Effect of Oxidation Under Accelerated Conditions on Fuel Properties of Methyl Soyate (biodiesel)

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ABSTRACT: Biodiesel derived from transesterification of soybean oil and methanol is an attractive alternative fuel for combustion in direct-injection compression ignition (diesel) engines. During long-term storage, oxidation due to contact with air (autoxidation) presents a legitimate concern with respect to maintaining fuel quality of biodiesel. This work examines the effects of oxidation under controlled accelerated conditions on fuel properties of methyl soyate (SME). SME samples from four separate sources with varying storage histories were oxidized at elevated temperature under a 0.5 standard cm^3/min air purge and with continuous stirring. Results showed that reaction time significantly affects kinematic viscosity (ν). With respect to increasing reaction temperature, ν, acid value (AV), PV, and specific gravity (SG) increased significantly, whereas cold flow properties were minimally affected for temperatures up to 150°C. Antioxidants TBHQ and α-tocopherol showed beneficial effects on retarding oxidative degradation of SME under conditions of this study. Results indicated that ν and AV have the best potential as parameters for timely and easy monitoring of biodiesel fuel quality during storage.

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KEY WORDS: Acid value, antioxidant, diesel fuels, fatty acid methyl esters, kinematic viscosity, oxidative stability, peroxide value, soybean oil.

Biodiesel (FA monoalkyl esters derived from vegetable oil or animal fat) is nearly ideal as an alternative fuel or fuel extender for combustion in direct-injection compression ignition (diesel) engines. Biodiesel has many fuel properties, including viscosity, gross heat of combustion, and cetane number, that are comparable to those of No. 2 diesel fuel (1–4). The lubricity characteristics of biodiesel allow improvement of antiwear properties in blends with low-sulfur No. 2 diesel fuel (5). In blends with conventional diesel fuel, biodiesel reduces exhaust emissions including particulate matter, hydrocarbons, polycyclic aromatic hydrocarbons, sulfur dioxide, carbon monoxide, and smoke (1,4,6–11). Biodiesel has a negative carbon dioxide balance and produces more than twice the energy required to create it (6,9).

The effects of oxidative degradation caused by contact with ambient air (autoxidation) during long-term storage present a legitimate concern in terms of maintaining fuel quality of biodiesel. Biodiesel derived from transesterification of soybean oil and methanol is a mixture of unsaturated and saturated long-chain (C_{18}) FA esters. Methyl soyate (SME) is composed of 80–85 wt% total unsaturated esters and has a relatively high degree of polyunsaturation. Unsaturated compounds are significantly more reactive to oxidation than saturated compounds; increasing the degree of unsaturation further increases reactivity (12).

Oxidative stability is not recognized as a parameter in the American Society for Testing and Materials (ASTM) provisional fuel standard guideline for biodiesel, PS121 (13), because cumulative effects of autoxidation on engine performance and emissions are difficult to quantify. Autoxidation is known to affect kinematic viscosity (ν), acid value (AV), and PV (14–17). Two of these parameters, ν and AV, are among the specifications listed within PS121, and extensive oxidation may increase either of these parameters beyond their maximal limits. Although PV itself is not listed as a parameter in the biodiesel fuel specification, formation of hydroperoxides caused by oxidative degradation during storage is known to influence cetane number (18,19), a parameter that is listed within PS121.

Oxidative degradation also presents a concern during storage of biodiesel/No. 2 diesel fuel blends (20,21). In addition to effects on ν, AV, and PV, extensive degradation may produce insoluble high-M.W. polymers that clog fuel lines and filters or lead to injector coking, incomplete combustion, and engine deposits.

The many ways in which autoxidation can compromise biodiesel fuel quality necessitates development of approaches for boosting resistance to oxidation. The work reported herein seeks to quantify effects of oxidative degradation on selected fuel properties under controlled, accelerated conditions. Samples from four independent producers of SME biodiesel with varying storage histories were collected and oxidized at temperatures in the range 50–200ºC. Reactions were conducted on mechanically stirred sample mixtures with a slow-bubbling air purge. Effects of reaction time and temperature on fuel properties were determined. Fuel properties evaluated before and after oxidation included ν (40ºC), AV, PV, specific gravity (SG, at 15.6ºC relative to water at 15.6ºC), cloud point (CP), and pour point (PP). Effects of TBHQ and α-tocopherol antioxidants on change in fuel properties following oxidation were also evaluated. Finally, results were analyzed quantitatively and on the basis of timeliness and ease of measurement to identify which fuel properties have the best potential for development as parameters for monitoring fuel quality during storage.

