Amelioration of Factors Limiting the Use of Lipid-Based Diesel Products

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Amelioration of factors limiting the use of lipid-based diesel products

by

Haixia Liu

A thesis submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Major: Food Science and Technology

Program of Study Committee:

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Earl G. Hammond

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Iowa State University

Ames, Iowa

2009

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Chapter 1. General Introduction

Background of this research

This research was sponsored by Center for Sustainable Environmental Technology (CSET) at Iowa State University and entailed cooperation with the University of Northern Iowa and its National Ag-Based Lubricants Center (UNI-NABL). The primary purpose of the project was to improve the performance of vegetable-oil-based biolubricants and biodiesel. The first part of this thesis focuses on the purification of oleic acid from high-oleic soybean oil by crystallization. This process makes possible improvements in the stability and melting properties of the products derived from the high-oleic oils. The second part of this thesis is based on a 1998 study at Iowa State University by Tekin and Hammond [1]. Our goal was to increase the yield of epoxy linoleate formed by the oxidation of a monolayer of methyl linoleate on silica gel. The epoxy linoleate acts as a precursor of lipid-based lubricants. The third part of this thesis is a study of the fouling on the injection nozzles of diesel engines when burning biodiesel or biodiesel-petroleum diesel mixtures as diesel fuel. We studied the impact of various fatty acids in soybean oil on fouling.

Literature review

Properties of high-oleic soybean oil

High-oleic acid soybean oil (HOSO) has the following fatty acids composition: oleic acid greater than 80%, linoleic 3%, linolenic 3% and saturated fatty acid less than 12%, compared to normal soybean oil with a composition of 23, 50, 7 and 15%, respectively [2]. The "silencing" of the expression of FAD2 genes greatly increases the levels of oleic acid and decreases the levels of linoleic and linolenic acid in the seeds.

Fatty acids differ from each other in terms of acyl chain length and number of double bonds, which lead to different physical properties [3]. Consequently, the fuel properties of biodiesel derived from mixtures of fatty acids are dependent on that composition. Various studies suggest
that biolubricants with high levels of methyl oleate will have excellent, if not optimal, performance [4].

HOSO displays considerable oxidative stability relative to conventional soybean oil. The oxidative stability of fatty acid esters is mainly affected by the number and position of double bonds in the acyl chain. The greater the concentration of oleic acid in high-oleic oil should contribute to greater stability to oxidation. Fatemi and Hammond [5] found that the relative rates of oxidation of methyl oleate, linoleate and linolenate in mixtures were about 1:10.3:21.6. Unsaturated fatty acid chains, especially those of linoleic and linolenic acids are responsible for the autoxidation process. Even low concentrations of polyunsaturated fatty esters have a disproportionately large effect on the oxidative stability of biodiesel [6].

The melting points of fatty acid esters affect cold-flow properties of biolubricants. In winter, crystallization of high-melting saturated fatty acid methyl esters may lead to plugging of filters and tubes. The melting temperatures of biodiesels originating from different vegetable oils vary significantly, highlighting the effects of fatty acid composition on melting points. The presence of saturated methyl esters longer than C12 significantly increases both the melting points and cloud points [7]. The introduction of double bonds prevents the easy alignment of the fatty acids in crystals, thus lowers melting points [8]. HOSO biolubricants have lower melting points than normal soybean biolubricants. The higher the amount of oleate esters with single double bonds and less saturated fatty acid esters may have contributed to its low melting point.

Isopropyl and butyl esters have lower melting points than corresponding methyl esters

Many solutions have been proposed to improve cold flow characteristics of biodiesel. One effective way is replacing methyl or ethyl esters, traditionally forms of biodiesel, with branched-chain alcohol moieties, such as isopropyl or 2-butyl esters [9]. The introduction of branch alcohols into biodiesel can reduce the melting points by 7-14°C compared with their methyl or ethyl counterparts [10]. Yao et al. [11] have noted that methyl oleate had melting point of -17°C, whereas isopropyl and butyl oleate had melting points of -33 and -32°C, respectively. They should have suitable stability for lubricants. As the alcohol chain lengthens from methyl through butyl, the additional methylene groups cause the end groups to take more unfavorable positions in the crystal, making the crystal less stable and lowering their melting point.
Most biolubricants consist of methyl esters and methanol is used for the transesterification reaction since it is inexpensive and widely available. Methanol is priced between $0.04-0.12/lb and has the fourth largest volume among organic chemicals in the U.S. [12]. Isopropyl alcohol and butyl alcohol, on the other hand, are priced between $0.20 to 0.37/lb [13], which makes it more expensive to make isopropyl and butyl esters. However, the weight yield and energy content for isopropyl esters is about 9.6% more than methyl esters and butyl ester is about 11.2% more because of isopropanol’s and butyl’s greater molecular weights. These weight and energy gains partially compensate for the increased cost of these alcohols.

Removal of undesired fatty acids from HOSO

The presence of palmitic and stearic esters in high-oleic oils are likely the cause for the rising of the cloud and pour points of the HOSO esters and limit the temperatures at which it can be used as lubricants and fuel. One way to remove palmitic acid is by fractional distillation. The separation of C12 to C22 fatty acid esters from each other by distillation is the most common and most efficient means of producing high-purity fatty acids. The boiling points of saturated and unsaturated fatty acid methyl esters were determined by Scott et al. [14] at pressures from 0.1 to 6 mmHg.

Since the effectiveness of distillation depends on differences of boiling point, chain length is more important than degree of unsaturation. It also might be possible to remove the palmitate esters from the other fatty esters by distillation because the separation will depend mostly on the chain length of the esters. The other major contaminants of the oleate esters have fatty acid chain lengths of C18 and cannot be removed by distillation.

A second possibility is the use of low temperature crystallization. Brown et al. [15] employed low temperature crystallization from acetone for the separation of predominantly saturated and unsaturated acid fractions from mixed acids of cottonseed oil. Singleton et al. [16] carried out an extensive investigation to determine the best condition separating oleic acid and linoleic acid of completely refined and hydrogenated cottonseed oils by crystallization.

As the temperature is lowered, the saturated palmitate and stearate esters will be the least soluble and the easiest to remove. It will be difficult to remove the traces of polyunsaturated esters by crystallization because they will be the most soluble. The use of a solvent, such as
acetone may be helpful. Yao et al [11] have shown that isopropyl oleate and butyl oleate have melting points of -38 to -39 °C, which are lower than that of methyl oleate (mp -20°C).

Maximum oxidation rate occurs on monolayer

The spontaneous reaction of molecular oxygen with unsaturated fatty acids has been recognized to be a problem in the storage of fats. Free radical-mediated lipid oxidation is the major cause of quality deterioration (rancidity) and decreased nutritional quality [17].

As early as the 1930s, Ellis reported that when fatty acids with two or more double bonds exposed to air in thin films, the absorption of oxygen became rapid and the oil was converted to a gelatinous residue [18]. For monoenes, such as oleic acid, the oxygen uptake of thin films was almost negligible at ordinary temperatures. Because of the considerable differences between the rates of oxidation of thin films compared with bulk lipids, many studies have been conducted to try to reduce the thickness of hydrocarbon surface films on media such as filter and chromatography papers, glass beads and dried gelatin, but such films were still several hundred molecules in thickness [19].

Honn et al. [20] investigated the rate of autoxidation of polyunsaturated oils on silica gel. They found that the rate of oxygen consumption per g of absorbed drying oil varied with the film thickness, and the rate of oil oxidation was greater when the oil was just sufficient to form a monomolecular layer on the silica gel. Compared with such monolayers, the rate of autoxidation of bulk oil was quite slow. Porter et al. [19] reported that the rate of autoxidation in a monolayer was 8-10 times greater than in bulk. Subsequently, Wu et al. [21, 22, 23] conducted a series of studies in which unsaturated fatty acid monolayers on silica surface were used. Generally, saturated fatty acids were assumed to oxidize perceptibly only at very high temperature [24], and their rates of oxidization were assumed to be zero under monolayer conditions. When C6 to C12 saturated fatty acids were mixed with linoleic acid, the autoxidation rate of the linoleic acid decreased as the chain length of the saturated acid increased. Increasing the chain length from C12 to C 16 resulted in reversal of this trend [23], however, if the proportions of linoleic acid were high, the kinetics and products would be the same as for a pure linoleate monolayer. The autoxidation of polyunsaturated fatty acids (PUFAs) and other esters on a silica gel monolayer has been suggested as a model of biological membranes and has been the focus of intense investigation [25].
Major products of monolayer oxidation

When PUFAs and their esters are exposed to oxygen in bulk phase, the primary products are lipid hydroperoxides. This oxidation process is a free radical chain reaction, which targets the methylene group between double bonds of the PUFAs. Although hydroperoxide is the major product of the bulk phase reaction, it is a minor product of monolayer oxidation [26]. When monolayer oxidation is initiated and the reaction is followed by the disappearance of linoleate, the monolayer autoxidation reaction follows first-order kinetics.

