

Oxidative Stability Measurement of High-Stability Oils by Pressure Differential Scanning Calorimeter (PDSC)

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High-stability oils are used as coatings on food products that require long shelf life. The high stability oils produced from high-oleic oils require less processing and bring additional nutritional benefits such as lower *trans* and saturated fat contents. Accurate and reproducible oxidative stability measurement of these oils is necessary to assess the performance. The accelerated oxidative stability measurement method often used in the fats and oils industry, the oxidative stability index (OSI, AOCS Cd 12b-92) is unreliable for higher stability oils due to poor reproducibility. This study presents a pressure differential scanning calorimetry (PDSC) method, which is highly reproducible and versatile and applies to oils from low to very high oxidative stability. PDSC has been used in industrial applications such as lubricants (ASTM D 6186-98) and measures the oxidative induction time (OIT) of oils under high temperature and pressure in the presence of pure oxygen. The OITs of a number of hydrogenated oils with different unsaturation and oxidative stability are measured. Unlike OSI data, the PDSC OIT measurement is highly reproducible and precise and requires only a small sample and a couple of hours. The regression analysis of the PDSC data indicated the natural log OIT of all samples linearly correlated with the temperature. The equation derived from this relationship helps to compare the oxidative stabilities of the same or different oils determined at different temperatures. The development of this method into an approved method will benefit the fats/oils and food industry.

KEYWORDS: Oxidative stability; high-stability oils; high-oleic oils; soybean oil; cottonseed oil; canola oil; fractionation; pressure differential scanning calorimetry (PDSC); oxidative induction time (OIT); active oxygen method (AOM); oil stability index (OSI)

Traditional high-stability oils are produced from commodity oils such as soybean and cottonseed that are relatively inexpensive. These starting oils, due to their low oxidative stability, require elaborate processing including hydrogenation and fractionation. Recently, Lampert reviewed the production, use, and applications of high-stability oils (1). High-stability oils are liquid at ambient temperature and used as moisture barriers, flavor carriers, lubrication or release agents, antioxidant or anticake agents, gloss enhancers, and viscosity modifiers. Recently, a number of vegetable oils with modified fatty acid compositions, especially high-oleic acid content, produced by breeding and or mutagenesis (non-GMO) have been commercialized (2). These new oils possess greater oxidative stability and offer an alternative source of high-stability oils. Due to a higher percentage of oleic acid, these oils require less processing to provide higher oxidative stability with relatively low *trans* and saturated fatty acid contents. In light of the recent U.S. FDA regulations to include the *trans* fat content on food product labels, oils having higher oxidative stability with low *trans* and saturates have become more important (3).

In our development of high-stability oils from high-oleic oils, the oil stability index (OSI) instrument was used extensively (AOCS Cd 12b-92) to measure the oxidative stability (4). The commercial high-stability oils are sold on the basis of their degree of oxidative stability expressed as active oxygen method (AOM) hours. The old AOCS official method to measure the oxidative stability by AOM has been replaced by the OSI procedure (5). The OSI instrument has a provision to calculate the AOM hours from the OSI time (6). The use of the OSI posed considerable difficulties in measuring the oxidative stability of high-stability oils, such as inordinately long times required to obtain results, water evaporation due to long run times, and contamination of glassware and tubes. For these reasons, the applicability of a relatively new method by pressure differential scanning calorimeter (ASTM D6186-98) for fats and oils in general and high-stability oils in particular was investigated (7). PDSC measures the oxidative induction time (OIT) of the oil under high temperature and pressure in pure oxygen. This method has been previously used to measure the oxidative stability of fats and oils and mineral oil derived materials (8–14). It was used to analyze the oxidative stability of soy methyl esters and various vegetable oils for industrial applications (11, 12). Tan et al. did a comparative study of OSI and OIT of edible

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oils and found a good correlation between the two methods (13). These authors also found that the rates of lipid oxidation were highly correlated with temperature (14). The earlier studies used nonstandardized PDSC test procedures for industrial applications. Also, the correlation of temperature and rate of oxidation obtained was limited to a given oil. In this study a standardized ASTM procedure previously applied in industrial applications was followed. The regression analysis of the data correlated the temperature with OIT, yielding a single equation applicable to all oils.