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EXPERIMENTAL PROCEDURES

Materials. SME samples were collected from four different fuel producers. To remove bias, identities of the producers will not be disclosed. Instead, the fuels were arbitrarily designated as SME-X where X ∈ (A, B, C, D) distinguishes the product by producer. Three samples were obtained from the ADEPT Group (Los Angeles, CA) and the fourth from the National Biodiesel Board (Jefferson City, MO). Listed in Table 1 are results from GC analyses of FA compositions of these materials. Antioxidants were ±α-tocopherol (95 wt%) from Aldrich Chemical Co. (Milwaukee, WI) and TBHQ (97%) from Sigma Chemical Co. (St. Louis, MO).

Methods. Oxidation reactions were conducted in the laboratory under varying time and temperature conditions. With respect to determining effects of oxidative degradation on biodiesel fuel properties, reaction conditions were designed to produce measurable changes in most fuel properties in a relatively short time. Sample mixtures were placed in a three-necked round-bottomed flask and heated by a mantle connected to a Variac controller (Bristol, CT). Reaction temperature was regulated manually using the controller and a thermometer immersed in the sample. Throughout the reaction, clean, dry air was bubbled slowly through the sample mixture and a water-cooled condenser used to minimize evaporative losses. Air flow rate was manually regulated at a constant 0.5 standard cm^3/min (SCCM) with an Aldrich digital flow meter. Contents of the flask were stirred by a magnetic stirrer from Cole-Parmer (Chicago, IL) to minimize wall effects and keep the mixture homogeneous through the duration of the reaction.

Apparatus and procedures for measuring ν at 40°C, CP, and PP data were summarized previously (22). AV data were measured in accordance with American Association of Cereal Chemists' (AACC) method 58-15 (23). The AACC method is essentially equivalent to the American Oil Chemists' Society (AOCS) method Cd 3a-63 except it allows use of a less hazardous solvent (95 vol% ethanol) for titration. AOCS method Cd 8-53 (24) was used to measure PV and method Cc 10a-25 (25) to measure SG at 15.6°C relative to water at 15.6°C.

TABLE 1
GC Analysis[a] of Methyl Soyate (SME) Samples[b]

Sample	16:0 (wt%)	18:0 (wt%)	18:1 (wt%)	18:2 (wt%)	18:3 (wt%)	Other[c] (wt%)
SME-A	11.2	4.3	22.6	51.2	9.9	0.8
SME-B	12.9	5.5	24.5	45.6	8.0	3.5
SME-C	11.7	4.3	24.8	50.8	8.4	—
SME-D	10.7	3.6	22.8	55.5	7.5	—

[a] Analyses were conducted on a PerkinElmer Autosystem GC with a 25 m × 0.32 mm i.d. BPX70 column from SGE (Austin, TX). Temperature program: hold at 50°C (5 min), ramp at 10°C/min to 250°C, hold at 250°C (10 min).
[b] In SME-X, 'X' designates biodiesel fuel producer; 16:0 = hexadecanoate; 18:0 = octadecanoate; 18:1 = oleate; 18:2 = linoleate; 18:3 = linolenate.
[c] 0.3% eicosanoate (20:0) for SME-A; 3.0% tetradecanoate for SME-B; trace (<0.1%) 20:0 for SME-C.

RESULTS AND DISCUSSION

Earlier work by Thompson *et al.* (14), Bondioli *et al.* (15), and du Plessis *et al.* (16,17) examined effects of long-term storage on fuel quality of biodiesel. These studies concluded that degradation can increase AV, PV, ν, anisidine value, UV absorption, and density (SG) for storage temperatures as low as 30°C. Results varied depending upon characteristics of the container, presence or absence of light, presence or absence of air, and treatment with an oxidation inhibitor (antioxidant). Test methods employed in these studies were designed to deliver results under realistic conditions. Consequently, these storage studies were conducted over very long time periods (90 d to 2 yr).

It is advantageous to develop an easy and timely means to measure effects of oxidation on fuel properties of biodiesel. The present work examines the approach of determining effects of oxidation of biodiesel under controlled accelerated conditions (that is, elevated temperature and continuous air purge) on ν, AV, PV, SG, and cold flow properties (CP and PP). Advantages of treating SME with antioxidants were also investigated.

