

ANALYSIS OF OXIDATIVE STABILITY OF METHYL SOYATE BY PRESSURIZED-DIFFERENTIAL SCANNING CALORIMETRY

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ABSTRACT. Biodiesel, an alternative diesel fuel that may be derived from soybean oil, is composed of long-chain saturated and unsaturated fatty acid alkyl esters. Extensive oxidative degradation can compromise viscosity, acid value, peroxide value, and other parameters in the current ASTM biodiesel fuel guideline. This work examines pressurized-differential scanning calorimetry (P-DSC) for analysis of oxidative stability of biodiesel. Heating scans were conducted under static air-atmosphere with 5°C/min ramping. Increasing pressure from 1000 to 5000 kPa did not significantly affect results and 2000 kPa was selected for the remainder of this study. Curves were analyzed for oxidation temperature (OT) of methyl soyate samples from four separate sources. With respect to unmodified methyl soyate, addition of antioxidants increased OT from 108.4-127.2°C to 137.2-163.4°C. Mixtures with added tert.-butylhydroquinone consistently gave higher OT values than those with $\pm\alpha$ -tocopherol; therefore, P-DSC may be useful for screening antioxidants. Although P-DSC results were consistent with corresponding oil stability index (OSI) data measured at 50°C, no correlation for predicting OSI directly from OT results was evident, with the possible exception of unmodified methyl soyate. This work establishes P-DSC as an analytical tool in evaluating the oxidative stability of biodiesel with and without antioxidants.

Keywords. Antioxidants, Biodiesel, Oil stability index, Oxidation temperature, Pressurized-differential scanning calorimetry.

Biodiesel (mono-alkyl esters of fatty acids derived from agricultural lipids) is an ideal alternative fuel or extender for compression-ignition engines. Lately, the effects of oxidation during storage on the fuel properties of biodiesel has drawn increased attention. To avoid start-up and operability problems in cold weather, biodiesel must contain a relatively high concentration of low-melting point compounds. For most practical feedstocks, this means high concentrations of unsaturated long chain (C₁₈) fatty esters. Unsaturated organic compounds are significantly more prone to oxidation than saturated compounds with the same chain length. In addition, polyunsaturated compounds are many times more reactive than monounsaturated compounds. For example, methyl linoleate is 12-20 times more reactive than methyl oleate (Gunstone, 1967) meaning that methyl soyate, the most studied form of biodiesel in the U.S., is likely to be prone to autoxidation (oxidation caused by contact with atmospheric oxygen) during long-term storage.

Autoxidation may be an important factor in determining fuel quality. Acid value (AV) and kinematic viscosity (ν), two parameters specified in the American Society for Testing and Materials (ASTM) provisional standard for

biodiesel (Howell, 1997), can increase significantly as a result of autoxidation. Extensive degradation during storage could increase either of these parameters to exceed their ASTM-specified maximum (AV = 0.80 mg KOH/g oil; ν = 6.0 mm²/s at 40°C) and drive the fuel outside of specification.

du Plessis et al. (1983; 1985) studied effects of long-term (90 d) storage of methyl and ethyl esters of sunflowerseed oil under various conditions including the presence or exclusion of air, temperature, light, contact with mild steel, and antioxidants. Results showed that AV, peroxide value (PV), ν , UV-absorption, and anisidine value increased while induction period decreased significantly when samples were in contact with air at 30°C or warmer. On the other hand, storage with exclusion of air retarded oxidation at temperatures up to 50°C. Mild steel (rust free) containers did not accelerate oxidation and addition of an antioxidant (TBHQ) had beneficial effects. Bondioli et al. (1995) conducted similar studies with methyl esters of rapeseed oil and determined that the path of oxidation was strongly influenced by characteristics of the storage container as well as temperature. That work showed that aging of the esters in glass containers at 40°C did not affect fuel quality with respect to ν , cetane number, specific gravity, flash point, cloud point, pour point or cold filter plugging point.