This paper briefly discusses the production of high-stability oils from conventional oils and high-oleic oils and their uses and advantages in food products. This study presents data that show the inadequacy of the OSI method to measure the oxidative stability of higher stability oils. The primary objective of this study is to measure the oxidative stability of fats and oils by PDSC and to assess its suitability and advantages over the OSI method.

MATERIALS AND METHODS

Conventional oils (soybean, cottonseed, canola, and sunflower) were obtained from Cargill, Inc. All vegetable oils used in this study were refined and bleached (RB) or refined, bleached, and deodorized (RBD). High-oleic canola oils CV-65, CV-75, and CV-85 used in this study were obtained from Cargill Specialty Canola Oils. Hydrogenated oils were produced by hydrogenation of RB oil with nickel catalyst (N-545, used at 0.13 wt %) obtained from Engelhard (Jackson, MS). The laboratory-scale hydrogenations were done in a Parr reactor (model 4563, Parr Instrument Co., Moline, IL) under 35 psig of hydrogen pressure at 155 °C. The hydrogenations were carried out to the desired iodine value by monitoring the refractive index. The catalyst was removed by filtration through filter aid after the reaction products had cooled to ~50 °C. The commercially hydrogenated oil samples were obtained from Cargill plants and were produced under similar hydrogenation conditions.

The oxidative stabilities expressed as AOM hours of various oils reported in this study were measured on an OSI instrument according to the AOCS method (AOCS Cd 12b-92) at 110 °C. The OSI times thus obtained were converted to AOM hours (6). The PDSC OIT measurements were made on TA Instruments (New Castle, DE) model DSC 2920. The standard PDSC OIT measurements were made according to ASTM method D 6186-98 (7). PDSC has been used to evaluate vegetable oils (8). In the past decade this method was evaluated and standardized for the oxidative stability measurement of vegetable oils and hydraulic fluids (9, 10). In this method a small sample (~3 mg) was placed in an open pan in a test cell, whereas an empty pan served as a reference. The sample is heated to a set temperature and held isothermally under 500 psi of pure oxygen atmosphere until an exothermic reaction occurred. The amount of time taken to initiate oxidation of the sample (shown as an inflection of heat flow from the baseline) was expressed as OIT, in minutes. The OIT is measured as the intersection of the extrapolated baseline and a line tangent to the oxidation exotherm constructed at its maximum rate. All OIT data presented in this study are mean values of duplicate samples.

The data were subjected to standard regression analysis using the SAS statistical package (SAS, Cary, NC). The correlation between temperature and OIT was determined. Best-fit equations were calculated for slopes, and the correlation coefficient, R^2 , was calculated for each correlation. The relationship between the Ln OIT and the temperature, and the prediction of OIT for a given temperature from the experimental OIT determined at a specific temperature, was determined from the best-fit equations.

RESULTS AND DISCUSSION

Traditionally, high-stability oils are produced from conventional oils by partial hydrogenation. The fatty acid composition and the oxidative stability of conventional oils are shown in

Table 1. Approximate Fatty Acid Composition (Weight Percent) and Oxidative Stability of Conventional and High-Oleic Oils (3)

oil type	saturates	C18:1	C18:2	C18:3	AOM (h)
soybean	15	23	55	7	12
cottonseed	27	19	53	1	15
sunflower	10	20	70	0	12
canola	7	62	22	10	12
high-oleic sunflower	9	81	10	0	60
mid-oleic canola	7	76	12	5	40
high-oleic canola	6	85	5	4	70

Table 1 (3). Due to their high oxidative susceptibility, these oils are not used in high-performance food products. The ease of oxidation depends on the fatty acid composition and the nature and concentration of antioxidants present in the oil. The rate of oxidation depends on the degree of unsaturation. The oxidative susceptibility increases exponentially from an allylic methylene to a bis-allylic methylene present between two double bonds in polyunsaturated fatty acids (15). This is supported by bond dissociation energies of carbon hydrogen bonds in a saturated aliphatic methylene, an allylic methylene, and a doubly allylic methylene, which are 96, 85, and 76 kcal/mol, respectively.