Effects of reaction time and temperature on ν at 40°C. Figure 1 is a graph of ν vs. time (t) data for oxidation of SME-D at reaction temperatures (T) of 50, 75, and 100°C. These data show that under conditions of this study, within $t = 6$ h oxidation of 200 mL of biodiesel significantly increased ν without exceeding the maximum limit of 6.0 mm^2/s specified by PS121 (13). Subsequent analysis of effects of oxidation on fuel properties was conducted with respect to a maximal reaction time of 6 h.

Examination of Figure 2 provides some insight into the kinetics of oxidation of 200 mL SME-D at $T = 100$°C under conditions of this study. Least-squares regression analysis (excluding the outlier at $t = 24$ h) yielded the line drawn through the data and represented by the following equation:

$$\ln[\nu_{Rel}] = 0.01 + 0.03258(t) \qquad [1]$$

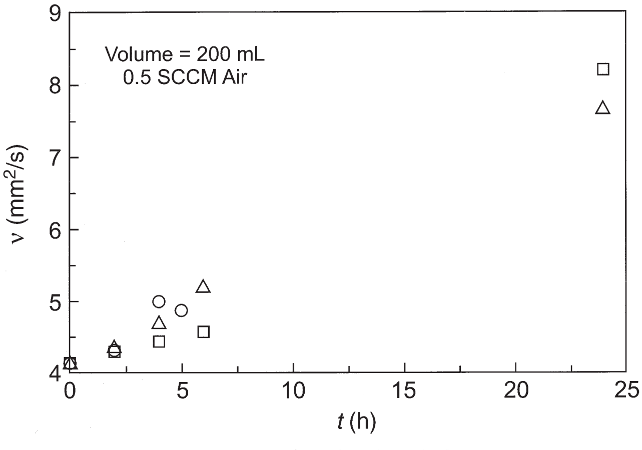

FIG. 1. Kinematic viscosity (ν) of oxidized methyl soyate esters (SME-D) at 40°C vs. reaction time (t). Reaction temperatures = 50°C (□); 75°C (○); 100°C (△). SCCM, standard cm^3/min.

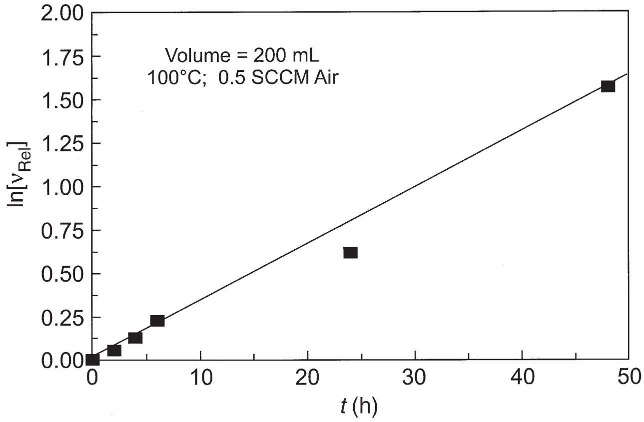

FIG. 2. Relative viscosity (ν_{Rel}) of oxidized SME-D vs. *t*. ν_{Rel} = ratio of viscosity of oxidized SME-D to that of nonoxidized esters (ν_0 = 4.1 mm^2/s at t = 0). See Figure 1 for abbreviations.

$$\nu_{Rel} = \nu/\nu_0 \qquad [2]$$

where ν_{Rel} = relative viscosity and ν_0 = viscosity before oxidation = 4.1 mm^2/s. For Equation 1, R^2 = 0.999, and the standard error of the *y*-estimate (σ_y) = 0.021. Including the outlier in the analysis reduced R^2 to 0.98. Similar analyses yielded the following results (not shown graphically):

$$\ln[\nu_{Rel}] = 0.001 + 0.01746(t) \qquad [3]$$

where R^2 = 0.9999 and σ_y = 0.0039 for oxidation at T = 50°C; and

$$\ln[\nu_{Rel}] = 0.03 + 0.02596(t) \qquad [4]$$

where R^2 = 0.994 and σ_y = 0.043 at T = 75°C. These results indicate that oxidation of SME-D follows first-order reaction reaction kinetics for $t \leq 48$ h, under conditions of this study.

Figure 3 is a plot of ν vs. reaction temperature for oxidation of 100 and 200 mL of SME-D (t = 6 h). After oxidation at T = 50°C, ν = 4.3 mm^2/s (100 mL) and 4.2 mm^2/s (200 mL). These results were within ± 0.2 mm^2/s of ν_0 measured before oxidation; therefore, it may be speculated that very little change in ν would be expected for oxidation at T below 50°C for air flow rate = 0.5 SCCM and t = 6 h.

