Dependence of Oil Stability Index of Fatty Compounds on Their Structure and Concentration and Presence of Metals

Gerhard Knothe* and Robert O. Dunn

USDA, ARS, NCAUR, Peoria, Illinois 61604

ABSTRACT: During storage and use, vegetable oil-derived industrial products such as biodiesel and biodegradable lubricants can be subjected to conditions that promote oxidation of their unsaturated components. The materials arising during oxidation and subsequent degradation can seriously impair the quality and performance of such products. Therefore, oxidative stability is a significant issue facing these vegetable oil-derived products, and enhanced understanding of the influence of various components of vegetable oils and storage parameters is necessary. In this work, the oil stability index (OSI) was used for assessing oxidation of monoalkyl esters of FA by varying several parameters. Neat fatty compounds and prepared mixtures thereof were studied for assessing the influence of compound structure and concentration. Small amounts of more highly unsaturated compounds had a disproportionately strong effect on oxidative stability. The recently developed concept of bis-allylic equivalents correlated more closely than the iodine value with the OSI times of mixtures of fatty esters. The OSI times of free acids were shorter than those of the corresponding alkyl esters. The presence of copper, iron, and nickel also reduced oxidative stability, but their effect was less than the presence of more highly unsaturated fatty compounds. Of these metals, copper had the strongest catalytic effect on OSI time. OSI may be an alternative to long-term storage tests for determining the influence of extraneous materials such as metals on oxidative stability.

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KEY WORDS: Biodiesel, bis-allylic position equivalent, fatty esters, free fatty acids, iodine value, metals, oil stability index, oxidative stability.

The oxidation of lipids is the subject of intense research (1). During exposure to air, unsaturated fatty compounds especially can form oxygenated species such as hydroperoxides and subsequent degradation products. The FA composition of a fatty material is a major factor influencing oxidation. Generally, the FA composition of products derived from vegetable oils or animal fats corresponds to that of the parent oil or fat. Thus, the oxidation reaction of unsaturated fatty compounds with varying amounts of double bonds affects the quality and utility of fatty materials in diverse areas such as nutrition and industrial applications. Some affected industrial applications are lubricants and biodiesel (monoalkyl, usually methyl, esters of veg-

etable oils or animal fats), a promising alternative fuel for use in compression-ignition (diesel) engines (2,3). The issue of oxidative stability affects biodiesel mainly by contact with air during storage and affects lubricants through contact of the lubricant with hot engine parts accelerating the oxidation process.

The oxidation of fatty materials such as biodiesel is affected by other factors, such as elevated temperature, light, the presence of metals, and other parameters that may accelerate oxidation (4–13). The exhaust emissions of a diesel engine operating on biodiesel are influenced by oxidation of the biodiesel fuel (14–15). Also, the term "oxidative stability" is more general and is distinguished from the term "storage stability" since oxidation may occur not only during storage but also during production and use.

Generally, the rate of oxidation of fatty compounds depends on the number of double bonds and their position (1). The oxidation chain reaction is usually initiated at the positions allylic to double bonds. Thus, FA with methylene-interrupted double bonds, for example, linoleic acid [(9Z,12Z)-octadecadienoic acid], are more susceptible to oxidation because they contain methylene groups that are allylic to two double bonds. FA with two such methylene groups, for example, linolenic acid [(9Z,12Z,15Z)-octadecatrienoic acid], are even more susceptible to oxidation.

A method for assessing oxidative stability is the oil stability index (OSI) (16–19; also frequently termed the "oxidative stability index"). The OSI method is based on determining the time (usually termed "induction time") before the maximum rate change of oxidation by measuring the increase in conductivity of deionized water caused by dry air bubbled through a heated sample that carries the resulting volatile acids into a separate container with the deionized water. The OSI method is considered to be an automated replacement for the active oxygen method (20), for which difficulties were noted in the literature (17). Although problems with the OSI method have been noted (21,22), it yields results that are useful for making semi-quantitative predictions. Other methods that have been studied for assessing oxidative stability include (pressurized-)DSC (23–25) and several others, including wet chemical methods such as the PV (26,27).

This paper investigates the influence of compound structure and concentration of individual fatty compounds as well as the presence of metals on the oxidative stability of fatty compounds using the OSI method. The most common FA esters that occur in vegetable oils and animal fats were investigated.