Because of their high polyunsaturated fatty acid content (>30%), conventional oils require severe hydrogenation to achieve high oxidative stability, resulting in high *trans* and saturates contents. Optimally, high-stability oils can be produced by converting all of the polyunsaturated into monounsaturated fatty acids while minimizing the *trans* formation. The resulting fat is fractionated by pressure filtration (dry fractionation) into solid and liquid fractions (16). One of the new developments in vegetable oils in the past decade is the ability to alter the fatty acid composition of oilseeds through advanced plant breeding and/or mutagenesis (2). The polyunsaturated fatty acid content in the high-oleic oils is dramatically reduced while oleic acid content is increased (**Table 1**). Consequently, the oxidative stability of these oils is 3–6 times that of conventional oils. The high-oleic oils produced through biotechnology provide an alternate source for high-stability oils. Due to their inherent higher oxidative stability, many high-oleic oils with >75% oleic acid content can be used as they are or with added antioxidant for low-range high-stability oil applications. However, the production of higher stability oils from high-oleic oils requires both hydrogenation and fractionation.

There are a number of processing and functional advantages for the production of high-stability oils from high-oleic oils. The process is simple and may not require hydrogenation and/or fractionation. The reduced level of processing would result in lower color and bland taste. Additionally, the high-stability oils made from high-oleic oils have nutritional advantages such as lower *trans* and saturates contents than traditional high-stability oils. Because of the lower *trans* and saturates contents and the lower level of use, the high-stability oils made from high-oleic oil may facilitate a “clean” label for many food products (3). The accurate and reproducible measurement of oxidative stability is essential to develop these oils. While developing the high-stability oils, we explored the oxidative stability measurement method by OSI and found it to be unsatisfactory due to poor reproducibility. This is mainly due to the prolonged test time required to measure the oxidative stabilities of high-stability oils.

Recently, Shahidi and Zhong reviewed the oxidative stability measurement methods (17). The original oxidative stability measurement by active oxygen method (AOM) measures the

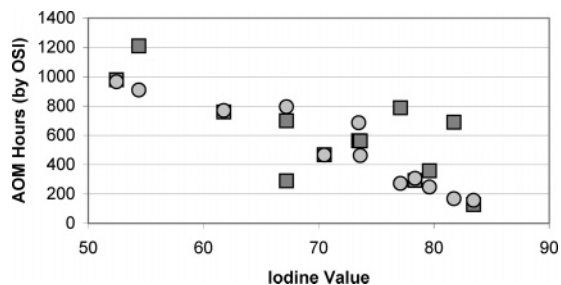


Figure 1. AOM hours from OSI plotted against iodine value of different samples. These measurements were made on duplicate/triplicate samples (as shown in circles and squares) to show the variation in reproducibility.

amount of time required for a sample to reach a peroxide value of 100 when kept at 97.8 °C (5). This method became obsolete and was replaced by the OSI method (6). In OSI, the oil is heated to a set temperature, air is blown through the oil, and the oxidative affluent is collected in water while the conductivity of the water is measured with time. This method has been tested and successfully used by a number of researchers (18–20). Accelerated oxidation methods are useful to predict the oxidative stability and shelf life. However, the results from these methods do not necessarily have one-to-one correlation with the ambient temperature storage due to the differences in rate-limiting conditions.

The OSI results obtained for hydrogenated oils measured in duplicate (one triplicate measurement) are presented in **Figure 1**. The duplicate sample measurements of a given material are shown with a circle and a square to distinguish the difference. The AOM hours of some of the duplicate samples agreed very well, but others varied by as much as hundreds of hours. The OSI results may be reproduced and correlate reasonably well between laboratories at low AOM values (<100 AOM h), but they cannot be reproduced reliably for very high stability oils. The AOCS method indicates that the OSI results are most reliable when measurement times are in the range of 4–24 h (6). Another concern is that the OSI measurements of these very high stability oils take days to weeks. These long run times invariably result in other problems such as loss of water in the conductivity cells and temperature and air flow fluctuations. The OSI method specified that the inordinate amount of time taken by the higher stability oils can be reduced by increasing the run temperature. However, in our experience the results obtained at different temperatures did not correlate well. For example, the AOM values obtained at 110 °C differed from the values obtained at 130 °C by 50 h, and the lower values were obtained for the samples run at 130 °C. Other problems with this method include the need to maintain conductivity meters, keeping tubing and sample tubes from contamination, and difficulties in keeping the air flow rate constant.