On the other hand, following similar oxidation at T equal to or exceeding 75°C, ν increased significantly. Furthermore, smaller sample volumes showed a higher degree of increase in ν. This was likely caused by a larger initial quantity of oxygen and its rate of replacement from the air-purge relative to fatty material on a molar basis during the reaction for the smaller volume samples. Only the 100-mL sample oxidized at T = 50°C remained within the limits for ν (1.0–6.0 mm^2/s) specified in PS121 (13).

Effects of reaction temperature on fuel properties of SME. A comparison of ν data measured before and after oxidation of 100 mL of SME-A, SME-B, SME-C, and SME-D at T = 75 and 125°C is shown in Table 2. Analogous to data in Figure 3, ν consistently increased with increasing T. In addition, regardless of temperature, all oxidized samples gave ν values that exceeded the aforementioned PS121 maximum limit (6.0 mm^2/s).

Figure 4 is a graph of AV vs. reaction temperature for oxidation of 100 mL of SME-D at t = 6 h. Prior to oxidation, AV equaled 0.16 mg KOH/g oil (Table 2). These data indicate that increasing T from 50 to 150°C results in a nearly linear increase in AV. Least-squares regression (omitting the outlier at 100°C) yielded the following expression:

$$\mathrm{AV} = -1.68 + 0.03832(T) \qquad [5]$$

where AV is in mg KOH/g oil, T is in °C, R^2 = 0.999, and σ_y = 0.053. Including the outlier in the regression analysis reduced R^2 to 0.98.

Given that Equation 2 predicts a zero AV-value at T = 43.8°C, it may be inferred that oxidation of SME-D at T less than 44°C (0.5 SCCM air-purge and t = 6 h) will not result in a significant increase in AV. Furthermore, under these conditions Equation 2 suggests that oxidation will not drive AV of SME-D above the maximum limit (0.80 mg KOH/g oil) specified in PS121 (13) for T less than 64.7°C.

A comparison of AV data measured before and after oxidation of SME-A, SME-B, SME-C, and SME-D at T = 75 and

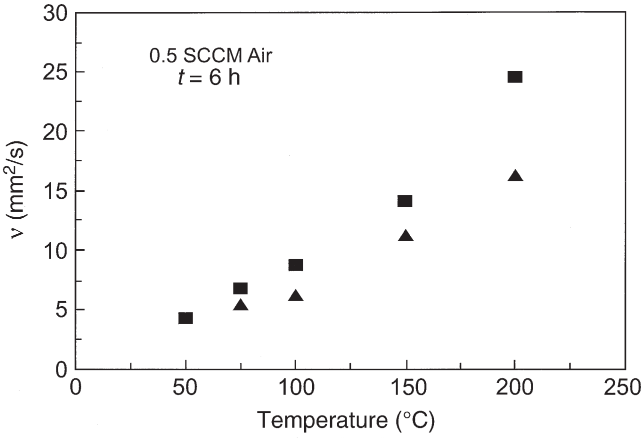

FIG. 3. Kinematic viscosity (ν) of oxidized SME-D at 40°C vs. reaction temperature (T). Volume = 100 mL (■); 200 mL (▲). See Figure 1 for abbreviations.

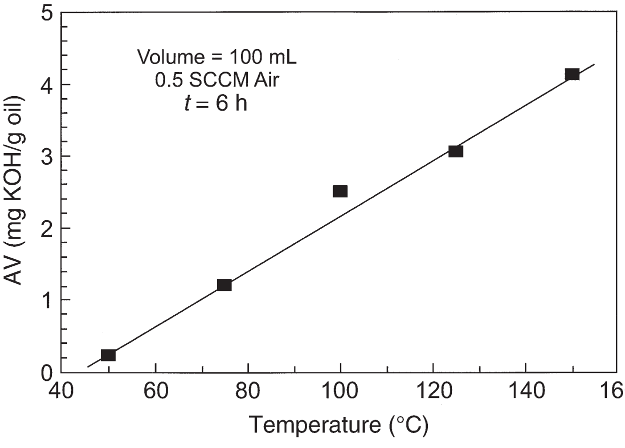

FIG. 4. Acid value (AV) of oxidized SME-D vs. reaction temperature (T). See Figure 1 for abbreviations.