*To whom correspondence should be addressed at USDA, ARS, NCAUR, 1815 N. University St., Peoria, IL 61604.
E-mail: knothegh@ncaur.usda.gov

Three neat metals—copper, iron, and nickel, commonly found in metal containers—were added to some samples to study the effect of exposure of fatty compounds to them. Methyl oleate (5 g) was selected as the standard fatty compound for oxidation studies.

EXPERIMENTAL PROCEDURES

All FA and esters, including triolein, were obtained from Nu-Chek-Prep, Inc. (Elysian, MN) and were of >99% purity (confirmed by GC–MS analyses of randomly selected samples). Copper, iron, and nickel metals in different specifications were purchased from Aldrich (Milwaukee, WI), used as received, and stored under nitrogen. The amounts of fatty compound and metal used for each experiment are given in Figure 1 and Tables 1–3.

The oxidative stability instrument was manufactured by Omnion (Rockland, MA) under license from Archer Daniels Midland Co. (Decatur, IL). Generally, the procedure of the AOCS OSI Method Cd 12b-92 (16) was followed. The apparatus as described in that method was modified slightly by extending the effluent vent by approximately 20–25 cm using an inverted Pasteur pipette placed in the stopper of the sample tube. This minimized evaporative loss of deionized water used as solvent in the conductance cell. Temperatures (70 and 90°C) were lower than prescribed in the method, and runs were often longer (up to 90 h) than suggested by the method. All OSI values given here were determined as averages of three replicates. Replications were usually carried out during the same run on the OSI instrument, as it can accommodate up to 24 simultaneous samples, but in some cases replicates were carried out in separate runs.

RESULTS AND DISCUSSION

The OSI (16) was selected as a relatively rapid and easy-to-use method for assessing oxidative stability. Some concerns exist, however, about its reproducibility (21,22). Therefore, all sam-
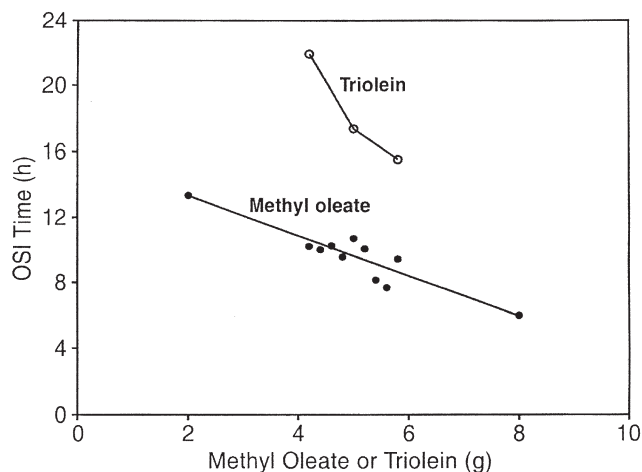

FIG. 1. Oil stability index (OSI) times at 90°C of varying amounts of neat methyl oleate and triolein.

TABLE 1
Oil Stability Index (OSI) Values of Neat Fatty Compounds (5 g) at 70 and 90°C

Compound	OSI value (h)	
	70°C	90°C
Methyl palmitoleate ($C_{16:1}$)	>90	22.06
Methyl petroselinate ($C_{18:1}$, Δ6)	>90	14.86
Oleic acid ($C_{18:1}$, Δ9)	38.82	6.63
Methyl oleate	55.63	10.70
Ethyl oleate	—	10.86
Propyl oleate	—	11.78
Butyl oleate	—	26.1
Triolein	>90	17.40
Methyl vaccenate ($C_{18:1}$, Δ11)	>90	15.86
Linoleic acid ($C_{18:2}$, Δ9, Δ12)	1.82	0.75
Methyl linoleate ($C_{18:2}$)	4.56	1.20
Methyl linolenate ($C_{18:3}$)	5.48	—[a]
Methyl 11-eicosenoate ($C_{20:1}$)	57.22	12.95
Methyl erucate ($C_{22:1}$)	59.46	13.86

[a]No OSI value determinable.

ples were run in triplicate, and averages are reported here. A possible alternative being studied is pressurized DSC (23–25). An OSI method for determining oxidative stability of methyl soyate treated with antioxidants has been reported (23).