Oxidative stability is not formally a fuel specification parameter in the aforementioned ASTM biodiesel provisional standard largely because its cumulative effects on engine performance and emissions can be difficult to quantify. However, the effects of autoxidation on ASTM-specified fuel quality parameters necessitates development of approaches to increase resistance to oxidation. The first operational step to meet this long term objective is development of a testing protocol to rapidly and accurately

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evaluate the effects of these approaches, preferably under accelerated conditions, on the oxidative stability of biodiesel.

Stavinoha (1998a, 1999) reviewed existing test methods that might be applied, directly or in modified form, to the evaluation of thermal and oxidative stability of biodiesel and biodiesel/middle distillate blends. Test methods were categorized according to the following temperature ranges: (1) 0° to 50°C, for simulating conditions within fuel tanks and storage facilities; (2) 60 to 80°C, for fuel system stability; and (3) up to 150°C, for thermal stability in fuel injectors and near the engine. The reviews recommended modified methods ASTM D2274 and D4625 because they allow testing effects of storage conditions on acid number, potential peroxide and formation of insoluble gums and sediments that may clog fuel lines and filters. Method ASTM D525 was also recommended for measurement of oxidation induction period because results correlate well with analogous tests popular in the fats and vegetable oils industry.

Stavinoha (1998b) also reviewed application of thermal analyses such as thermogravimetric analysis and differential scanning calorimetry (DSC) as procedures for accelerated oil stability tests. Most of these reports were for analysis of fats and oils (triglycerides); thus, some test method conditions such as relatively high temperatures may not be appropriate.

Recently, a pressurized-DSC (P-DSC) based test method (ASTM D5483) for measuring oxidation induction time (OIT) was developed for application to lubricating oils. Increasing pressure in the DSC cell has at least two benefits, suppression of pressure-sensitive reactions (e.g., volatilization) and acceleration of sample-atmosphere reactions including oxidation. Hassel (1976) demonstrated that P-DSC analysis of five vegetable oils [120°C, 500 psig (3450 kPa), O₂ purge] yielded good correlations with results predicted by active oxygen method (AOM) in minutes instead of days.

The work herein explores the suitability of P-DSC as an accelerated oxidation stability test method for biodiesel. Methyl soyate samples from four separate sources and with varying histories were analyzed under static conditions (zero air purge). Results were optimized with respect to effect of pressure (1000-5000 kPa) and compared with corresponding oil stability index (OSI) measurements at atmospheric pressure. Finally, P-DSC was evaluated as an accelerated test method for determining the effects of α -tocopherol and *tert*-butylhydroquinone (TBHQ) antioxidants on the stability of methyl soyate.

MATERIALS AND METHODS

Methyl soyate samples with various histories were obtained from four different manufacturers. Products and vendor identities are not disclosed to remove bias from presentation of results. Three of the products, SME-A, SME-B and SME-C were from ADEPT (Los Angeles, Calif.) and SME-D from the National Biodiesel Board (Jefferson City, Mo.). Results from gas chromatographic analysis of these materials are presented in table 1. The α -tocopherol (95%) was from Aldrich (Milwaukee, Wis.); *tert*-butylhydroquinone (TBHQ, 97%) was from Sigma (St.

Table 1. Gas chromatographic (GC) analysis of methyl soyate samples* (concentrations are in wt %)

Sample	16:0	18:0	18:1	18:2	18:3	Other†
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	—

* SME-X = methyl soyate from manufacturer 'X'; 16:0 = palmitate; 18:0 = stearate; 18:1 = oleate; 18:2 = linoleate; 18:3 = linolenate.

† Other includes 0.3% eicosanoate (20:0) for SME-A; 3.0% myristate for SME-B; and trace (< 0.1%) 20:0 for SME-C.

Louis, Mo.). Mixtures containing antioxidants were treated with 2,000 ppm loading.