The OSI times measured for a number of hydrogenated samples of similar iodine values are plotted in **Figure 2**. The variation in OSI values increased for hydrogenated oils having lower iodine values. These data indicate greater difficulty in measuring the oxidative stability of higher stability oils requiring long run times. All of the samples used in these tests were hydrogenated soybean oils from different plant batches. We cannot rule out the possibility that a small part of the variation might result from differences in hydrogenation conditions and the resulting structural differences of these samples with similar iodine values (e.g., variation in bis-allylic methylene content of the materials having the same iodine value).

For the above reasons, the PDSC method was used to evaluate the oxidative stability of various vegetable oils and their

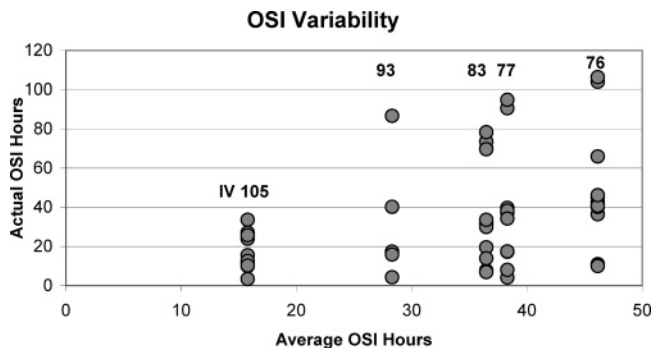


Figure 2. Actual OSI hours of different samples of the same iodine value obtained from different hydrogenation batches plotted against average OSI hours to show increase in variability with decrease in iodine value.

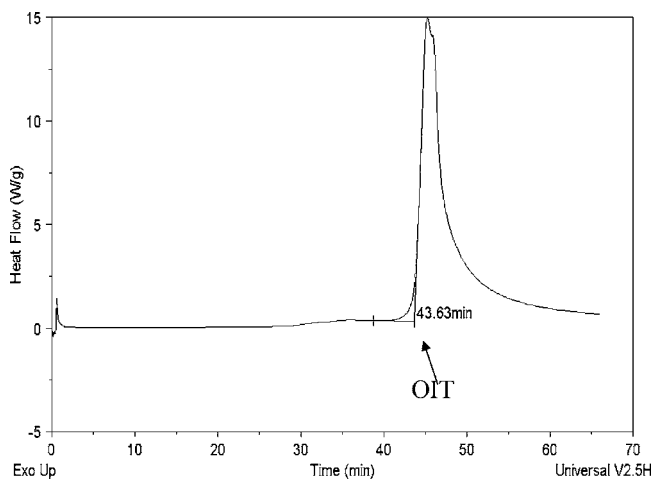


Figure 3. Typical PDSC oxidative stability curve of a sample measured at an isothermal temperature of 180 °C showing the OIT of 43.6 min.

derivatives. PDSC measures the energy release from the oxidation reaction rather than any specific chemical product(s) from oxidation. The amount of time taken to initiate oxidation of the sample (as observed from spurt of energy release as heat flow from the baseline) is measured as the OIT, in minutes. A typical PDSC scan of a sample with OIT measurement is shown in **Figure 3**. The OIT is very sensitive to the experimental conditions (21). One of the advantages of using a pressurized cell at elevated temperatures is to minimize the loss of volatile components, such as antioxidants, by evaporation. Tan et al. did a comparative study of OSI and differential scanning calorimeter OIT of edible oils and found a good correlation between the two methods (13). These authors also found that the rates of lipid oxidation for a given oil were highly correlated with temperature (14). Both the reproducibility and repeatability of the PDSC method are excellent. The OIT variation from the mean value of duplicate samples measured at different temperatures from 130 to 200 °C is ± 2 min. The PDSC OIT of the same sample is highly reproducible for both low- and high-stability oils measured at different temperatures.