Wu et al. [22] thoroughly studied the rates and products of PUFA monolayer autoxidation. The autoxidation products contained trace amount of conjugated hydroperoxides but were primarily 9, 10-and 12, 13-epoxyoctadecenoic acid in roughly equal quantities. The epoxidation was stereospecific, with cis and trans olefins giving cis and trans epoxides, respectively. Hydroxyepoxy compounds and their derivatives also were found among the oxidation products.

The high yield of epoxides may make it feasible to utilize PUFA monolayers to produce this useful product. Epoxides are widely used to make lubricants, surfactants, plasticizers and coatings. Tekin and Hammond [1] explored the use of surface oxidation as an inexpensive route to produce useful oleochemicals, they identified and quantified autoxidation products on linoleic monolayers at various temperatures and achieved 18.7% yields of monoepoxides at 40°C. In addition to epoxy esters (E-FAME), other nonscission products (NSP) obtained after peroxide reduction were hydroxy (H-FAME), hydroxy-epoxy (HE-FAME), dihydroxy (DH-FAME) and trihydroxy esters (TH-FAME). The peroxide values reached maximum value faster as the temperature increased, but lower temperatures gave greater PV maxima. Methyl 9-oxo-nanonoate was the major scission products (SPs).

Main factors affecting oxidation products on linoleate monolayers

The rate of autoxidation is very slow at low temperature, and every 10°C increase in temperature causes approximately a 2-fold increase in the reaction rate. Tekin and Hammond [1] showed that between 7 and 40°C, a higher yield of expoxide and other NSPs was obtained as the temperature increased, but 40°C was the highest temperature they investigated. Wu et al. [22] found that at 60°C, one achieved higher yields of expoxides.
The effects of antioxidants, such as tocopherol and BHA on the oxidation of PUFA monolayers were reported by several investigators [19, 27]. The presence of antioxidants produced induction periods whose lengths were proportional to the antioxidant content.

Transition metal ions increased the rate of oxidation of PUFA monolayers. The oxidation is initiated by the formation of free radicals by reaction of hydroperoxides with the metal ions. Pretreatment of the silica with chelating agents can reduce the effect of the metals. Ascorbic, phosphoric, and citric acids and ethylene-diaminetetraacetic acid (EDTA) are effective chelating agents. Washing the silica gel with acid solutions also can reduce the effective metal content [19]. Koprucuoglu et al. [28] investigated the effects of various transition metals on methyl linoleate monolayers. Copper and iron ions increased the rate of oxidation and the levels of hydroperoxides and scission products. Vanadium ions decreased the time needed to achieve maximum hydroperoxide level and increased the proportion of E-FAME and HE-FAME. Vanadium is a common catalyst for olefin epoxidation with peroxides.

Characteristics of engine injector deposits

Several accelerated fuel-injector deposit formation tests were developed to understand fuel deposit formation on fuel injectors after long time running. Blassnegger [29] associated Rancimat induction time with oxidative stability by performing 500-h fuel injector bench tests with rapeseed methyl ester (RME, B100). The lower stability B100, with a Rancimat induction time of 1.8 to 3.5 h, produced injector deposits and reduced the amount of fuel injected per stroke. Thomas [30] reported that a 1000-h operation of Transport Refrigeration Units equipment with B100 biodiesel formed hard, black deposits that interfered with optimum spray patterns of the injectors. Terry et al. [31] observed fuel filter blocking and fuel separation caused fuel pump and injector operational problems on fuel system components in 500-h test procedure on fuel blends.

The chemical and physical processes that lead to deposit formation are complex and not well understood. Gamlin et al. [32] employed thermogravimetric analysis (TGA) and pressure differential scanning calorimetry (PDSC) to measure oxidative stability and to determine deposit formation kinetics of oils. Oxidation changed the chemical and physical properties of biodiesel. There was a possible change in mechanism for thermal degradation reactions of the biodiesel when the temperature increased [33].
Yamane et al. [34] assessed oxidation stability of different unsaturated fatty acid components by Rancimat test. Unsaturated fatty acid components exert a large influence on oxidation deterioration as well as thermal and autoxidation stability. Pillar et al. [35] reported that the residues of polyunsaturated fatty acids were comprised of metal carboxylate and non-volatile oxygenated compounds. Methyl stearate decomposed into carboxylic acids and alcoholic acid at 220°C. Oxidative decomposition of methyl oleate at 220°C formed secondary species such as aldehydes, ketons and acids; at temperature below 250°C, the thermo-oxidative decomposition process undergone by methyl linoleate and lenolenate were analogous to those of methyl oleate.

References


Chapter 2. Purification of Oleate Esters Produced from High-oleic Soybean Oil

Haixia Liu · Earl G. Hammond · Tong Wang

Abstract

High-purity oleate esters can decrease the melting points and improve the oxidative stability of lubricants. High-oleic soybean oil (HOSO) was esterified to butyl or isopropyl esters. Fractional distillation and low-temperature crystallization were applied to improve the purity of oleate of HOSO esters. Although the purity of butyl esters of HOSO attained 91.8% by fractional distillation, the rate of distillation must be slow which made this approach not very feasible. After subjecting the esters to a two-step crystallization at reduced temperatures, the percentage of oleate in the HOSO esters was increased from 83.2 to 92.5%. The percentage of saturated fatty acids decreased to less than 2.2%, but polyunsaturates percentage remained almost unchanged.

Key words High-oleic Soybean oil · Butyl ester · Isopropyl ester · Fractional distillation · Low temperature crystallization

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Introduction

In response to the rapid depletion of fossil fuel reserves and environmental concerns, considerable research has been done on using vegetable oils as feedstocks for manufacture fuels and lubricants. Such lubricants could be attractive for their combined biodegradability, renewability and excellent lubricity [1], but higher rates of oxidation, poor cold-temperature properties and a narrow range of available viscosities have limited the adoption of biolubricants [2]. Biolubricants that are highly unsaturated have low melting points, depending on the number and position of double bonds in the fatty acid chains, but they oxidize and become viscous much more rapidly than mineral oil-based fluids. Saturated fatty acids and their derivatives have high melting points that increase with chain length but are quite stable to oxidation.

Altering the fatty acid composition of the raw material is often used to achieve better properties of biolubricants [3]. In general, increasing oxidative stability requires decreasing the contents of unsaturated fatty acids, whereas improving cold-temperature flow characteristics requires a fuel with low content of saturated fatty acids. HOSO, which contains more than 80% oleic acid, partially satisfies these requirements. HOSO and similar oils from other oilseed species are generally derived from genetically modified oilseed crops. A mutation in the gene that encodes a desaturase enzyme blocks the conversion of oleic acid to linoleic and linolenic acids that are commonly found in plants [4].

The fatty acid composition can be further altered by low-pressure distillation and low-temperature crystallization from low-melting solvents. Separation of fractions from HOSO esters by low-temperature crystallization is based on the differences among the melting points of the various fatty acids or their esters. At a certain temperature, the higher melting component will crystallize and can be separated from the liquid fraction. The solvents used to facilitate the separation can be removed by distillation. Fractional distillation is the separation of a mixture into its component parts or fractions by their boiling points and heating them to a temperature at which several fractions of the compound will evaporate. Generally, components boil at more than 25°C difference in boiling temperature under a pressure can be separated by distillation [5].

Isopropyl and butyl esters have lower melting points compared with the corresponding methyl esters. These properties of isopropyl and butyl esters can be used to improve cold-temperature flow characteristics of biodiesel [6, 7]. The objective of the present study was to
remove saturated fatty acids and improve the purities of isopropyl and butyl esters in HOSO by means of fractional distillation or crystallization.

**Materials and Methods**

Chemicals and reagents

HOSO was obtained from University of Northern Iowa's National Ag-Based Lubricants Center (NABL). Isopropyl alcohol, 1-butanol and acetone (all certified grade) and sodium metal were purchased from Fisher Scientific (Pittsburgh, PA). Sodium sulfate was purchased from Sigma-Aldrich, Inc, (St. Louis, MO). Standard mixtures of fatty acid methyl esters were purchased from Nu-Chek Prep (Elysian, MN).