P-DSC analyses were conducted with a TA Instruments (New Castle, Del.) DSC 2910 cell base fitted with a HP 2910 high-pressure (maximum 7 MPa) DSC cell. A TA model 3100 PC-based controller was employed for data acquisition and analysis. High-pressure DSC analyses were conducted in "batch" mode; that is, following pressurization with air the cell was sealed off and its contents scanned in static (zero purge) air. For each scan, 2 to 3 mg of sample was hermetically sealed in an aluminum pan and tested against an identical empty pan. Pan covers were punched with a pin-hole (diameter ~ 0.5 mm) to allow continuous contact between sample and air in the cell and to "restrict diffusion" of volatiles (Keller and Saba, 1998). Preliminary studies indicated that onset temperatures from scans with restricted-diffusion type pans were nearly identical to those made with open solid fat index (SFI)-type pans and that use of SFI-type pans caused varnish deposits inside the cell. After sealing sample and reference pans in the cell, "dirty" air was purged at slightly above atmospheric pressure before pressurization. Following pressurization, cell contents were equilibrated at 25°C, then ramped at 5°/min to 175°C. During each scan, hot air was bled off by a spring-loaded purge valve to maintain constant pressure. Following depressurization, the cell was purged a second time with cool, fresh air then allowed to cool down at atmospheric pressure. Results from each scan were analyzed for oxidation onset temperature (OT). The OT data presented in this work are means from replicate scans conducted on at least three fresh samples.

Oil Stability Index (OSI) measurements were conducted on an oxidative stability instrument from Omnion Inc. (Rockland, Massachusetts) under license from Archer Daniels Midland (Decatur, Illinois). Prior to measurement, samples were vacuum-distilled to remove volatiles that may interfere with analysis in a Kugelrohr apparatus from Aldrich. The OSI values were inferred by extrapolation of onset time (h) using a modified AOCS method Cd 12b-92 described elsewhere (Dunn, 1997). The OSI results presented in this work are means from replicates conducted on two fresh samples.

Gas chromatographic analyses of methyl soyate samples were performed on a Perkin-Elmer (Norwalk, Connecticut) Autosystem GC with a 25 m \times 0.32 mm ID BPX70 column from SGE (Austin, Texas). These analysis were conducted under the following temperature program: (1) hold at 50°C for 5 min; (2) ramp at 10°/min to 250°C; (3) hold at 250°C for 10 min.

RESULTS AND DISCUSSION

P-DSC ANALYSES

Figure 1 is a plot overlaying P-DSC results for unmodified SME-D, SME-D + 2000 ppm Tocopherol and SME-D + 2000 ppm TBHQ at 2000 kPa pressure. Heat flows were offset on the y-axis to distinguish between individual curves.

Effects of evaporation, indicated by tailing, split peaks and a change in baseline due to loss of sample mass were observed for some samples. However, these effects were apparent at temperatures higher than that of the initial oxidation peak and did not interfere with measurement of OT values by extrapolation of peak onset temperatures. For the curves in figure 1, mean OT values were 126°C for unmodified SME-D, 146.2°C for SME + Tocopherol and 157.76°C for SME-D + TBHQ. Variances (σ^2) were in the range 0.0061 to 1.4.

Figure 2 is a plot of results from P-DSC scans of SME-D with and without antioxidants at four pressures, 1000, 2000, 3500 and 5000 kPa (145, 290, 508 and 725 psig). These results show that resistance to oxidation with respect to increasing sample temperature at 5°C/min is not a

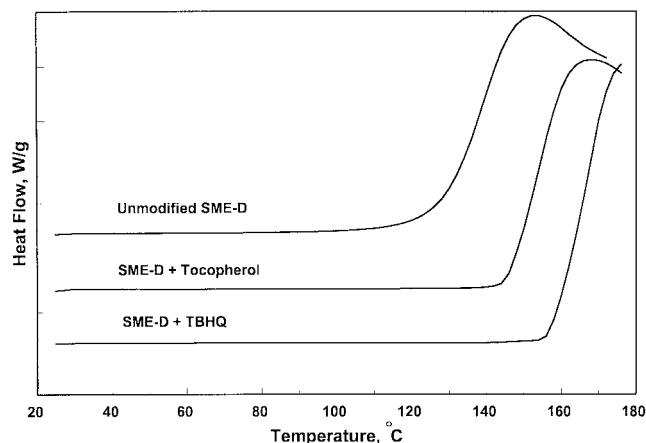


Figure 1—Heating scans from pressurized-differential scanning calorimetry (P-DSC) analyses of methyl soyate sample SME-D with and without added antioxidants (2000 ppm). Pressure = 2000 kPa; Ramp = 5°C/min. Tocopherol = $\pm\alpha$ -tocopherol; TBHQ = *tert*-butylhydroquinone.

