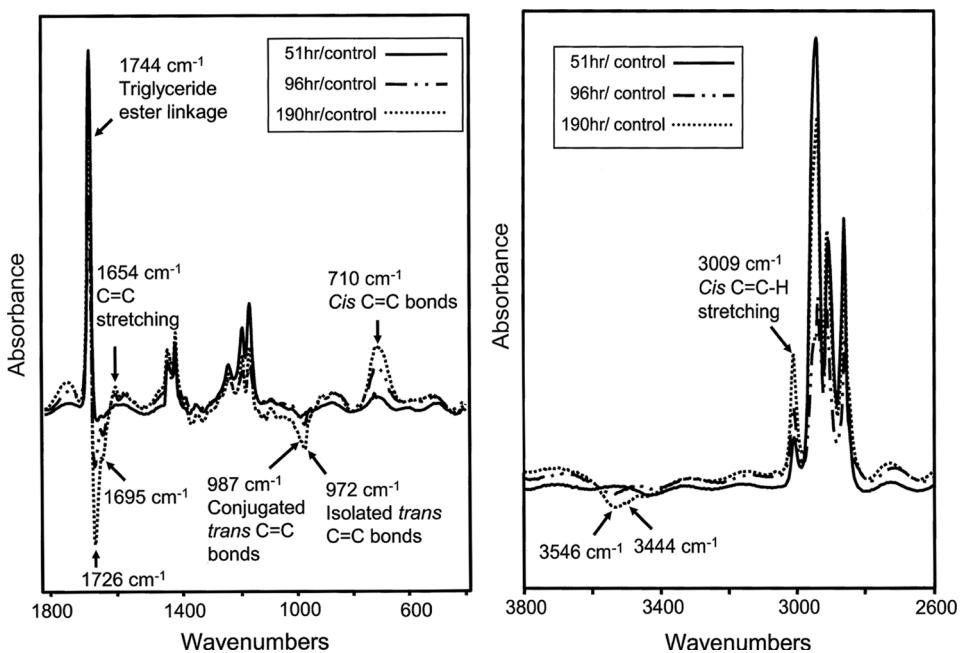


FIGURE 2 Subtractive IR spectra of UVO (McDonald's) biodiesel heated at $110\text{--}120^\circ\text{C}$ for times indicated.

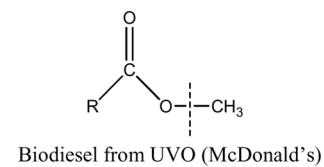
alcohols^[4,10] or fatty acids^[4], the breakdown products of hydroperoxides. This broad peak is similar in shape and position to the one present in the parent UVO, which is known to contain free fatty acids. The oxidized samples are found to be acidic, with pH values around 4–5. All of this supports the formation of free fatty acids due to the thermal oxidation.

ii. *Carbonyl region.* As shown in Fig. 2, the most significant change taking place in the carbonyl region ($1650\text{--}1750\text{ cm}^{-1}$) is the appearance of two peaks at 1726 cm^{-1} and 1695 cm^{-1} , which increase in intensity with increasing heat treatment time or oxidation. These new peaks suggest the presence in the oxidized samples of at least two separate carbonyl-containing compounds other than the esteric carbonyls originally present. The carbonyl peak associated with the triglyceride ester linkage occurs at 1744 cm^{-1} . It is known that normal aliphatic aldehyde, ketone, and carboxylic acid carbonyls absorb at lower frequencies compared to those in the esters and that their absorptions generally appear in the range of $1700\text{--}1740\text{ cm}^{-1}$.^[11] Conjugation with double bonds shifts carbonyl absorptions to lower frequencies.^[11] The new peaks at 1726 cm^{-1} and 1695 cm^{-1} may therefore be attributed to the formation of aldehydes, ketones, fatty acids, and other oxidation products formed via different breakdown mechanisms of hydroperoxides.^[4] The 1726-cm^{-1} peak may be assigned to saturated carbonyls, and the 1695-cm^{-1} peak the carbonyls conjugated with double bonds.^[12] In their studies of the oxidation of a commercial soy methylester biodiesel, Fang and McCormick proposed that the unsaturated ketones may be generated from aldol condensation, a reaction between an aldehyde and a ketone. This condensation may be one of the major routes for insoluble polymer formation.^[4]

iii. *Peaks associated with cis and trans C=C bonds.* The *cis* C=C bond peaks are located at 3009 cm^{-1} and 710 cm^{-1} , which are observed to decrease with oxidation time, indicating a loss of *cis* double bonds. Spectral changes are also observed in the region between 900 and 1000 cm^{-1} , where the C=C–H bending vibrations of *trans* double bonds take place. Two new peaks at 972 cm^{-1} and 987 cm^{-1} become apparent as the oxidation