Preparation of isopropyl and butyl esters

Five-hundred g of HOSO was dried under vacuum at 100°C to remove residual water. Isopropyl esters were made by using a 3:1 molar ratio of isopropanol to water-free oil. To prepare the catalyst in an amount equal to 1% of the weight of HOSO, about 1-1.5 g of freshly trimmed sodium metal was washed with freshly distilled diethyl ether and then dissolved in 50 mL of CO₂-free isopropanol prepared by boiling the alcohol in an Erlenmeyer flask with a few boileezers. After boiling, the alcohol was cooled while protected with Drierite. A Bunsen valve, which consisted of a short piece of rubber pressure tubing with a vertical cut in its side, was connected to the reaction flask to protect the reaction mixture from moisture while releasing the hydrogen gas that was generated. The catalyst was added to the HOSO and alcohol, and heated at 70-80°C for 8 h. After esterification, adequate dry ice was added to the reaction mixture to neutralize the catalyst. Then the esters were washed with 500 mL water three times to remove extra isopropanol. Sodium sulfate was added to dry the esters.

For butyl esters, n-butanol, sodium butyloxide and other reagents were prepared in the same manner as for the isopropyl esters. Since butanol has low solubity in water, after esterification, the residual butanol was removed by evaporation with a rotary evaporator.

Measurement of melting points of the fatty acid esters
Melting points of butyl and isopropyl esters were measured with a differential scanning calorimeter (DSC 7 equipped with an Intracool System II, Perkin Elmer, Norwalk, CT). Approximately 3 mg of each sample was weighed accurately into an alumina pan, and an empty pan was used as reference. After equilibration at 25°C for 1 min, the sample was rapidly heated to 80°C at 40°C/min and held for 3 min and then cooled to -60°C at 10°C/min rate and equilibrated for 20 min. When reheated at 5°C/min rate, the peak and final melting temperatures were recorded.

Gas chromatographic analysis

The fatty acid compositions of the esters were examined by gas chromatography (GC). Esters in hexane solution were injected into a HP 5890 Series II instrument (Hewlett-Packard, PA) with a SP-2330 fused silica column (15 m x 0.25 mm and 0.20 μm film thickness (Supelco, Bellefonte, PA, USA). The injector and FID detector were at 230°C, and the oven temperature was programmed from 140 to 220°C at 10°C/min. The flow rates of hydrogen, helium and air were set at 32, 23 and 438 mL/min, respectively. One μL samples of esters diluted in hexane were injected. Chromatographic peaks of FAME were identified by comparing the retention time with GC reference mixture 17A from Nu-Chek.

Fractional distillation

The butyl esters were distilled in a round-bottom flask containing a Teflon-coated magnetic stirring bar. The fractionating column consisted of three concentric tubes 25 cm length. The distillation flask was heated with a heating mantle and the column with a heating tape, and the condenser was cooled with water. Thermometers were inserted in the top of the column and in the distillation flask. Joints were lubricated with high-vacuum grease. The pressure of distillation was stabilized at 0.4 Torr by using a vacuum pump and automatic pressure control. The distillation rate was controlled by power input to the heaters. Fraction compositions were measured by GC.

Low-temperature crystallization
Solvent concentration selection: Butyl esters with various volume percentages of acetone were placed in a cold bath at -30°C for 24 h. The mixtures were filtered through a jacketed Bucher funnel cooled with dry ice and acetone at the temperature of crystallization, and the fatty acid compositions of the filtrates and precipitates were analyzed by GC.

Two-step crystallization: Esters with 80 % (vol) of acetone were placed in a cold bath for 24 hours at a selected temperature. The optimal fractionation temperature was chosen, to give a thick slurry of crystals without the gel formation. After filtering through a jacketed Buchner funnel fitted with Whatman #1 quantitative filter paper, the filtrates were set at the second optimal fractionation temperature. The second temperature was chosen to be higher than the melting point of the ester being processed. Fractions were examined by GC.

Scale-up fractionation of butyl esters: Three-hundred mL of esters with 80 volume % acetone were fractionated by the 2-step crystallization. A metal submersed filter (40 mesh screen, stainless steel) was used. The fatty acid profiles of the filtrates and precipitates were analyzed by GC.

Results and Discussion

Fatty acid compositions of esters from HOSO

The fatty acid compositions of isopropyl and butyl esters were examined by GC. The percentages of the esters are listed in Table 1.

Fractional distillation of butyl esters of HOSO

The boiling points of methyl esters, propyl esters and isopropyl esters with various fatty acid chain lengths have been summarized by Singleton [8]. The boiling points of butyl palmitate,
butyl stearate and butyl oleate were extrapolated from Singleton’s data. When the vapor temperature was close to the boiling point of butyl palmitate, collection of the first fraction was begun. The first fraction was ended when the head temperature increased sharply under constant pressure.

The distillation speed, head temperature and fatty acid composition of distilled fraction and pot residue of three trials are presented in Table 2. These data indicated that the boiling point of butyl palmitate at 0.4 mmHg is about 120-123°C. To achieve good separation, the distillation speed must be very slow. When the distillation speed was a drop/10sec, the butyl palmitate fraction was accompanied by considerable amount of butyl oleate. When the distillation speed was reduced to a drop/30 sec, the purity of the concentration of the butyl palmitate in the first fraction approximately doubled and the amount of butyl oleate accompanying it decreased. When the pot residue was analyzed after the butyl palmitate was distilled, the butyl oleate content was only slightly reduced for the fast distillation, but for a slow distillation the purity of the butyl oleate in the pot residue reached about 92%. The difference of boiling points of butyl palmitate and the other butyl esters of HOSO is less than 20°C at the pressures we used. It appears that distillation will be too slow and inefficient to remove butyl palmitate from HOSO. Distillation also does little to separate the butyl stearate, which actually increased in the pot residue as other components were partly removed.

Melting points of isopropyl esters, butyl esters and filtrate of butyl esters

The melting points of isopropyl and butyl esters were determined by DSC. Figure 1 shows the DSC curve of butyl oleate (>98%). The pure compound gives a melting curve with a single peak that requires about -37°C to melt. This range is probably caused by the difference in crystal size and the high surface energy of the smaller crystals. The results for isopropyl oleate were similar to those of Figure 1, but the peak melting point was 2.3°C lower. Figures 2 and 3 show the DSC curves for isopropyl and butyl esters prepared from the HOSO. These compounds have multiple melting peaks, reflecting their complexity. The double peaks at low temperatures suggest polymorphic forms of the esters. The sharp downward curves that are lower than the baseline indicate the release of heat as a low-melting polymorph changes into a more stable one. Notice the shallow ripples to the right of the main peaks. These are the melting of the saturated compounds, primarily palmitate and stearate esters. The pure butyl and isopropyl palmitates and
stearates are above 0°C (Chemical Abstracts), so these ripples must be mixture and polymorphs of the saturated esters. In any event, these compounds limit the temperature at which the ester mixture can be used. Even though their amounts are small, their crystallization can cause clouds and even gelation of the ester mass well above the temperatures of the main peak. The small amounts of linoleate and linolenate esters are obscured by the polymorphic forms, but the presence of these esters may encourage the formation of the low-melting polymorph which was not observed in the pure oleate ester peak.

Solvent concentration selection for crystallization

Preliminary experiments showed that fractionation without solvent or fractionation with low proportions of solvent yielded gels that could not be filtered when the esters were cooled to crystallization temperatures. The crystals formed by isopropyl esters at low solvent concentrations were very fine, filled the whole container and made filtration difficult. On the other hand, butyl esters formed relatively big crystals that settled to the bottom. The good filtration properties of butyl esters made it ideal to investigate the feasibility of using low solvent concentrations. The solvent concentration affected the gel formation temperature as shown in Table 3. Table 3 shows that the gel formation temperature decreased with the increased percentage of solvent. The more solvent used, the lower the gel formation temperature. The efficiency of separation of crystals formed at low temperature could be improved by diluting the sample with solvent.

Table 4 shows that although lower solvent concentration yielded a slightly higher purity of butyl oleate, the filtrates became richer in both butyl stearate and butyl oleate as the solvent concentrations increased. These samples yielded almost dry precipitates with the same filtration times (about 5 min for 100 mL sample). The yields of oleate in three samples have been measured (Table 5) and the results also showed the efficiency of separation of crystals formed at low temperature can be improved by diluting sample with solvent.

Two-step crystallization of HOSO esters

Multisteps of crystallization were required because saturates (about 10% in original oil) in the sample can push esters to form gel at low temperature. Since 2-3% saturates was enough to lead
to the formation of a gel, only diluting esters to a relatively low concentration can make one-step filtration reach the desired purity of oleate ester.