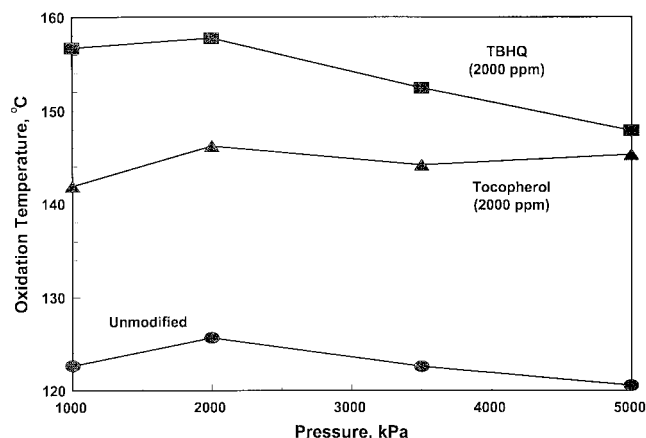


Figure 2—Effect of P-DSC cell pressure on oxidation temperature (OT) of SME-D with and without added antioxidants. Ramp = 5°C/min. See figure 1 for abbreviations.

strong function of pressure. A slight maximum was observed near 2000 kPa for each curve. Pressures less than 5000 kPa may be preferable because σ^2 values increased at higher pressures for mixtures with added antioxidants (from 1.4 to 2.2 for SME-D + Tocopherol and from 0.88 to 6.3 for SME-D + TBHQ). In addition, higher pressures tended to narrow the separation between OT values for Tocopherol and TBHQ. Although a pressure of 2000 kPa was selected for follow-up analyses, these results indicate 3500 kPa would be equally suitable.

Figure 3 is a bar-graph comparing results for the four methyl soyates with and without added antioxidant, at pressure = 2000 kPa. These data gave σ^2 values in the range 0.0061 to 1.4. Adding 2000 ppm of either antioxidant substantially increases OT with respect to unmodified methyl soyate mixtures. TBHQ was consistently superior to Tocopherol with respect to increasing resistance to oxidation; however, P-DSC results showed that the magnitude of the increase in OT between TBHQ and was significantly less than that between Tocopherol and the corresponding unmodified methyl soyate.

Statistical comparison of the results in figure 3 showed the following trends for unmodified methyl soyates, in descending order:

$$\text{SME-B} > \text{SME-D} \approx \text{SME-A} > \text{SME-C}$$

where ' \approx ' indicates the hypothesis of equivalent means is acceptable with respect to probability (P) = 0.11. For mixtures with added Tocopherol:

$$\text{SME-A} > \text{SME-B} > \text{SME-D} > \text{SME-C}$$

and for mixtures with TBHQ:

$$\text{SME-A} > \text{SME-B} \approx \text{SME-D} (P = 0.38) > \text{SME-C}$$

Although results for mixtures with added antioxidants were consistent with respect to each other, they are not consistent with respect to unmodified mixtures. Thus, the magnitude of increase in resistance to oxidation due to

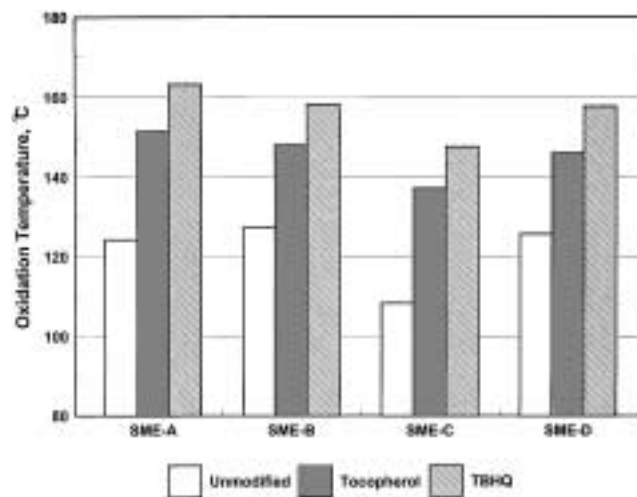


Figure 3—OT results for methyl soyate samples SME-A, SME-B, SME-C, and SME-D with and without added antioxidants (2000 ppm). Pressure = 2000 kPa; Ramp = 5°C/min. See figures 1 and 2 for abbreviations.