The AOM hours determined by OSI are correlated with OIT from PDSC in **Figure 4**. The OIT determined at 130 °C correlated well with the AOM hours determined by OSI ($R^2 = 0.94$). This reconfirms that the OSI method is useful for the oils that have lower oxidative stability. The OSI result reproducibility for the oils having >150 AOM hours was poor and did not correlate well with the PDSC data.

The PDSC natural log OIT of a given sample, measured at different temperatures, correlates linearly with temperature. This relationship for a number of samples recorded at different

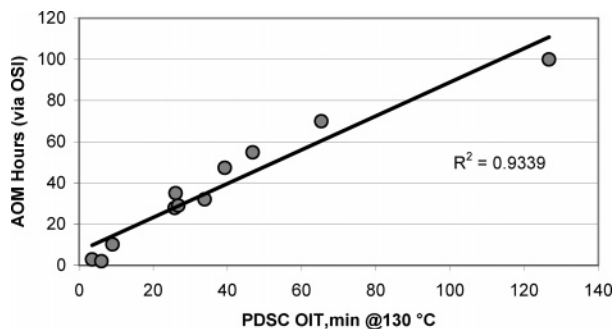


Figure 4. Oxidative stability of different samples AOM hours plotted against PDSC OIT. The AOM hours correlate well with OIT, especially at lower AOM values ($R^2 = 0.94$).

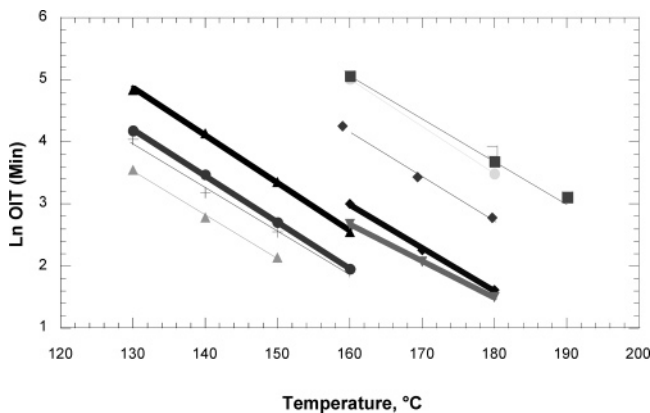


Figure 5. Natural log of PDSC OIT plotted for various samples run at different temperatures. Ln OIT decreases linearly with increased temperature with comparable slopes for all samples studied.

temperatures is shown in **Figure 5**. To relate the sample Ln OIT with the temperatures, the sample temperatures are normalized to a centered temperature, 0. The centered temperature is a mean temperature value of a given sample measured at different temperatures. For example, if the OIT of an oil sample was determined at four different temperatures of 130, 140, 150, and 160 °C, then the normalized centered temperature, 0, would be 145 °C. The expression of data in terms of normalized centered temperature is useful, as the OIT of these samples, irrespective of the temperatures they were measured at, will stack on top of each other to make the comparison easier. The Ln OIT of all samples showed a linear relationship with temperature with statistically comparable slopes as shown in **Figure 6**. A plot of natural log OIT spread with mean centered against the centered temperature of these samples resulted in a linear equation with a slope of 0.075139. This correlation between the Ln OIT and temperature for a number of samples studied is shown in **Figure 7**. The oxidative induction times of all the samples measured at different temperatures have excellent correlation with temperature ($R^2 > 0.99$) and hold good for a variety of fat and oil samples. The equation derived from this relationship is

$$\text{OIT @ } X \text{ } ^\circ\text{C} = \text{OIT @ } Y \text{ } ^\circ\text{C} \times 2.71828^{(-0.071539\Delta^\circ\text{C})}$$

$$\Delta \text{ } ^\circ\text{C} = X - Y$$

where X = desired PDSC temperature and Y = determined PDSC temperature. This equation facilitates the conversion of OIT determined at a temperature Y to any desired temperature X by multiplying the OIT @ Y by base of the natural log(e), 2.71828, raised to the power of the slope multiplied by the