Isopropyl esters of HOSO formed very fine crystals and the separation of crystals was very slow: One hundred milliliter isopropyl ester solution containing 80% acetone took more than 1 h to filter whereas butyl esters of HOSO, which formed big crystals at the bottom of the container, only took 5 min to filter. The butyl esters seemed to be freer of filtrate than the isopropyl esters. The fine and soft precipitates in isopropyl ester and its poor filtration properties were responsible for the first fractionation temperature of isopropyl ester being higher than that of the butyl ester.

The second fractionation temperature of isopropyl esters was selected to be lower than that of butyl ester because the isopropyl had a lower melting point than in corresponding butyl ester. The composition of the filtrate after two steps showed that the stearic ester was removed more readily than palmitic ester.

After two-step fractionation, the purity of the oleate ester reached 91.9% for the isopropyl ester and 92.5% for the butyl ester, but there was still about 2% palmitate esters left in the filtrates. When the filtrate temperatures of the butyl and isopropyl esters were lowered to -38 °C and -40°C, respectively, there were little difference in fatty acid compositions of the precipitate and filtrate. This may be because the precipitate had reached a eutectic composition. At this temperature, all the constituents crystallize simultaneously from molten liquid solution.

Figure 4 shows a DSC melting curve for the twice fractionated butyl esters of HOSO. Comparison with Figure 3 shows that the size of the high melting peaks on the right side of Figure 4 have been greatly reduced and moved to lower temperatures by the fractionation.

The concentrations of linoleic and linolenic esters remained little changed during the two-step crystallization. The melting points of the esters of these two polyunsaturates are lower than oleic acid and can not be removed by this procedure. Although theoretically they can be removed by filtering out oleate esters, this is not practical because of the low percentage of polyunsaturates.

Scale-up experiment of crystallization

A metal filter was used in reverse filtration mode to observe the possibility of scaling up separation. The compositions of filtrates from these two methods of butyl esters were shown in Table 7. There were no significant differences between these two methods for butyl ester, but for isopropyl ester, the metal filter could not separate precipitates very well and many crystals came
with the filtrate although the metal filter that had finer pores than the filter paper used in the Bucher funnels. Isopropyl ester esters formed crystals that were too fine to be filtered by metal filter. A Buchner funnel did better because the crystal pad that formed on the bottom of the funnel made a finer filter.

**Conclusion**

The saturated fatty esters in HOSO esters can be mostly removed and the purity of oleate of can be improved from 83.2 to 92.5% by employing 2-step low-temperature crystallization. Fractional distillation was not very effective because the low distillation speed.

**Acknowledgement**  This study was carried out with financial support from the Center for Sustainable Environmental Technology (CSET) at Iowa State University.

**References**

Table 1. Fatty acid compositions (%) of isopropyl and butyl esters of HOSO

<table>
<thead>
<tr>
<th>Sample</th>
<th>Palmitate</th>
<th>Stearate</th>
<th>Oleate</th>
<th>Linoleate</th>
<th>Linolenate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isopropyl esters</td>
<td>7.34</td>
<td>3.12</td>
<td>83.12</td>
<td>1.37</td>
<td>1.84</td>
</tr>
<tr>
<td>Butyl esters</td>
<td>7.06</td>
<td>3.11</td>
<td>83.31</td>
<td>1.30</td>
<td>2.29</td>
</tr>
</tbody>
</table>

Table 2. Distillation rate and fatty acid composition of the first distillation fractions of butyl esters from HOSO

<table>
<thead>
<tr>
<th>Distillation rate</th>
<th>Head temperature*</th>
<th>Major compositions of distillates (%)</th>
<th>Major compositions of residue oil (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distillation</td>
<td>C16:0  C18:0  C18:1</td>
<td>C16:0  C18:0  C18:1</td>
<td></td>
</tr>
<tr>
<td>Drop/10sec</td>
<td>120°C</td>
<td>17.18  2.11  75.01</td>
<td>6.48  2.70  85.65</td>
</tr>
<tr>
<td>Drop/22 sec</td>
<td>117-123°C</td>
<td>30.36  1.45  62.58</td>
<td>1.99  2.71  89.49</td>
</tr>
<tr>
<td>Drop/30 sec</td>
<td>121°C</td>
<td>37.84  1.28  54.35</td>
<td>0.16  2.78  91.81</td>
</tr>
</tbody>
</table>

*The head temperatures correspond to the vapor temperatures.

Table 3. Gel formation temperatures of butyl ester of HOSO with various solvent concentrations*

<table>
<thead>
<tr>
<th>Concentration of acetone (%)</th>
<th>Gel formation Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>-30</td>
</tr>
<tr>
<td>50</td>
<td>-32</td>
</tr>
<tr>
<td>60</td>
<td>-33</td>
</tr>
<tr>
<td>70</td>
<td>-34</td>
</tr>
<tr>
<td>80</td>
<td>-34</td>
</tr>
</tbody>
</table>

*Gel formation was recognized when the crystals filled the whole container and did not allow a liquid section to separate.
Table 4. Fatty acid composition (%) of the major constituents of filtrates and precipitates of butyl esters of HOSO at various solvent concentrations

<table>
<thead>
<tr>
<th>Fractions</th>
<th>Proportion of acetone (v/v, %)</th>
<th>Filtrate</th>
<th>Percentage of methyl esters in the mixture</th>
<th>Precipitate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>C16:0</td>
<td>C18:0</td>
</tr>
<tr>
<td>Filtrate</td>
<td>50</td>
<td>2.45</td>
<td>0.42</td>
<td>90.78</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>2.58</td>
<td>0.47</td>
<td>90.68</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>2.70</td>
<td>0.57</td>
<td>90.66</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>2.91</td>
<td>0.65</td>
<td>90.58</td>
</tr>
</tbody>
</table>

Table 5. The yields of oleate in 100 mL of sample by low-temperature crystallization of samples with various solvent percentages

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fractionation temperature (°C)</th>
<th>Percentage of oleate in the filtrate oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butyl esters of HOSO with 50% acetone</td>
<td>-30</td>
<td>63.7</td>
</tr>
<tr>
<td>Butyl esters of HOSO with 80% acetone</td>
<td>-30</td>
<td>88.7</td>
</tr>
<tr>
<td>Isopropyl esters of HOSO with 80% acetone</td>
<td>-27</td>
<td>55.6</td>
</tr>
</tbody>
</table>
Tabl 6. Fractionation at two temperatures and the ester compositions (%) of isopropyl and butyl esters of HOSO in 80 vol % acetone

<table>
<thead>
<tr>
<th>Samples</th>
<th>Steps</th>
<th>Fractionation temperature (°C)</th>
<th>Percentage of esters in filtrate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C16:0</td>
<td>C18:0</td>
</tr>
<tr>
<td>Isopropyl esters</td>
<td>First</td>
<td>-27</td>
<td>5.78</td>
</tr>
<tr>
<td></td>
<td>Second</td>
<td>-37</td>
<td>2.06</td>
</tr>
<tr>
<td>Butyl esters</td>
<td>First</td>
<td>-30</td>
<td>2.99</td>
</tr>
<tr>
<td></td>
<td>Second</td>
<td>-36</td>
<td>1.91</td>
</tr>
</tbody>
</table>

Table 7. Major compositions (%) of filtrates by Bucher funnel and metal filter methods

<table>
<thead>
<tr>
<th>Samples</th>
<th>Fractionation temperature</th>
<th>Filtration method</th>
<th>Percentage of esters in filtrate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>C16:0</td>
</tr>
<tr>
<td>Isopropyl ester</td>
<td>-27 °C</td>
<td>Bucher funnel</td>
<td>5.78</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Metal filter</td>
<td>7.00</td>
</tr>
<tr>
<td>Butyl ester</td>
<td>-30 °C</td>
<td>Bucher funnel</td>
<td>2.99</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Metal filter</td>
<td>2.80</td>
</tr>
</tbody>
</table>
Fig 1. DSC thermogram of pure butyl oleate (98%) *

*Data provided by Linxing Yao

Fig 2. DSC thermogram of isopropyl esters of HOSO
Fig 3. DSC thermogram of butyl esters of HOSO

Fig 4. DSC thermogram of filtrate of butyl esters* of HOSO

*GC (%) composition of filtrate butyl esters: 2.99% palmitate, 0.66% stearate, 90.27% oleate, 1.29% linoleate and 2.23% linolenate.
Chapter 3. Optimization of the Oxidation of Methyl Linoleate Monolayers to Yield Useful Products

Haixia Liu · Earl G. Hammond · Tong Wang

Abstract

Methyl linoleate monolayer has a highest lipid oxidation rate. It can be employed to produce useful oxidation products including epoxides and hydroxides. Methyl linoleate (20% by weight) was coated to silica gel H to form monolayers and heated at 35, 40, 50 and 60°C. Methyl palmitate (5% by weight of methyl linoleate) was added as internal standard. The identification of oxidation products was by comparison to standards. The oxidation rate increased with temperature. The temperature for optimal yields of epoxides (20.26%) and total non-scission products (NSPs, 38.79%) was 50°C. Citric acid and EDTA (0.01% and 0.02% by weight of oil) were added as chelating agents to minimize the effects of iron on oxidation. Citric acid at 0.01% achieved higher PV and also reduced the loss of NSPs to scission products (SPs) after reaching the maximum peroxide value. The addition of 20 ppm vanadium (by weight of silica gel) increased the yield of epoxides (23.85%); however, it also led to lower peroxide values and longer induction period.