addition of antioxidant is not proportional the relative resistance of a given unmodified methyl soyate mixture. Apparently, the presence of antioxidant alters the reaction pathways relative to those for unmodified methyl esters. This was evident given the change in the shape of the heating scans (fig. 1) in the onset region from a broad, slow transition for unmodified SME-D to a sharper transition for mixtures with added antioxidant.

OXIDATIVE STABILITY INSTRUMENT ANALYSES

Figure 4 is a plot overlaying oxidative stability instrument results for unmodified SME-D and SME-D + 2000 ppm added Tocopherol at 50°C and atmospheric pressure. The downward shift in the Tocopherol curve at ~98 h was a dilution effect caused by adding fresh distilled water to prevent exposing the conductivity probe to air due to evaporation. The OSI parameters were determined by extrapolation of onset time for each conductivity curve. For the two mixtures shown in figure 4, mean OSI values were 12.9 and 177.2 h with corresponding σ^2 values of 0.25 and 9.1.

Figure 5 is a bar-graph comparing OSI results at 50°C for all four methyl soyate products with and without added antioxidant. These results gave σ^2 values in the range 5.0E-05 to 9.1 and tended to increase with OSI. Curves for SME-A and SME-D with added TBHQ showed no onset time, indicating that OSI of these two mixtures exceeds 500 h under the conditions measured. Analogous to P-DSC results, adding 2000 ppm of either antioxidant increases OSI with respect to unmodified methyl soyate and adding TBHQ was consistently more effective than Tocopherol. However, the magnitude of the increase in OSI between added antioxidants Tocopherol and TBHQ generally exceeded that between unmodified esters and added Tocopherol. Obviously, TBHQ was more significantly affected by increasing temperatures during P-DSC analysis than Tocopherol, with respect to improving resistance to oxidation. In other words, although Tocopherol was less effective than TBHQ, its relative effectiveness was also less temperature dependent.

Statistical comparison of the results in figure 5 showed the following trends for unmodified methyl soyates, in descending order:

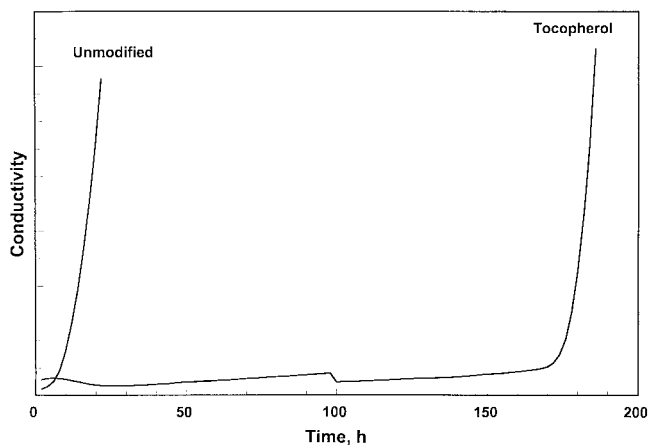


Figure 4—Conductivity versus time curves from oxidative stability instrument analyses of unmodified SME-D and SME-D + 2000 ppm α -tocopherol. Block temperature = 50°C.