proceeds. The peak at 987 cm^{-1} is attributed to conjugated *trans* C=C bonds, and the peak at 972 cm^{-1} is attributed to the isolated *trans* C=C bonds.^[11,12] Fig. 2 shows that in the early stages of oxidation, the amount of conjugated *trans* bonds is more than that of isolated *trans* bonds. At later stages, the proportion is reversed, and the amount of isolated *trans* bonds increases rapidly. These results suggest that the biodiesel under study may have undergone a *cis*-to-*trans* isomerization during oxidation, agreeing with the literature.^[2] This isomerization may be accompanied by an initial formation of conjugated *trans* bonds, which are then progressively converted to the isolated *trans* bonds as oxidation continues. Figure 2 also shows that with oxidation, the weak C=C absorption at 1650 cm^{-1} decreases. This decrease may be attributed to a net loss of C=C bonds. Since a *cis* isomer absorbs more strongly than a *trans* isomer for this absorption, a decrease in this peak intensity may partially reflect a decrease in the amount of *cis* double bonds. Additionally, symmetrically substituted C=C bond does not absorb at all at this frequency. As a result, interpretation of a change in this peak intensity may be difficult.

Additionally, net decreases in peak intensity related to ester linkage at 1744 cm^{-1} , and methyl groups in the biodiesel at 1377 cm^{-1} and 1196 cm^{-1} , are observed. These changes suggest a net breakage of the methyl–ester linkages as a possible oxidative breakdown mechanism for biodiesel:



In their biodiesel oxidation study, Fang and McCormick attributed this breakage as a result to possible reverse transesterification, per-ester formation, or hydrolysis.^[4] The latter processes may lead to free fatty acid formation.

Even though the oxidation conditions and biodiesels studied here are limited, the preliminary spectral results indicate that they have produced products commonly associated with biodiesel oxidation and can help illustrate the information obtainable by

FTIR spectroscopy in monitoring or investigating biodiesel oxidation. Relative changes may also be measured based on the changes in intensity of the corresponding IR absorptions, allowing the assessment of the relative oxidative state of a biodiesel sample. For instance, since *trans* double bonds do not occur naturally in fatty acid hydrocarbon chains, the ratio of the intensity of the *trans* double bonds to that of the *cis* double bonds may be used as an index of biodiesel oxidation. Figure 3 (left) shows the ratios of the peak at 972 cm^{-1} (due to the isolated *trans* double bonds) to the peak at 710 cm^{-1} (due to the *cis* double bonds) as a function of heat treatment time for a control biodiesel sample and a sample containing 0.15 g/kg VE. It can be seen that the *trans*-to-*cis* peak ratio and thus the *trans*-to-*cis* content ratio increase with oxidation, consistent with an ongoing *cis*-to-*trans* isomerization during oxidation. A comparison of the data points in Fig. 3 (left) shows that the antioxidant, VE, has reduced the *trans*-to-*cis* peak or content ratio and slowed down the biodiesel oxidation. As another example, the ratios of the new peak at 3546 cm^{-1} to the peak at 3470 cm^{-1} are plotted in Fig. 3 (right) as a function of the heat treatment time for these samples. The peak at 3546 cm^{-1} is attributed to the oxidation products containing OH groups (alcohol or fatty acids). The peak centered at 3470 cm^{-1} is assigned to the overtone of esteric carbonyl absorption^[13] and serves as the reference peak. Similar information in terms of the oxidative state of the biodiesel and the antioxidant effect can be derived using this peak ratio. It is clear, however, that the major challenges for extracting reliable quantitative information from these FTIR spectra include

identifying the peaks of the major oxidative products and resolving the overlapping peaks in the regions (hydroxyl, carbonyl, or *trans*/*cis* region, etc.) of interest. The former may be dealt with by spiking the control biodiesel sample with compounds that are spectroscopically representative of those oxidative products, and the latter may be dealt with by applying modern deconvolution software packages such as GRAMS/Al. These packages can resolve overlapping peaks, provide integrated peak intensities, and calculate the concentrations of unknowns.

The density, cloud point, and viscosity of all the samples were found to increase as a result of heat treatment or thermal oxidation (representative data are shown in Table 1). The increase in these values may indicate the formation of more polar, oxygen-containing molecules and the formation of polymers (gums and sediments) responsible for clogging fuel lines or pumps.^[3] The color of the samples changes from light yellow to dark yellow or orange, depending on the degree of oxidation. Results from density measurements and color inspections show that adding an antioxidant, such as VE, to the control biodiesels slows down the oxidation-induced changes in these properties.