Key words  Epoxides · Nonscission products · Methyl linoleate · Monolayer · chelating agents · Vanadium
Introduction

The importance of oxidative stability and low melting point in the application of lipid-based fuels and lubricants has been discussed in previously chapter. Another potential way to improve the lubricant properties is through chemical modification of the olefinic groups of the oleochemical. For example, hydrogenation and epoxidation have been used to synthesize improved products.

The properties of some esters of epoxidized oleochemicals have been extensively studied. These studies showed that epoxides, such as epoxidized methyl oleate, linoleate, and linolenate, have great potential for use as a fuel additive or lubricating fluid [1]. There is evidence that epoxidation of olefinic materials improves their oxidative stabilities, strengthens their attachment to metal surfaces, and improves their low-temperature properties [2]. The conventional method of preparing epoxidized vegetable oils is by reacting the double bonds of fatty acids with peroxy acids, which is formed by treating hydrogen peroxide with acetic acid; however, epoxide, hydroxy and hydroxy-epoxides can also be obtained by oxidation of linoleate in monolayers. Compared with commercial epoxidized methyl linoleate, which is fully epoxidized, the main products of monolayer oxidation were a mixture of 9,10 and 12,13-monoepoxyoctadecenoic acids [3].

The uptake of oxygen and the rate of oxidation are greatly accelerated when the ratio of solid to oil is close to that of a monolayer [4, 5]. Tekin and Hammond [6] showed that epoxy fatty made up about 19% of the products recovered by air oxidation when linoleate esters were spread as a monolayer on a silica gel surface. The non-scission products (NSPs) in surface oxidation, included epoxides, hydroxides and hydroxy epoxides, and their yield amounted to 52% of the recovered volatiles by GC. The surface oxidation of methyl linoleate in monolayer may provide an alternative way to produce useful products, especially epoxides. Further work done by Koprucioglu et al. [7] investigated the effects of various transition metal ions on surface oxidation of methyl linoleate and showed that copper and iron ions accelerated oxidation time and increased scission products (SPs) concentration. However, vanadium addition reduced the formation of these products.

Temperature and the presence of some metal ions affect the oxidation rate and the surface oxidation products. Chelating agents can be used to remove some undesirable prooxidant metals.
and decrease the accumulation of SPs [6, 8]. Although other NSPs may also be valuable, the major concern in this study was the yield of epoxides. The objective of this study was to optimize the parameters that may affect the yield of epoxides from methyl linoleate monolayer oxidation.

**Materials and Methods**

Chemicals and reagents

Methyl linoleate and methyl palmitate were purchased from Nu chek Prep, INC.; citric acid from Haarmann & Reimer Corp., ethylenediamine tetraacetic acid (EDTA) and sodium sulfate from Fisher Scientific Co. (Pittsburgh, PA). Vanadyl acetylacetonate (95%) and Silica gel H were purchased from Sigma-Aldrich, Inc, (St. Louis, MO).

General method

*Preparing methyl linoleate monolayers*

Three g of methyl linoleate and 150 mg of methyl palmitate (5% by wt of methyl linoleate), as an internal standard, were dissolved in 50 mL of hexane and added to 12.00 g of silica gel H [3]. After stirring for 2 min, the hexane was evaporated on a rotary evaporator. This lipid embedded silica was subjected to various conditions for oxidation studies.

*Peroxide value measurement*

Peroxide values were determined by iodometric titration (AOCS Cd 8-53). At suitable times, 1 g samples of silica were withdrawn and the hydroperoxides were reduced with iodide. Silica gel was removed by filtration. The chloroform-acetic acid layer was washed three times with water to remove acetic acid. Then the chloroform layer was dried with anhydrous sodium sulfate. The residual lipid was characterized by GC for the reduced products.

*GC analysis*

Samples of the chloroform layer were evaporated and the residue dissolved in hexane. Approximately 1 µL was injected into a HP 5890 Series II instrument (Hewlett-Packard, PA) with
a SP-2330 fused silica column (15 m length, 0.25 mm i.d., and 0.25 μm film thickness). The injector and FID detector were at 300 °C, and the oven temperature was programmed from 40 to 220 °C at a rate of 10°C/min. The flow rates of hydrogen, helium, air, split and septum purge were set at 31.7, 23.1, 438, 326 and 2.78 mL/min. Chromatographic peaks of FAME were identified by comparing the retention times with those of Tekin and Hammond (11).

Effect of temperature on the yields of epoxides and other NSPs

Autoxidation of methyl linoleate monolayers was performed at 35, 40, 50 or 60°C. Samples of silica of approximately 1 g were withdrawn at times estimated to give similar degrees of oxidation. Each sample was weighed and the hydroperoxides were reduced and the product was analyzed by GC.

Effect of chelating agents on the yield of epoxides and accumulation of SPs

Citric acid or EDTA was added to 12 g silica gel at 0.01 or 0.02% of the weight of methyl linoleate (3g) required to form a monolayer in 30 mL water and thoroughly mixed for 2 min. The water was removed by baking the silica at 110°C for 2 h. Methyl linoleate was added to the silica gel, and oxidized at 50°C. Approximately 1 g of samples were taken and weighed and analyzed periodically.

Effect of vanadium on the yield of epoxides

Silica gel (12 g) was treated with citric acid at the 0.01% level of the weight of methyl linoleate (3 g) required for a monolayer. The citric acid was dissolved in 30 mL of water and after mixing 5 min with the silica, the water was removed by vacuum filtration. An additional 100 mL of water was added again and removed by filtration. This washing of the silica gel was repeated 3 times. Then based on the weight of the silica gel used, 20 or 40 ppm of vanadium as vanadyl acetylacetonate was added in 30 mL of water and mixed thoroughly. The silica gel was then dried at 110°C for 2 h. and then used for monolayer preparation and oxidized at 50°C and analyzed as above.

Statistical analysis
Statistical analysis was performed by using the ANOVA in R (Software version 2.5). For each oil sample, two determinations were made.

**Results and Discussion**

Optimizing temperature for maximum yield of epoxides and other NSPs

Methyl linoleate monolayers were oxidized at 35, 40, 50 and 60°C. Previous results [6] showed that the higher the temperature, the faster the rate of oxidation, so sampling time was adjusted to take temperature into account. Figure 1 showed the changes in PV with time at various temperatures. The PV reached the maximum value faster at high temperature, but low temperature yielded higher PV’s. This occurred because the reaction was slow, and hydroperoxides decomposed more slowly at low temperature. At 50 and 60°C, the oxidation started immediately with no obvious induction period; but, at 35 and 40°C, there was a slight induction period during first day of oxidation.

The disappearance of methyl linoleate was coordinated with the changes of PV (Fig. 2). At high temperature, methyl linoleate quickly oxidized. The rate constants of autoxidation of methyl linoleate monolayers were 0.516, 0.779, 1.68, and 3.02 min⁻¹ for 35, 40, 50 and 60°C, respectively, as measured by the slope of the ln[linoleate] vs. time.