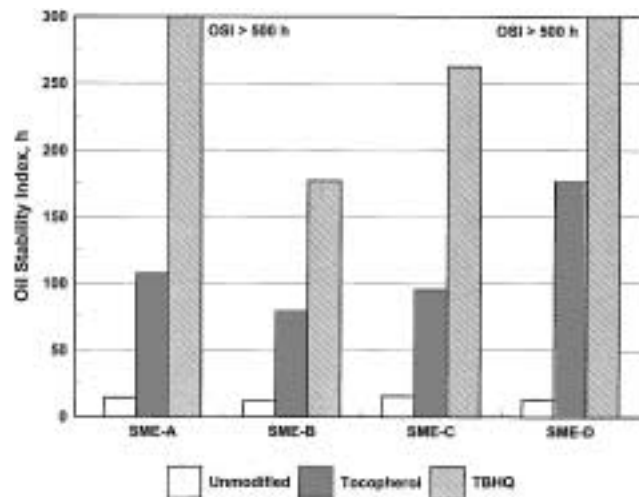


Figure 5—Oil stability index (OSI) results for methyl soyate samples SME-A, SME-B, SME-C, and SME-D with and without added antioxidants (2000 ppm). Block temperature = 50°C. Tocopherol = α -tocopherol. See figure 1 for abbreviations.

$$\text{SME-C} > \text{SME-A} > \text{SME-D} \approx \text{SME-B} \quad (P = 0.18)$$

For methyl soyate mixtures with added Tocopherol:

$$\text{SME-D} > \text{SME-A} > \text{SME-C} > \text{SME-B}$$

and for mixtures with added TBHQ:

$$\text{SME-A, SME-D} > \text{SME-C} > \text{SME-B}$$

where OSI > 500 h for SME-A and SME-D treated with TBHQ. Results for mixtures with added Tocopherol were consistent with those for added TBHQ; however, results for added antioxidants were not consistent with those for unmodified mixtures. Thus, the magnitude of increase in resistance to oxidation due to addition of antioxidant is not proportional to the relative resistance of a given unmodified methyl soyate mixture. These results were analogous to those for P-DSC analyses with the exception that the OSI were measured under nearly isothermal conditions. This suggests that the effects of antioxidants on oxidation reaction pathways of methyl soyate are not solely dependent on temperature.

Finally, from the point of view of this work, initial tocopherol and other natural antioxidant concentrations and other factors that are relevant to methyl soyate's oxidative stability prior to addition of Tocopherol or TBHQ were viewed as part of the "varying history" of the samples prior to experimentation. Nevertheless, the relatively large disparities between OSI results for samples with and without added antioxidant suggest that initial concentrations of natural antioxidants was nearly zero.

CORRELATION OF OSI AND OT RESULTS

In general, resistance to oxidation as measured by induction period is inversely related to both temperature and pressure, with temperature being the predominant factor. Litwinienko et al. (1999), studied the autoxidation of long chain fatty acids and ethyl fatty acid esters and reported that an Arrhenius relationship may be used to

correlate induction periods with respect to results from non-isothermal DSC results. This study also showed that activation energy (E_a) may be determined from non-isothermal DSC results. This suggested that an Arrhenius equation may be tested for predicting induction period (OSI) from non-isothermal P-DSC data (OT).

Neglecting effects of pressure on induction period, the following equation was tested:

$$\text{OSI} = A_0 \times \exp\{(E_a/R) \times (1/OT)\} \quad (1)$$

where

A_0 = constant
 R = universal gas constant
 OT is in K.

If equation 1 is rewritten as:

$$\ln[\text{OSI}] = A_1 + B/OT \quad (2)$$

where

$A_1 = \ln[A_0]$
 $B = E_a/R$

then a plot of $\ln[\text{OSI}]$ versus $1/OT$ that produces a straight line will have intercept equal to A_1 and slope equal to B .

Figure 6 is a plot of $\ln[\text{OSI}]$ versus $1/OT$. Nearly linear behavior was observed for unmodified methyl soyate and least squares regression analysis yielded the following:

$$\ln[\text{OSI}] = -1.63 + 1670/OT \quad (3)$$

for the line drawn through the data. Equation 3 had a regression coefficient (R^2) = 0.572, a value that gave a relatively low probability (0.16) supporting a linear correlation. However, the standard error of the y-estimate (σ_y) = 0.074; that is, equation 3 may be employed to estimate OSI to ± 1.1 h. Only one methyl soyate sample (SME-A) had a confidence interval for OSI that was less than ± 1.1 h, with respect to ± 0.05 level of significance. Finally, Litwinienko et al. (1999) reported E_a values of 106 to 128 kJ/mol for saturated ethyl stearate. Even taking into account reduction for unsaturated and polyunsaturated hydrocarbon chains, the value inferred from the slope of