TABLE 2
Kinetic Viscosity [ν (40°C)], Acid Value (AV), and Peroxide Value (PV) of SME Before (t = 0) and After Oxidation at 75 and 125°C[a]

		ν (mm^2/s)			AV (mg KOH/g oil)			PV (meq/kg oil)		
Ester	Antioxidant[b]	t = 0	75°C	125°C	t = 0	75°C	125°C	t = 0	75°C	125°C
SME-A	None	4.4	6.9	11.3	0.65	1.61	4.22	5.9	13.4	9.7
SME-B	None	4.4	6.4	10.3	0.69	1.47	4.11	16.7	20.2	6.5
SME-C	None	5.2	7.1	11.6	0.58	1.52	4.56	28.2	9.4	7.8
SME-D	None	4.1	6.8	11.1	0.16	1.21	3.05	57.0	18.2	10.3
SME-D	TBHQ	4.3	4.3	8.6	0.26	0.36	3.89	30.8	33.2	33.1
SME-D	α-Tocopherol	4.3	6.5	10.2	0.20	1.05	4.44	36.1	38.4	36.1

[a] Purge gas = air at 0.5 SCCM (cc/min at 25°C, 1 atm); volume = 100 mL; reaction time (t) = 6 h; see Table 1 for other abbreviations.
[b] Loading = 2000 ppm.

125°C is shown in Table 2. Analogous to the data in Figure 4, AV consistently increased with increasing T. Also, regardless of temperature, all oxidized samples gave AV results that exceeded the aforementioned PS121 limit (0.80 mg KOH/g).

Figure 5 is a graph of PV vs. reaction temperature for oxidation of SME-D under conditions identical to those for Figure 4. Least-squares regression gave the following equation:

$$PV = 28.5 - 0.1451T \qquad [6]$$

where PV is in meq/kg oil, T is in °C, $R^2 = 0.994$, and $\sigma_y = 0.62$. In contrast to AV results, PV decreases linearly with respect to increasing T, approaching zero near T = 196°C.

A comparison of PV data measured before and after oxidation of SME-A, SME-B, SME-C, and SME-D at T = 75 and 125°C is shown in Table 2. Verifying results shown in Figure 5, PV consistently decreased with increasing T from 75 to 125°C. At T = 75°C, PV for SME-A and SME-B increased following oxidation, where values for SME-C and SME-D decreased. At T = 125°C, only SME-A showed an increase in PV following oxidation.

During initial stages in the oxidation of fatty derivatives, primary products such as hydroperoxides increase in concentration, causing PV to increase. These stages are defined collectively as the induction period. Following the induction period, decomposition of the hydroperoxides yields a mixture of secondary products including short-chain carboxylic acids, ketones, epoxides, and mono- and dihydroxy compounds (12). Eventually, the rate of disappearance of hydroperoxides exceeds formation, causing PV to decrease from a maximum. This phenomenon was observed previously for SME (26), methyl esters of palm olein (27), and various alkyl esters of safflower oil (28).

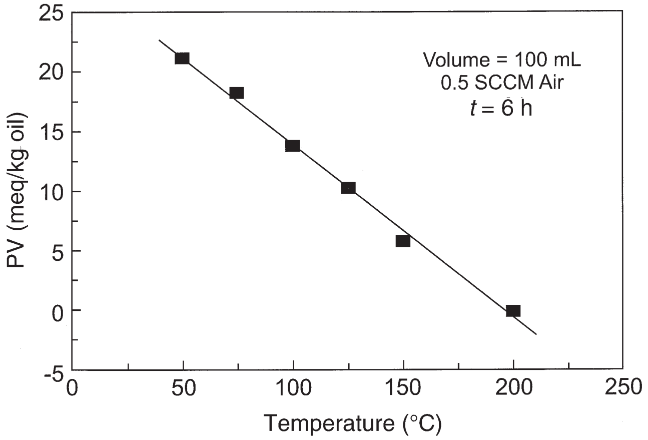

FIG. 5. PV of oxidized SME-D vs. reaction temperature (T). See Figure 1 for abbreviations.

Another condition that affects formation and decomposition of hydroperoxides is the relative availability of oxygen. Canakci *et al.* (29) reported that for oxidation of SME at 60°C for 6 h, increasing oxygen flow rate from 0.26E-06 to 1.8E-06 kg/s increased PV. Apparently, increasing oxygen flow rate increased the quantity of available oxygen for reaction. Similar responses were reported for ν and AV data.