CONCLUSION

We prepared a biodiesel from UVO (McDonald's restaurant) and investigated the responses of control and VE-added samples to heat treatment at $110\text{--}120^\circ\text{C}$ for a period of 2 weeks using FTIR spectroscopy. The preliminary spectral results indicate that the heating conditions and the biodiesel under

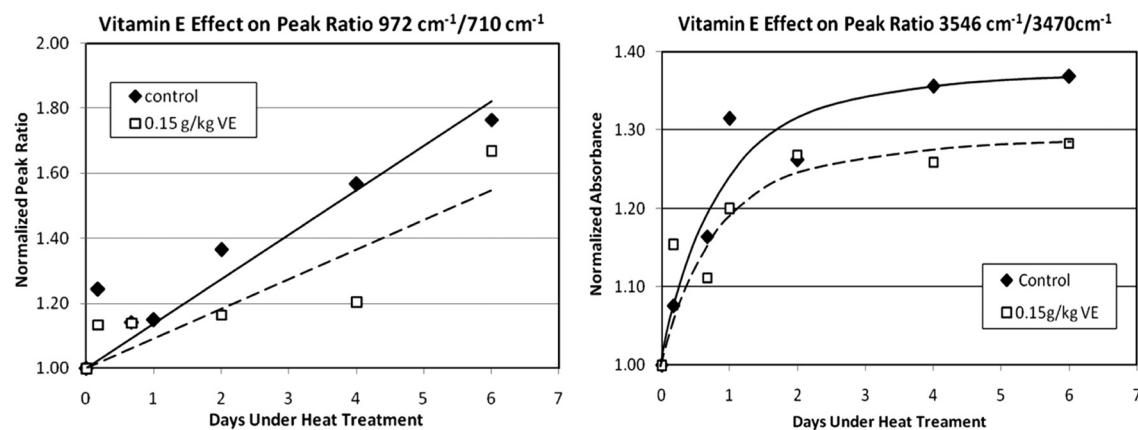


FIGURE 3 Vitamin E effect on the biodiesel oxidation as illustrated by the IR peak ratios $972\text{ cm}^{-1}/710\text{ cm}^{-1}$ (left) and $3546\text{ cm}^{-1}/3470\text{ cm}^{-1}$ (right).

TABLE 1 Changes in Physical Properties of UVO (McDonald's) Biodiesel Induced by Thermal Oxidation

Variable		Before heat treatment	After being heated for 2 weeks at 110–120°C
Density	Control	0.790	0.887
	0.25 g/kg VE	0.790	0.877
	1.00 g/kg VE	0.775	0.881
	2.00 g/kg VE	0.785	0.869
	Cloud point	Control 0.70°C 0.25 g/kg VE 0.70°C 1.00 g/kg VE 0.70°C 2.00 g/kg VE 0.70°C	4.0°C 4.5°C 4.5°C 4.5°C
Color	Control	Light yellow	Orange
	0.25 g/kg VE	Light yellow	↑
	1.00 g/kg VE	Light yellow	
	2.00 g/kg VE	Light yellow	Yellow
Viscosity		Flows easily	Becomes Sluggish

Note. VE = Vitamin E.

study produced the oxidative products containing hydroxyl (–OH) groups (hydroperoxides and alcohols or fatty acids), at least two new types of carbonyls (possibly saturated and unsaturated aldehydes, ketones, or fatty acids) and a *cis*-to-*trans* isomerization (followed by a ongoing conversion from conjugated *trans* double bonds to isolated *trans* double bonds). These products or processes are commonly associated with biodiesel oxidation. Additionally the IR results suggest a possible thermal oxidation-induced breakage of the methyl ester linkages. Relative changes in *trans*-to-*cis* content and alcohol/fatty-acid-to-ester content are measured based on the changes in the ratios of their corresponding IR peaks. Both of these content changes show increases with increasing oxidation. Adding VE to the biodiesel control sample is found to help improve biodiesel's oxidation stability. Results from IR spectroscopy are in good agreement with literature and with those from measured physical properties (density, cloud point, color, and viscosity). This study therefore demonstrates the feasibility of using FTIR, a fast and reagent-free method, to identify and quantify oxidative products, thus assessing the oxidation state of biodiesel and providing insight into the oxidative degradation mechanisms. This is especially true if (a) quantitative methods

can be developed using modern deconvolution software packages and (b) model compounds that simulate oxidative products and relationships can be established between the FTIR spectral changes and the changes detected by conventional chemical methods.

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