Figure 3 shows the yield of epoxides with time at various temperatures. In general, the yield of epoxides increased during the early stages of oxidation, but decreased after maximum value was reached. Hydroperoxides were accumulated when methyl linoleate was oxidized, then epoxides were produced using the hydroperoxides as an oxidizing agent. When the methyl linoleate was mostly oxidized, the concentration of hydroperoxides fell, and the yield of epoxides decreased as they disappeared into other products. The maximum yield of epoxides increased when the temperature was raised from 35 to 50°C, whereas at 60°C, the maximum yield of epoxides decreased. This is because hydroperoxides decomposed too fast at 60°C and less epoxides were produced. Therefore, the optimal temperature for maximum yield of epoxides was ~50°C. Other NSPs also reached highest value at this temperature. Figure 4 represents a typical chromatograph of oxidation products.
Epoxy methyl esters (E-FAME), hydroxy methyl esters (H-FAME), hydroxy-epoxy methyl esters (HE-FAME), dihydroxy methyl esters (DH-FAME) and trihydroxy methyl esters (TH-FAME) were the major NSPs. The details of changes of oxidation products at 50°C are shown in Table 1. PV and the yields of NSPs increased with time during oxidation within 24 h. The NSPs almost all reached a maximum value at 24 h of oxidation at 50°C, but H-FAME reached maximum value at 50°C for 16 h. The maximum yield of epoxides achieved 20.26% at 50°C for 24 h, which was higher than 18.74 % achieved by Tekin and Hemmond at 40°C for 3 days [6]. The PV also reached maximum value, 1218 meq/kg oil, at this condition. The concentration of methyl linoleate decreased to 15-20% during 24 h at 50°C. After 24 h, the yield of epoxides and other NSPs all decreased, but the accumulation of SPs increased because the E-FAME and other major products were converted slowly to SPs. The longer the oxidation, the less the total peak was, which included unoxidized linoleate, NSP, and SP. After 48 h of oxidation, the total peak area decreased to 55%. This decrease was probably caused by evaporation of some volatile SP, lower detector responses to various NSP, and the formation of polymers that can not be extracted from the silica or eluted from GC column [6].

Effect of chelating agents on the yield of epoxides and accumulation of SPs

Proxidant metals were removed by citric acid or EDTA at two concentrations. Figure 5 showed the changes in PV of methyl linoleate monolayers with time at 50°C in the presence of these chelating agents. Compared with control group (untreated silica gel as support), all chelation agent treatments, except the one with 0.01% citric acid, led to an induction period during oxidation. Presumably, this is because at least some portion of the proxidant metals in the silica gel was chelated. The primary proxidant metal in silica is thought to be iron ions [3]. Inactivation of the ions that are present prolongs the induction period. Two EDTA treatment groups have longer inductions period than those treated with citric acid. With the chelating agents, higher maximum peroxide values were achieved, the PV with 0.01% citric acid treatment was 1562.5 meq/kg, which was significantly (p <0.05) higher than control group at 1211.8 meq/kg.

The graphs (Fig. 5 to Fig. 9) show mean values and standard deviations of individual means are shown graphically as vertical bars. Figure 6 shows the yields of epoxides at 50°C with various chelating agents. Citric acid treatment groups had slightly higher yields of epoxides
compared with the control group, but the difference was not statistically significantly at p >0.1. The yield of epoxides achieved 20.9% with 0.01% citric acid treatment at 24 h (20.1% for the control group). Chelation of proxidant metals suppressed the decomposition of the hydroperoxides and yielded more epoxides. EDTA treatment groups did not increase in epoxide yields. Probably, this is because the chelation, in this case, prolonged the induction period, and the general yield of oxidation products. Tekin and Hammond [6] showed that undesirable SPs were increased by addition of iron and copper to silica gel. Figure 7 shows the changes in SPs during oxidation. With all chelating agents, the accumulation of SPs decreased, but not significantly (p >0.1) with the citric acid treatments, compared with controls. EDTA treatment can decrease the accumulation of SPs significantly (p <0.05). This showed that by removing proxidant metals (i.e., iron and copper ions), NSPs survived longer and there was less decomposition to SPs. Overall, 0.01% citric acid treatment can slightly increase the yield of epoxides and decrease the accumulation of undesirable SPs although on both points are not significant compared with control group.

Effects of vanadium on the yield of epoxides

Vanadium was added in vanadyl acetylacetonate form in water solution to silica that had been treated with citric acid and then thoroughly washed. Figure 8 shows the changes of PV with 20 and 40 ppm vanadium at 50°C. Zero ppm vanadium addition was the control group. It is obvious that the addition of vanadium to silica gel decreased PV significantly (p <0.05). This is probably because vanadium catalytically used linoleate hydroperoxides to make epoxides from methyl linoleate thereby decreasing PV. The addition of 20 ppm had less effect on the PV than 40 ppm of vanadium. If vanadium reduces the PV, it will slow the overall reaction because the hydroperoxides generate the free radicals that drive the overall reaction. Actually the long induction periods (Fig. 9) indicate that vanadium might have acted as antioxidant in this application.

Figure 9 shows the yields of epoxides caused by addition of 20 and 40 ppm vanadium at 50°C. It also showed induction for the first several hours compared with the control, but the vanadium addition also caused higher yields of epoxides, achieved at 32 h. The maximum yields of epoxides for 0 (control), 20 and 40 ppm vanadium addition were 20.1%, 23.9 and 21.4%,
respectively. The addition of 20 ppm vanadium increased the yield of epoxides modestly but significantly (p <0.05).

**Conclusion**

The optimal temperature for the yields of epoxides and other NSPs was 50°C. Citric acid 0.01% treatment improved the yield of epoxides and decreased the accumulation of SPs, but the effect was modest. The addition of 20 ppm vanadium increased the yield of epoxides and achieved 23.85% at 50°C for 32 h. Citric acid and vanadium treatments all led to a induction period.

**Acknowledgement**  This study was carried out with financial support from the Center for Sustainable Environmental Technology (CSET) at Iowa State University.

**References**

Fig. 1. Change in PV of monolayers of methyl linoleate with time at various temperatures in monolayers.

Fig. 2. Decrease in the percentage of methyl linoleate with time at various temperatures in monolayers.
Fig. 3. Changes of the yields of epoxides over time at various temperatures in monolayers

Fig. 4. A typical gas chromatograph of the oxidation products produced during methyl linoleate monolayer oxidation.
Fig. 5. Changes in PV of methyl linoleate monolayers over time at 50°C with various chelating agents and concentration.

Fig. 6. Epoxide yields of methyl linoleate monolayers over time at 50°C with various chelating agents and concentration.
Fig. 7. Accumulation of scission products of methyl linoleate monolayers over time at 50°C in various chelating agents and concentration

Fig. 8. Changes of PV of methyl linoleate monolayer with over at 50°C at different vanadium concentration
Fig. 9: Epoxide yields of methyl linoleate monolayer over time at 50°C in different vanadium concentration.

Table 1. Changes in PV, percentage of methyl linoleate, and percentage of oxidation products during surface oxidation at 50°C$^a$

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>0</th>
<th>8</th>
<th>16</th>
<th>24</th>
<th>32</th>
<th>40</th>
<th>48</th>
</tr>
</thead>
<tbody>
<tr>
<td>PV(meq/kg)</td>
<td>--</td>
<td>403.1</td>
<td>1189.0</td>
<td>1218.0</td>
<td>1075.6</td>
<td>944.3</td>
<td>880.9</td>
</tr>
<tr>
<td>linoleate</td>
<td>100</td>
<td>78.8</td>
<td>43.5</td>
<td>21.9</td>
<td>12.3</td>
<td>6.9</td>
<td>5.8</td>
</tr>
<tr>
<td>E-FAME</td>
<td>--</td>
<td>5.4</td>
<td>16.5</td>
<td>20.3</td>
<td>18.8</td>
<td>18.1</td>
<td>16.0</td>
</tr>
<tr>
<td>H-FAME</td>
<td>--</td>
<td>2.8</td>
<td>4.3</td>
<td>3.4</td>
<td>2.1</td>
<td>1.2</td>
<td>1.0</td>
</tr>
<tr>
<td>HE-FAME</td>
<td>--</td>
<td>2.1</td>
<td>5.4</td>
<td>8.3</td>
<td>8.0</td>
<td>8.5</td>
<td>7.8</td>
</tr>
<tr>
<td>DH-FAME</td>
<td>--</td>
<td>1.0</td>
<td>2.2</td>
<td>2.7</td>
<td>2.4</td>
<td>2.5</td>
<td>2.8</td>
</tr>
<tr>
<td>TH-FAME</td>
<td>--</td>
<td>0.3</td>
<td>0.9</td>
<td>1.9</td>
<td>1.3</td>
<td>0.9</td>
<td>3.5</td>
</tr>
<tr>
<td>Total NSP</td>
<td>--</td>
<td>12.7</td>
<td>31.5</td>
<td>38.8</td>
<td>37.0</td>
<td>34.4</td>
<td>35.6</td>
</tr>
<tr>
<td>Total SP</td>
<td>--</td>
<td>1.6</td>
<td>6.3</td>
<td>9.4</td>
<td>10.1</td>
<td>10.3</td>
<td>13.7</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>93.1</td>
<td>81.2</td>
<td>70.1</td>
<td>59.5</td>
<td>51.6</td>
<td>55.2</td>
</tr>
</tbody>
</table>

$^a$Calculated based on GC area relative to the area and concentration of methyl palmitate. GC correction factors for the oxidation products were 1.17 for E-FAME (11).
Chapter 4. Residues Accumulating When Biodiesel and its Component Methyl Esters Are Heated in a Muffle Furnace at 200°C for 15 min

Haixia Liu1 · Earl G. Hammond1, 2 · Tong Wang1

Abstract

After long operation of biodiesel engine, hard and dark deposits accumulate on injector tips, which affect engine performance. The type and composition of biodiesel have major effect on the formation of deposits. The major compounds of thermal stable residues of biodiesel from muffle furnace heated at 200°C for 15 min were analysed by GC-MS. Those compounds were mostly fragments of fatty esters, in which the terminal ends are acids, aldehydes. Methyl linolenate formed significantly greater amounts of residue than neat biodiesel, methyl palmitate, methyl stearate, methyl oleate, and methyl linoleate. The GC profile of methyl linolenate residues included more compounds than from other oils.