The temperature range (100–140°C) prescribed in the OSI method (16) appears to be too high to correlate well with "real-world" storage conditions. Also, OSI values obtained at 110°C reportedly do not correlate with content of unsaturated FA in various fatty materials (17). A relatively low temperature (50°C) has been applied to the OSI method (23). In light of these results, the temperatures selected for the present study were 70 and 90°C. Earlier studies (23) showed that variances

TABLE 2
OSI Values at 90°C of Some Prepared Mixtures (5 g total weight) of Fatty Compounds

Mixture	Components	Wt%	OSI value (h)	IV[a]	BAPE[b]	APE[c]
A	Methyl stearate	10	1.83	111.88	40	180
	Methyl oleate	60				
	Methyl linoleate	20				
	Methyl linolenate	10				
B	Methyl stearate	20	1.53	112	50	160
	Methyl oleate	40				
	Methyl linoleate	30				
	Methyl linolenate	10				
C	Methyl stearate	30	1	120.92	70	140
	Methyl oleate	20				
	Methyl linoleate	30				
	Methyl linolenate	20				
D	Methyl stearate	45	0.55	112.54	75	110
	Methyl oleate	10				
	Methyl linoleate	15				
	Methyl linolenate	30				
E	Methyl stearate	90	3.65	17.24	10	20
	Methyl linoleate	10				

[a]Calculated from Equation 2 in Reference 35.
[b]BAPE = bis-allylic position equivalents. Calculated from Equation 7 in Reference 35.
[c]APE = allylic position equivalents. Calculated from Equation 5 in Reference 35. See Table 1 for other abbreviation.

TABLE 3
OSI Values of 5 g Methyl Oleate at 90°C in the Presence of Metals

Metal	Metal form[a]	Amount of metal (mg)	OSI value (h)
None	—	—	10.70[b]
Cu	150 mesh	10	5.55
Cu	150 mesh	20	5.60
Cu	1 micron	1	4.25
Cu	1 micron	10	3.85
Cu	1 micron	20	3.90
Fe	Filings	10	5.55
Fe	Filings	20	5.55
Fe	<10 micron	1	8.20
Fe	<10 micron	10	9.75
Fe	<10 micron	20	8.90
Ni	3 micron	10	5.60
Ni	3 micron	20	5.60
Ni	Submicron	1	11.40
Ni	Submicron	10	8.90
Ni	Submicron	20	8.8

[a]Information provided by vendor. Term "submicron" for Ni not further defined by vendor. 150 mesh = 106 micron.
[b]Value from Table 1. See Table 1 for abbreviation.

of the OSI times tended to increase with increased OSI times. Therefore, experiments conducted in the present work were terminated after 90 h (23). Results are reported in Tables 1–3 and Figure 1.

Pure compounds or prepared mixtures thereof were studied to better assess the effect of these compounds on oxidation. In "real" mixtures of fatty compounds, these effects are obscured to some degree by their more complex nature, as they are mixtures of numerous fatty compounds and often some other materials.

Influence of structure and amounts of fatty compounds. The OSI method (16) prescribes the use of 5 g of material for one sample. However, the effluent (at constant air flow) generated by the method depends on the concentration of the materials being oxidized, i.e., on the number of double bonds per 5 g sample. Therefore, on a molecular basis, the OSI values of compounds with equal numbers of double bonds per molecule but different M.W. are not directly comparable unless a correction is made for the differing M.W. (this may be seen as a shortcoming of the OSI method). Such corrections may affect the interpretation of oxidative stability studies in general.

With increasing M.W. and a constant number of double bonds per molecule, the "molar" concentration of double bonds decreases, and OSI should therefore increase. Conversely, with decreasing M.W. and a constant number of double bonds, the "molar" concentration of double bonds increases, and OSI should therefore decrease. Two approaches are possible for studying the influence of "molar" concentration of double bonds to obtain the correction for differing M.W. just noted. One is to compare OSI times of pure compounds of different M.W. but identical number of double bonds per molecule. The other is to use the same pure material but to vary the sample amounts beyond the 5 g prescribed in the OSI method since this approach has the same effect as varying the "molar" concentration of double bonds but not the number of double bonds per molecule.

The OSI values of both neat methyl 11-eicosenoate and methyl 13-docosenoate (methyl erucate) were longer than the

OSI value of methyl oleate (Table 1). This confirms the prediction that OSI times are increased when the molar concentration is lower as a result of the higher M.W. of the compounds tested. More pure compounds of similar nature would thus need to be studied to confirm the prediction.