It is likely that the air flow rate of 0.5 SCCM (= 9.9E-08 kg/s) translated into a low rate of replacement of oxygen relative to its consumption during the reaction. Thus, under conditions of this study it is possible that formation of hydroperoxides was retarded, keeping PV low. Second, once the induction period expired, formation of secondary products decreased PV.

Another implication of a relatively low rate of oxygen replacement is an increased likelihood that thermal decomposition predominates during the reaction. Thermal degradation can result in increased ν and AV, while increases in PV generally depends on the presence of oxygen. PV data from this work showed that, although thermal degradation is more prominent at higher temperatures, oxidative degradation is significant for SME-A and -B at T up to 75°C.

Bondioli *et al.* (15) studied oxidative stability of rapeseed oil FAME and reported that storage temperature strongly influenced the path of oxidation. Aging of the esters under relatively mild conditions (40°C, darkness, glass containers) did not affect fuel quality with respect to CP, PP, ν, flash point, SG, or cold filter plugging point. CP and PP data measured before and after oxidation of SME-A, SME-B, SME-C, and SME-D at T = 75 and 125°C (Table 3) agree with these conclusions.

Although not all results are shown in Table 3, oxidation of SME-D at T in the range 50–150°C yielded mean values for CP of 0 ± 1.7°C and PP of −0.4 ± 0.55°C. In contrast, oxidation of SME-D at T = 200°C decreased CP to −10°C and PP to −12°C, values that deviated significantly from correspond-

TABLE 3
Specific Gravity and Cold Flow Properties of SME Before and After Oxidation at 75 and 125°C[a]

		SG[c]		CP (°C)			PP (°C)		
Ester	Antioxidant[b]	$t = 0$	75°C	$t = 0$	75°C	125°C	$t = 0$	75°C	125°C
SME-A	None	0.8884	0.9107	–1	–1	3	–2	–2	2
SME-B	None	0.8871	0.9044	1	0	2	–1	–1	1
SME-C	None	0.8962	0.9134	–2	–2	2	–4	–2	2
SME-D	None	0.8813	0.9111	0	–1	1	–2	–1	–1
SME-D	TBHQ	0.8875	0.8875	–2	–3	–1	–2	–2	–1
SME-D	α-tocopherol	0.8879	0.9082	–2	–2	0	–2	–2	0

[a] Reaction conditions same as for Table 2. CP = cloud point; PP = pour point; SG = specific gravity; see Table 1 for other abbreviations.
[b] Loading = 2000 ppm.
[c] At 15.6°C relative to distilled water at 15.6°C.

ing results at lower temperatures. Apparently, oxidation at 200°C caused decomposition into products with low m.p., such as those with lower M.W. or an increased degree of branching in their molecular structure.

In contrast to cold flow property results, oxidation generally increased SG of SME (Table 3). For SME-A, SME-B, SME-C, and SME-D, the mean SG value before oxidation was 0.887 ± 0.0065. Although the increase in SG after oxidation at $T = 75$°C was statistically significant ($P < 0.03$ for SME-C) for all four samples, the average increase was relatively small (0.0217). On the other hand, oxidation of SME-D at $T = 50$°C (not shown in Table 3) resulted in no significant increase in SG (0.8889, $P = 0.44$ for equivalent means).

Effect of antioxidants on oxidation of SME. Results from oxidation of SME-D treated with 2000 ppm of antioxidants TBHQ and α-tocopherol are shown in Tables 2 and 3. At $T = 75$°C, oxidation of 100 mL of SME-D + TBHQ did not result in ν or AV values exceeding corresponding maximal fuel specifications (6.0 mm^2/s; 0.80 mg KOH/g) with respect to PS121 (13). Although α-tocopherol was effective in reducing effects of oxidation on ν and AV, oxidation at $T = 75$°C increased both parameters slightly in excess of the aforementioned PS121 specifications. PV, CP, PP, and SG results showed very little deviation before or after oxidation regardless of T.

These results showed that oxidation of 100 mL of SME-D + TBHQ at $T = 75$°C likely did not exceed its induction period. Although less likely, oxidation of SME-D + α-tocopherol at the same T may not have exceeded its induction period even though both ν and AV were outside of the aforementioned PS121 limits.

The results also showed an increase in PV with increasing T, implying that available oxygen was sufficient given the relatively low rate of hydroperoxide formation expected for SME-D treated with antioxidants.

Monitoring of oxidative stability during storage. Periodic monitoring of biodiesel during storage may be necessary to ensure effects of autoxidation do not compromise fuel quality. Although the results reported in this work were for oxidation at $T = 50$°C and higher, they may be useful in determining which parameters have the best prospects for development of methods for monitoring biodiesel fuel quality under realistic storage conditions. The following four recommendations should be examined more thoroughly in future studies.