Key words Thermal stable residues · Muffle furnace · Biodiesel · Methyl esters of fatty acids
Introduction

Biodiesel produced from vegetable oils can be more prone to reactions that lead to engine deposits, water separation, accelerated microbial growth, filter plugging, and corrosion of fuel-system components [1, 2]. Among these problems, the most common one is the accumulation of deposits on the fuel injector tips, which can alter the fuel injection pattern and flow volume. Sobolev et al. [3] reported that the deposit-forming tendency was a function of the type of hydrocarbon composition of the diesel fuels. Increased concentration of sulfur compounds and aromatic hydrocarbons in the fuel increased the deposit formation. Labeckas et al. [4] found that vegetable oil biodiesel was more prone to form deposits than petroleum-based diesel. Thomes [5] reported that the deposits on fuel injectors after 1000-h operation of transportable Refrigeration Units operating on B100 biodiesel were mostly carbon (70%) and oxygen (20%). Less than 1% by weight of metals was detected. Biodiesel itself is about 11% oxygen, so the deposit has gained oxygen likely due to oxidation. Pillar et al. [6] reported that in the presence of oxygen, polyunsaturated esters decomposed to leave a significantly greater amount of thermally-stable residue than saturated esters.

Injector tip temperature is one of the most important parameters affecting the performance of injector tip fouling. Kong [7] reported that during engine operation, the injector tip can experience temperatures of 150 to 250°C. Temperatures ranging from 80 to 150°C are believed to be required for deposit formation [8].

The objective of the present study was to investigate the formation of deposits when biodiesel and its component methyl esters were heated in muffle furnace. The major compounds of the residues were investigated by mass spectroscopy, and the amounts of the residues were estimated.

Materials and Methods

Chemicals and reagents

Fatty acid methyl esters were purchased from Nu-Chek Prep (Elysian, MN), and squalene was from Sigma-Aldrich, Inc (St. Louis, MO). Soybean biodiesel with no additives was obtained from University of Northern Iowa's National Ag-Based Lubricants Center (NABL).
Gas chromatographic analysis

The fatty acid compositions of the esters were examined by gas chromatography (GC). Esters in hexane solution were injected into a HP 5890 Series II instrument (Hewlett-Packard, PA) with a SP-2330 fused silica column (15 m length, 0.25 mm i.d., and 0.25 μm film thickness). The injector and flame detector were at 230°C, and the oven temperature was programmed from 140 to 220°C at 10°C /min. The flow rates of hydrogen, helium and air were set at 32, 23 and 440 ml/min, respectively. One μL samples of esters diluted in hexane were injected.

Gas chromatography-mass spectrometry (GC-MS) analysis

The GC-MS analyses were performed by using Waters GCT instrument coupled with an HP 6890 GC column (30 m length, 0.25 mm id., and 0.25 μm film thickness) and an Agilent 7963 autosampler (Agilent Technologies Inc., Palo Alto, CA). The oven temperature was programmed from 40 to 300°C at 10°C /min. The helium flow was 1.0 mL/min, which would be a linear velocity of about 35 cm/sec. The sample was injected in spiltless mode (purge time = 1 min). Two microliters were injected at an injector temperature of 260°C. The data were acquired in electron ionization mode (EI), scanning the mass range from 35 to 650 Daltons at 2 scans per sec.

Detection of the weight of the oxidation products of biodiesel and fatty esters and their composition by GC-MS

Approximately 10.00 ± 0.05 mg of biodiesel was measured into a 10-mL Pyrex® flask. The flask was place in the center of a muffle furnace using tongs. The temperature was set at 200°C using a thermocouple (Digi-Sense, Cole-Parmer). The samples were left in the furnace for 15 min at 200 ± 2 °C. After retrieval, residues in the flasks were extracted three times with 0.5 ml acetone. The volume of the acetone extract was reduced to 0.5 mL under nitrogen and analyzed by GC-MS. To determine the weight of the acetone residue, 4.04 μg squalene were added as internal standard and the residue was examined by gas chromatography.
Results and Discussion

GC-MS analysis of the biodiesel residue from the muffle furnace

Preliminary experiments showed that when biodiesel was heated at 250°C for 10 min no detectable residue remained, but the amount of material that accumulated increased rapidly as the temperature was lowered. At 150°C there was about 1% residue after 30 min. We chose to measure the residue after heating at 200°C for 15 min. Table 1 lists the MS identification of the volatile compounds of the biodiesel residue. Most of these compounds are fragments of fatty esters, in which the terminal ends are acids, aldehydes, or alcohols. There were many small peaks that could not be identified.

The five major fatty acids and their percentages in the biodiesel were: methyl palmitate (13.29%), methyl stearate (3.11%), methyl oleate (23.18%), methyl linoleate (56.02%) and methyl linolenate (3.86%). The amount of residue accumulation from heating the biodiesel and its major methyl esters at 200 °C for 15 min are given in Table 2. These results show that polyunsaturated esters left greater amounts of residue than the saturated esters. Methyl linolenate formed greater amounts of residue than biodiesel or the other constituent esters. Methyl palmitate and stearate left less than 0.1% residue. Pillar et al. [6] also found polyunsaturated fatty acids decomposed to leave more residues than saturated one due to oxidation. Polyunsaturated fatty acids are probably the main source of injector deposits in diesel engines.

For palmitate and stearate, the gas chromatographs showed peaks near that of methyl stearate. Possibly they are unoxidized esters. The residues from methyl oleate mostly had peaks with retention times longer than methyl stearate. The GC profiles of biodiesel and the polyunsaturated methyl esters showed peaks with shorter retention times than the original methyl esters, showing extensive decomposition. Mass spectra of the residues left from heating the methyl esters await use of the mass spectrometer and will be added later.

Conclusion

The major compounds from oxidized biodiesel were fragments of fatty esters, in which the terminal ends are acids, aldehydes, or alcohols. Polyunsaturated fatty acids formed more residues than saturated fatty acids.
Acknowledgement  This study was carried out with financial support from the Center for Sustainable Environmental Technology (CSET) at Iowa State University. Dr. Steve Vesey in chemistry instrument facility of Iowa State University helped on GC-MS analysis of oxidized biodiesel samples.

Reference

7. Private Email from Charng Kong S. to White, P. J. and Wang T. in June 13, 2008
Table 1. GC-MC analysis of residues of biodiesel that had been heated in the muffle furnace at 200 °C for 15 min

<table>
<thead>
<tr>
<th>Retention time (min)</th>
<th>Relative height (mm)</th>
<th>Possible compounds and structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.51</td>
<td>3</td>
<td>diacetone</td>
</tr>
<tr>
<td>7.83</td>
<td>25</td>
<td>hexanoic acid</td>
</tr>
<tr>
<td>8.38</td>
<td>15</td>
<td>2,3-butanediol diacetate</td>
</tr>
<tr>
<td>9.27</td>
<td>6</td>
<td>hexanoate ester</td>
</tr>
<tr>
<td>10.27</td>
<td>17</td>
<td>methyl octanoate</td>
</tr>
<tr>
<td>11.31</td>
<td>8</td>
<td>heptyl alcohol fragment</td>
</tr>
<tr>
<td>11.83</td>
<td>22</td>
<td>heptanoic acid</td>
</tr>
<tr>
<td>13.31</td>
<td>70</td>
<td>methyl 8-oxooctanoate</td>
</tr>
<tr>
<td>14.18</td>
<td>41</td>
<td>methyl 8-hydroxyoctanate</td>
</tr>
<tr>
<td>14.44</td>
<td>9</td>
<td>methyl 8-oxononanoate</td>
</tr>
<tr>
<td>14.69</td>
<td>162</td>
<td>monomethyl 9-nonandioic acid</td>
</tr>
<tr>
<td>15.28</td>
<td>34</td>
<td>monomethyl octanedioic acid</td>
</tr>
</tbody>
</table>
Table 1. GC-MC analysis of residues of biodiesel that had been heated in the muffle furnace at 200 °C for 15 min (Continue)