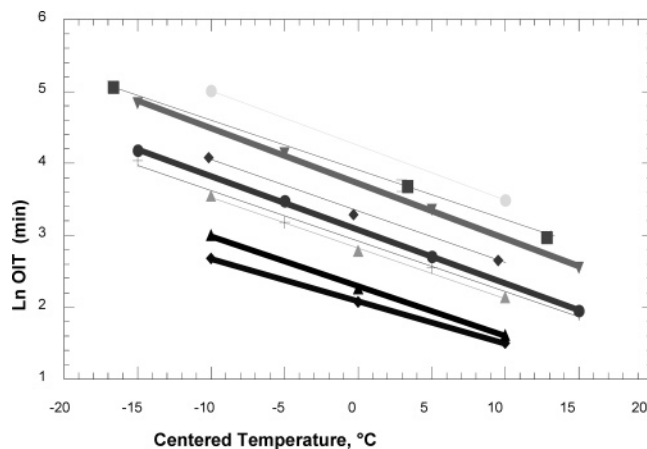


Figure 6. Ln OIT data presented in **Figure 6** plotted against centered temperature. Slopes of different samples are similar and stacked up one over the other at the normalized temperature center of the slope.

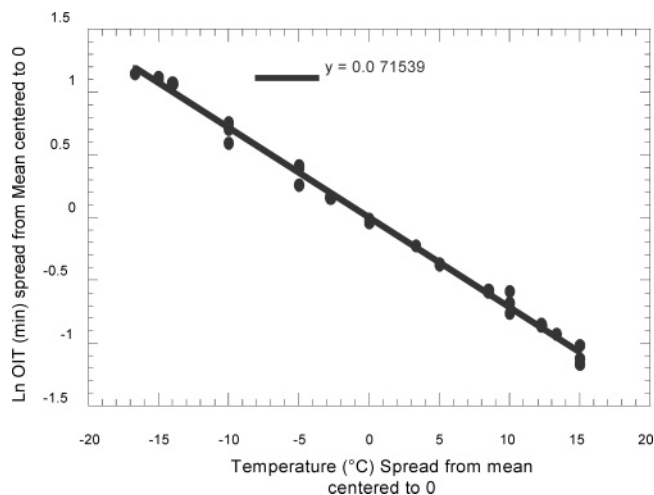


Figure 7. Plot of centered temperature of all samples measured at different temperatures plotted against the centered natural log of PDSC OIT. This plot shows the linear relationship between the temperature and Ln OIT with an excellent correlation ($R^2 = 0.9946$), and the slope of the line is 0.071539/°C.

difference in temperature between the desired and determined temperatures. The real advantage of this method is that the oxidative stability measured as OIT at any given temperature can be converted to any other temperature for comparison purposes.

The oxidative stability measurement method by PDSC requires a smaller sample size and only a couple of hours instead of many days it takes for other methods. In this method, the OIT measured at different temperatures of the same sample or different samples can be correlated. This convertibility of OIT times from determined to desired temperature is very useful to compare the same sample run at different temperatures by different laboratories and also to compare the low oxidative stability materials with very high stability materials. This method is very useful in screening the effectiveness of antioxidant formulations and, possibly, resulting food products. This method is reliable, applies to all stability ranges, and can be run at low (from 130 °C) to high temperature (210 °C). Adaptation of this method by the fats/oils and food industries will greatly enhance the efficiency and reliability of oxidative stability measurement while reducing the cost and time.