(i) Both ν and AV showed the greatest potential in terms of timely and relative ease of measurement. Either of these parameters should provide insight to determine whether storage conditions are adequate or need to be upgraded. Either parameter should also provide quantitative information on status of the fuel before its oxidation induction period has expired.

(ii) SG may also be useful. However, changes in SG measured at 15.6°C before and after reaction were relatively small under the conditions of this study.

(iii) CP and PP are not useful for evaluating the nature of the fuel before its induction period has expired. They may be useful once the fuel begins to exhibit extensive thermal degradation.

(iv) During storage, availability of unreacted oxygen is an important condition. It is likely that fuel kept in very full, sealed storage containers will have longer induction periods.

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REFERENCES

1. Masjuki, H.J., A.M. Zaki, and S.M. Sapuan, Methyl Ester of Palm Oil as an Alternative Diesel Fuel, in *Fuels for Automotive and Industrial Diesel Engines: Proceedings of the 2nd Institute of Mechanical Engineering Seminar*, Institute of Mechanical Engineering, London, 1993, pp. 129–137.
2. Peterson, C.L., R.A. Korus, P.G. Mora, and J.P. Madsen, Fumigation with Propane and Transesterification Effects on Injector Coking with Vegetable Oils, *Trans. ASAE 30*:28–35 (1987).
3. Schwab, A.W., M.O. Bagby, and B. Freedman, Preparation and Properties of Diesel Fuels from Vegetable Oils, *Fuel 66*:1372–1378 (1987).
4. Clark, S.J., L. Wagner, M.D. Schrock, and P.G. Piennaar, Methyl and Ethyl Soybean Esters as Renewable Fuels for Diesel Engines, *J. Am. Oil Chem. Soc. 61*:1632–1638 (1984).
5. Van Gerpen, J.H., S. Soylu, and M.E. Tat, Evaluation of the Lubricity of Soybean Oil-Based Additives in Diesel Fuel, *Proceedings, Annual International Meeting of the ASAE*, American

Society of Agricultural Engineers, St. Joseph, MI, 1996, paper no. 996134.