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Mass (amu)</th>
<th>Mass Formula</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.75</td>
<td>68</td>
<td>CH$_3$-O-C-(CH$_2$)$_7$-C=O</td>
<td>methyl mono 9-oxodecanedioic acid</td>
</tr>
<tr>
<td>15.98</td>
<td>20</td>
<td>CH$_3$-O-C-(CH$_2$)$_8$-C=O</td>
<td>methyl 10-oxodecanic acid</td>
</tr>
<tr>
<td>16.53</td>
<td>127</td>
<td>CH$_3$-O-C-(CH$_2$)$_7$-C-O</td>
<td>monomethyl nonanedioic acid</td>
</tr>
<tr>
<td>17.03</td>
<td>15</td>
<td>CH$_3$-O-C-(CH$_2$)$_8$-CH$_3$</td>
<td>methyl 8-(2-furyl)octadecanoate</td>
</tr>
<tr>
<td>17.89</td>
<td>19</td>
<td>CH$_3$-O-C-(CH$_2$)$_9$-C=O</td>
<td>4-(4-methoxycarbonyl butyl)-4-butanolide</td>
</tr>
<tr>
<td>17.95</td>
<td>18</td>
<td>CH$_3$-O-C-(CH$_2$)$_10$-C-O-CH$_3$</td>
<td>dimethyl dodecanedioate</td>
</tr>
<tr>
<td>20.17</td>
<td>11</td>
<td></td>
<td>unknown mass 208 probably cyclic</td>
</tr>
<tr>
<td>21.08</td>
<td>69</td>
<td></td>
<td>unknown mass 208 probably cyclic</td>
</tr>
<tr>
<td>22.10</td>
<td>6</td>
<td>CH$_3$-C-(CH$_2$)$_7$-CH=CH-(CH$_2$)$_8$-CH$_3$</td>
<td>methyl 9-hexadecenoate</td>
</tr>
</tbody>
</table>
Table 1. GC-MC analysis of residues of biodiesel that had been heated in the muffle furnace at 200 °C for 15 min (Continue)

<table>
<thead>
<tr>
<th>% Residues</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>23.00</td>
<td>22 methyl 9,10-dihydroxy octadecenoate</td>
</tr>
<tr>
<td></td>
<td>$\text{CH}_3-\text{O}=\text{C}-(\text{CH}<em>2)</em>{n}-\text{CH}=\text{CH}-(\text{CH}<em>2)</em>{n}-\text{CH}_3$</td>
</tr>
<tr>
<td>23.73</td>
<td>9 methyl octadecatrienoate (methyl linolenate)</td>
</tr>
<tr>
<td></td>
<td>$\text{CH}_3-\text{O}=\text{C}-(\text{CH}<em>2)</em>{n}-\text{CH}=(\text{CH}-(\text{CH}<em>2)</em>{n}-\text{CH}_3$</td>
</tr>
<tr>
<td>24.40</td>
<td>11 Methyl 12-epoxy octadecadienoate (M.W. 306)</td>
</tr>
<tr>
<td></td>
<td>$\text{CH}_3-\text{O}=\text{C}-(\text{CH}<em>2)</em>{n}-\text{CH}=\text{CH}-\text{CH}_2-\text{O}-(\text{CH}<em>2)</em>{n}-\text{CH}_3$</td>
</tr>
<tr>
<td>25.13</td>
<td>22 Methyl 12-epoxy octadecenoate (M.W. 308)</td>
</tr>
<tr>
<td></td>
<td>$\text{CH}_3-\text{O}=\text{C}-(\text{CH}<em>2)</em>{n}-\text{CH}=\text{CH}-\text{CH}_2-\text{O}-(\text{CH}<em>2)</em>{n}-\text{CH}_3$</td>
</tr>
</tbody>
</table>

Table 2. The amount of residues formed from biodiesel and its constituent methyl esters after heating for 15min at 200°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>% Residues*</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOSO biodiesel</td>
<td>0.531±0.043&lt;sup&gt;b&lt;/sup&gt;**</td>
</tr>
<tr>
<td>Methyl palmitate</td>
<td>0.079±0.017&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>Methyl stearate</td>
<td>0.055±0.018&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>Methyl oleate</td>
<td>0.382±0.009&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Methyl linoleate</td>
<td>0.566±0.005&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Methyl linolenate</td>
<td>1.786±0.052&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

* % residues = amount of residues/sample weight

** N=2, LSD<sub>0.05</sub>=0.073; Different letters represent significantly difference at P <0.05
Chapter 5. General Conclusions

By means of fractional distillation, the purity of oleate in butyl esters of HOSO can be improved from 83.3 to 91.8%. The major compound removed by distillation was butyl palmitate. The boiling point of butyl stearate was too close to butyl oleate and could not be separated. The rate of distillation must be as low as 30 sec/drop to avoid the loss of oleate with palmitate. The purification of butyl oleate of HOSO was more successful than isopropyl oleate by low-temperature crystallization because of good crystal formation properties of butyl esters of HOSO. Acetone at 80% (v/v) was helpful to increase the filtration efficiency. After a two-step low temperature crystallization, the percentage of oleic acid in the HOSO was increased from 83.2 to 92.5%. The percentage of palmitate decreased from 7.1 to 1.9% for butyl esters of HOSO, but it could not be further improved by crystallization because at this concentration, the mixture reached eutectic composition. Stearate was nearly completely filtered out and only had 0.3% left in the filtrates. For both fractional distillation and low temperature crystallization, the percentages of linoleate and linolenate remained unchanged.

The optimum temperature for formation of epoxides and other nonscission products (NSPs) from methyl linoleate monolayer oxidation was 50°C. At this temperature, the yield of epoxides reached 20.3% and peroxide value (PV) also reached a maximum value after 24 h oxidation. The percentage of epoxides decreased to 15-20% at this condition at 24 h. After 24 h, the yield of NSPs and PV decreased, but the accumulation of scission products (SPs) increased because some NSPs were converted to SPs. The prooxidant iron in silica gel can be chelated by citric acid or EDTA. A citric acid treatment at 0.01 % slightly increased the yield of epoxides and decreased the accumulation of SPs, but the addition of chelating agents also led to an induction time for oxidation. Vanadium acted presumptively as catalyst to convert hydroperoxides to epoxides during oxidation. It led to long induction time and very low PV, but the yields of epoxides reached 23.85% at 50°C for 32 h with 20 ppm in silica gel.

Biodiesel and methyl esters of its five major components were heated in a muffle furnace at 200°C for 15 min to assess the residue accumulation at engine fuel injector. The thermal stable residues from biodiesel were analysed by GC-MS. Those compounds recovered were mostly
fragments of fatty esters, in which the terminal ends were acids, aldehydes, or alcohols, and many unknown deposits in small amount. By comparison to the amounts of residues from biodiesel, the residues from methyl palmitate, and methyl stearate were smaller. Polyunsaturated fatty acids formed more residues than saturated fatty acids. Methyl linoleante left 25-fold more residues than methyl palmitate and methyl stearate, suggesting that polyunsaturated fatty acids are likely responsible for the injector tip deposit. Residues can be avoided by minimizing the time the engine runs in the 215-230°C range.
Acknowledgement

I would like to express my sincere gratitude to my advisor, Dr. Earl G. Hammond, for his guidance during my research and study. His great spirit and enthusiasm for research has motivated all his advisees, including me. His encouragement, patience, immense knowledge and his great efforts to explain things clearly and simply helped me during the time of research and writing this thesis. I also would like to express my great gratitude to my major professor, Dr. Tong Wang. Her clear, sharp mind and insights in oil studies always lead me deep thought about my research. She provided suggestions and good advice whenever I needed them.

Dr. Lawrence A. Johnson and Dr. Eve S. Wurtele deserve special thanks as my program of study committee members. Dr. Steve Vesey, in the chemistry chromatograph analytical instrument facility, has helped me with GC-MS analysis of the oxidized biodiesel samples.

My thanks also go to all people who have helped and inspired me in the past two years. My labmates in Dr. Hammond’s, Dr. Wang’s and Dr. White’s labs made for a convivial place to work.

I would like to give my special thanks to my husband, Dr. Wenjun Ma, my children Ruiyang Ma, Iris Ma and my parents. Their patient and love enabled me to complete this thesis.