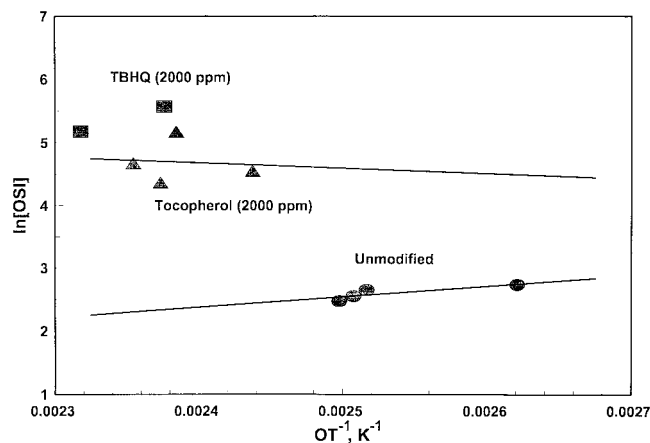


Figure 6—Correlation of OSI and OT results with respect to Arrhenius-type equation: $\ln[\text{OSI}] = A_1 + B/OT$, where A_1 and B are constants and OT is in K. See figures 1, 2 and 5 for abbreviations.

equation 3 for unmodified methyl soyate ($E_a = 13.9$ kJ/mol) appears to be underestimated.

The regression line from analysis of methyl soyate + 2000 ppm Tocopherol mixtures is also shown in figure 6. These results predicted a negative slope ($E_a < 0$), a conclusion that was counterintuitive and may be attributable to scatter predominantly in the OSI data. Methyl soyate + 2000 ppm TBHQ mixtures lacked the degrees of freedom for regression analysis.

Overall, there is little evidence to support the notion that induction period (OSI) may be reliably predicted from OT results. Obviously, varying oxidation reaction pathways when increasing temperature during measurement of OT may produce unpredictable results for a given methyl soyate mixture. On the other hand, variances between (raw) replicate OSI measurements tended to increase significantly as OSI increased to very high values such as those observed for mixtures with added antioxidants. Unmodified methyl soyates gave relatively low OSI values (< 16 h) whose σ^2 values were also low (0.0025-0.18); therefore, these mixtures yielded a correlation that can estimate OSI within 1.1 h directly from OT data.

CONCLUSIONS

1. Pressurized-DSC is a rapid and accurate technique for measuring OT and other parameters that can correlate oxidation reaction and oxidation stability of methyl soyate.
2. Pressurized-DSC results were generally consistent with those from oxidative stability instrument measurements. Methyl soyate mixtures with added antioxidants were more resistant to oxidation than unmodified mixtures while TBHQ was more effective than $\pm\alpha$ -tocopherol.
3. Pressurized-DSC results obtained with temperature ramping (OT values) showed very little probability of reliable correlation with OSI. One possible exception was noted for unmodified methyl soyate, whose OSI may be estimated within 1.1 h directly from OT.
4. Pressurized-DSC results may be an efficient tool for screening antioxidants. Although OT data showed a smaller increase between TBHQ and $\pm\alpha$ -tocopherol treated methyl soyate than corresponding OSI data, the increase was significant and results consistent for testing the relative effectiveness of antioxidants rapidly.
5. Continued development of P-DSC based techniques for measuring oxidative stability of biodiesel should explore scans under isothermal conditions, air/oxygen purge gas (dynamic mode) and open SFI-type pans. Data reported in this work (OT measured in static mode) will be useful in estimating temperatures and other parameters for future isothermal studies.
6. Oxidative stability instrument conditions should be modified for more accurate evaluation of induction periods for biodiesel-antioxidant mixtures. Results reported in this work indicate that obtaining reproducibility increases in difficulty as OSI increases. Although increasing temperature is the most likely solution for accelerating the reaction,

increasing temperature may also alter pathways so that the results will not correlate with oxidative stability measurements under non-accelerated conditions.

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