6. Sheehan, J., V. Camobreco, J. Duffield, M. Graboski, and H. Shapouri, in *Final Report, Life Cycle Inventory of Biodiesel and Petroleum Diesel for Use in an Urban Bus*, NREL-SR-580-24089, National Renewable Energy Laboratory, Golden, CO, 1998, pp. 206–261.
7. Knothe, G., R.O. Dunn, and M.O. Bagby, Biodiesel: The Use of Vegetable Oils and Their Derivatives as Alternative Diesel Fuels, in *Fuels and Chemicals from Biomass*, American Chemical Society Symposium Series No. 666, edited by B.C. Saha and J. Woodward, American Chemical Society, Washington, DC, 1997, pp. 172–208.
8. Krahl, J., A. Münack, M. Bahadir, L. Schumacher, and N. Elser, Survey About Biodiesel Exhaust Emissions and Their Environmental Benefits, in *Proceedings, Third Liquid Fuel Conference: Liquid Fuel and Industrial Products from Renewable Resources*, edited by J.S. Cundiff, E.E. Gavett, C. Hansen, C. Peterson, M.A. Sanderson, H. Shapouri, and D.L. VanDyne, American Society of Agricultural Engineers, St. Joseph, MI, 1996, pp. 136–148.
9. Krahl, J., J. Bünger, H.-E. Jeberien, K. Prieger, C. Schütt, A. Münack, and M. Bahadir, Analysis of Biodiesel Exhaust Emissions and Determination of Environmental and Health Effects, in *Ibid.,* pp. 149–165.
10. Scholl, K.W., and S.C. Sorenson, Combustion of Soybean Oil Methyl Ester in a Direct Injection Diesel Engine, in *Soc. Automot. Eng. Spec. Publ. SP-958: New Developments in Alternative Fuels and Gasolines for SI and CI Engines* (Paper No. 930936), Society of Automotive Engineers, Warrendale, PA, 1993, pp. 211–223.
11. Mittelbach, M., P. Tritthart, and H. Junek, Diesel Fuel Derived from Vegetable Oils, II: Emission Tests Using Rape Oil Methyl Ester, *Energy Agric. 4*:207–215 (1985).
12. Gunstone, F.D., Chemical Properties of Fatty Acids and Their Esters, in *An Introduction to the Chemistry and Biochemistry of Fatty Acids and Their Glycerides*, 2nd edn., Chapman & Hall Ltd., London, 1967, pp. 105–114.
13. ASTM PS121, Provisional Specification for Biodiesel Fuel (B100) Blend Stock for Distillate Fuels, in *Annual Book of ASTM Standards*, American Society for Testing and Materials, West Conshohocken, PA, 2000.
14. Thompson, J.C., C.L. Peterson, D.L. Reece, and S.M. Beck, Two-Year Storage Study with Methyl and Ethyl Esters of Rapeseed, *Trans. ASAE 41*:931–939 (1998).
15. Bondioli, P., A. Gasparoli, A. Lanzani, E. Fedeli, S. Veronese, and M. Sala, Storage Stability of Biodiesel, *J. Am. Oil Chem. Soc. 72*:699–702 (1995).
16. Du Plessis, L.M., J.B. M. de Villiers, and W.H. Van der Walt, Stability Studies on Methyl and Ethyl Fatty Acid Esters of Sunflowerseed Oil, *Ibid. 62*:748–752 (1985).
17. Du Plessis, L.M., and J.B.M. de Villiers, Stability Studies on Methyl and Ethyl Esters of Sunflower Seed Oil, in *Vegetable Oil as Diesel Fuel Seminar III*, edited by M.O. Bagby and E.H. Pryde, USDA Northern Regional Research Center, Peoria, 1983, pp. 57–62.
18. Van Gerpen, J.H., Cetane Number Testing of Biodiesel, in *Proceedings, Third Liquid Fuel Conference: Liquid Fuel and Industrial Products from Renewable Resources*, edited by J.S. Cundiff, E.E. Gavett, C. Hansen, C. Peterson, M.A. Sanderson, H. Shapouri, and D.L. VanDyne, American Society of Agricultural Engineers, St. Joseph, MI, 1996, pp. 197–206.
19. Clothier, P.Q.E., B.D. Aguda, A. Moise, and H. Pritchard, How Do Diesel-Fuel Ignition Improvers Work? *Chem. Soc. Rev. 22*:101–108 (1993).
20. Stavinoha, L.L., and S. Howell, Potential Analytical Methods for Stability Testing of Biodiesel and Biodiesel Blends, in *Soc. Automot. Eng. Spec. Publ. SP-1482: Alternative Fuels 1999*, Society of Automotive Engineers, Warrendale, PA, 1999, pp. 79–83.
21. Stavinoha, L.L., *Report, Oxidative and Thermal Stability Testing Methods for Biodiesel: Summary Overview*, Southwest Research Institute, San Antonio, TX, 1998, pp. 1–4.
22. Dunn, R.O., and M.O. Bagby, Low-Temperature Properties of Triglyceride-Based Diesel Fuels: Transesterified Methyl Esters and Petroleum Middle Distillate/Ester Blends, *J. Am. Oil Chem. Soc. 72*:895–904 (1995).
23. AACC 58-15, Free Fatty Acids, in *Approved Methods of the American Association of Cereal Chemists, Vol. 2*, 9th edn., American Association of Cereal Chemists, St. Paul, MN, 1995.
24. AOCS Cd 8-53, Peroxide Value, in *Official Methods and Practices of the American Oil Chemists' Society*, 3rd edn., American Oil Chemists' Society, Champaign, IL, 1974.
25. AOCS Cc 10a-25, Specific Gravity of Oils and Liquid Fats, *Ibid.*
26. Monyem, A., M. Canakci, and J.H. Van Gerpen, Investigation of Biodiesel Thermal Stability under Simulated In-Use Conditions, *Proceedings, Annual International Meeting of the ASAE*, American Society of Agricultural Engineers, St. Joseph, MI, 1999, Paper No. 996112.
27. Gan, L.H., K.S. Ooi, L.M. Gan, and S.H. Goh, Effects of Epoxidation on the Thermal Oxidative Stabilities of Fatty Acid Esters Derived from Palm Olein, *J. Am. Oil Chem. Soc. 72*:439–442 (1995).
28. Miyashita, K., and T. Takagi, Autoxidation Rates of Various Esters of Safflower Oil and Linoleic Acid, *Ibid. 65*:1156–1158 (1988).
29. Canakci, M., A. Monyem, and J. Van Gerpen, Accelerated Oxidation Process in Biodiesel, *Trans. ASAE 42*:1565–1572 (1999).

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