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LITERATURE CITED

- (1) Lampert, D. High Stability Oils: What Are They? How Are They Made? Why Do We Need Them? In *Physical Properties of Fats, Oils and Emulsifiers*; Widlak, N., Ed.; AOCS Press: Champaign, IL, 1999.
- (2) Loh, W. Biotechnology and Vegetable Oils: First Generation Products in the Market Place. In *Physical Properties of Fats, Oils and Emulsifiers*; Widlak, N., Ed.; AOCS Press: Champaign, IL, 1999.
- (3) Kodali, D. R. *Trans Fats*—Chemistry, Occurrence, Functional Need in Foods and Potential Solutions. In *Trans Fats Alternatives*; Kodali, D. R., List, G. R., Eds.; AOCS Press: Champaign, IL, 2005.
- (4) Kodali, D. R.; DeBonte, L. R.; Fan, Z. High Stability Canola Oils. U.S. Patent 5,885,643, 1999.
- (5) AOCS. *Official Method, Fat Stability, Active Oxygen Method Cd. 1-57*; AOCS: Champaign, IL, 1993.
- (6) AOCS. *Official Method, Oil Stability Index (OSI), Cd. 12b-92*; AOCS: Champaign, IL, 1993.
- (7) ASTM. *D 6186-98 Standard Test Method for Oxidation Induction Time of Lubricating Oils by Pressure Differential Scanning Calorimeter (PDSC)*; American Society for Testing and Materials: Philadelphia, PA, 1998.
- (8) Kowalski, B. Determination of Oxidative Stability of Edible Vegetable Oils by Pressure Differential Scanning Calorimetry. *Thermochim. Acta* **1989**, *156*, 347–358.
- (9) Rhee, I. S. Development of a New Oxidation Stability Test Method for lubricating Oils Using a Pressure Differential Scanning Calorimeter (PDSC). *NLGI Spokesman* **2001**, *65*, 16–23.
- (10) Fox, N. J.; Simpson, A. K.; Stachowiak, G. W. Sealed Capsule Differential Scanning Calorimetry—An Effective Method for Screening the Oxidation Stability of Vegetable Oil Formulations. *Lubrication Eng.* **2001**, *57*, 14–20.
- (11) Dunn, R. O. Analysis of Oxidative Stability of Methyl Soyate by Pressurized Differential Scanning Calorimetry. *Trans. ASAE* **2000**, *43*, 1203–1208.
- (12) Adhvaryu, A.; Erhan, S. Z.; Liu, Z. S.; Perez, J. M. Oxidation Kinetic Studies of Oils Derived from Unmodified and Genetically Modified Vegetables by Using Pressurized Differential Scanning Calorimetry and Nuclear Magnetic Resonance Spectroscopy. *Thermochim. Acta* **2000**, *364*, 87–97.
- (13) Tan, C. P.; Che Man, Y. B.; Selamat, J.; Yusoff, M. S. A. Comparative Studies of Oxidative Stability of Edible Oils by Differential Scanning Calorimetry and Oxidative Stability Index Methods. *Food Chem.* **2002**, *76*, 385–389.
- (14) Tan, C. P.; Che Man, Y. B.; Selamat, J.; Yusoff, M. S. A. Application of Arrhenius Kinetics to Evaluate Oxidative Stability in Vegetable Oils by Isothermal Differential Scanning Calorimetry. *J. Am. Oil Chem. Soc.* **2001**, *78*, 1133–1138.
- (15) Kodali, D. R. Biobased Lubricants: Chemical Modification of Vegetable Oils. *INFORM (Champaign, IL)* **2003**, *14*, 121–123.
- (16) Tirtiaux, A.; Gibon, V. Dry Fractionation: The Boost Goes On. Presented at World Conference and Exhibition on Oilseed and Edible Oils Processing, Istanbul, Turkey, Oct 1996.
- (17) Shahidi, F.; Zhong, Y. Lipid Oxidation: Measurement Methods. In *Bailey's Industrial Oil and Fat Products, 6th ed., Vol. 1. Edible Oil and Fat Products: Chemistry, Properties and Health Effects*; Shahidi, F., Ed.; Wiley: New York, 2005.
- (18) Hill, S. H.; Perkins, E. G. Determination of Oxidation Stability of Soybean Oil with the Oxidative Stability Instrument: Operation Parameter Effects. *J. Am. Oil Chem. Soc.* **1995**, *72*, 741–743.
- (19) Akoh, C. C. Oxidation Stability of Fat Substitutes and Vegetable Oils by the Oxidative Stability Index Method. *J. Am. Oil Chem. Soc.* **1994**, *71*, 211–216.
- (20) Isbell, T. A.; Abbott, T. P.; Carlson, K. D. Oxidative Stability Index of Vegetable Oils in Binary Mixtures with Meadfoam Oil. *Ind. Crops Prod.* **1999**, *9*, 115–123.
- (21) Blaine, R. L.; Lundgren, C. J.; Harris, M. B. *Oxidation Induction Time—A Review of DSC Experimental Effects*; TA Instruments Monograph TA-235: TA Instruments: New Castle, DE.

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