The position of the double bond was shown to play a role in oxidation (28). In that work, the OSI values of several monoene methyl esters deviated substantially from that of methyl oleate at 90°C. Deviations were observed in the present work also, but of lesser magnitude (Table 1) and also sometimes in reverse order compared to the other study (methyl petroselinate had a lower OSI time than methyl oleate in Ref. 28). One possible explanation may be that compounds of high purity (>99%) were investigated in the present work, whereas the materials studied previously (28) contained other components, including small amounts of dienes.

Free acids had lower OSI times than the corresponding esters (Table 1). The presence of a saturated FFA in methyl linoleate reportedly promoted oxidation (29). This result presents another reason for limiting free acids in the specifications of standards for products such as biodiesel.

The influence of varying amounts of neat methyl oleate on OSI times is depicted in Figure 1. The amounts were varied mainly to simulate changes in molar concentration of double bonds with changing M.W., although two samples (2 and 8 g) were chosen to test extreme variations of this kind. Although scatter is recognizable in the range of 4.2–5.8 g sample, a trend toward lower OSI values for greater amounts of compound exists. Least-squares regression analysis for the data in Figure 1 gives Equation 1,

$$OSI = -1.22 \times M + 15.68 \qquad [1]$$

in which OSI is the OSI time and M is the weight of the sample in grams. For this equation, $R^2 = 0.8420$ (corrected for population), and $\sigma_y = 0.7488$ (standard error of the y-estimate). Although the low R^2 indicates nonlinear behavior, scatter in the results for 4.2–5.8 g methyl oleate is the likely cause. Omitting the extreme values of 2 and 8 g, methyl oleate yields Equation 2,

$$OSI = -1.15 \times M + 15.32 \qquad [2]$$

with $R^2 = 0.3013$ and $\sigma_y = 0.8467$. However, the very similar slope and intercept in Equations 1 and 2 strongly suggest that, even in the case of the range 4.2–5.8 g methyl oleate, there is a downward trend in OSI with increasing sample mass. This is due to the aforementioned increase in the molar concentration of double bonds that reduces OSI values, as there are more allylic positions available to react with oxygen.

To study the downward trend of OSI times with increasing sample amount further, three sample weights of triolein were investigated. The triolein samples confirmed the trend toward reduced OSI times for greater amounts of sample. Triolein, the TAG of oleic acid, had an OSI time greater than that of methyl oleate. A reason for the higher OSI times of triolein may be its

higher viscosity compared with methyl oleate, which can affect mass transfer of oxidation products to the air–oil interface, how fast air bubbles traverse the sample, the size of the bubbles, and the rate at which oxygen from the bubbles dissolves into the oil.

To elucidate the effect of M.W., the OSI times of methyl oleate, methyl 11-eicosenoate, and methyl erucate were compared. In this sequence, the OSI times decreased with decreasing chain length. This corresponds to the decrease in OSI with increasing amounts of methyl oleate discussed above, because in both cases the amount of double bonds available for oxidation increases. No statistical evaluation was carried out here, because only a few values were available and they corresponded to the range 4.2–5.8 g methyl oleate. Methyl palmitoleate gave a higher OSI time than the aforementioned three compounds, which may be related to its shorter terminal alkyl chain. The OSI values for methyl, ethyl, propyl, and butyl oleate did not follow a clear trend, which bears further investigation.

The rate of oxidation of fatty compounds depends on the number of double bonds per molecule and their relative location (1,30). The bis-allylic positions in common PUFA, such as linoleic acid (double bonds at $\Delta 9$ and $\Delta 12$, giving one bis-allylic position at C-11) and linolenic acid (double bonds at $\Delta 9$, $\Delta 12$, and $\Delta 15$, giving two bis-allylic positions at C-11 and C-14), are even more prone to oxidation than allylic positions. Indeed, the relative rates of oxidation given in the literature are 1 for oleates (methyl, ethyl esters), 41 for linoleates, and 98 for linolenates (1).

Mixtures of FAME. The results of OSI studies for some mixtures containing varying amounts of the most common FAME are given in Table 2. Mixtures A–D containing four methyl esters ($C_{18:0}$, $C_{18:1}$, $C_{18:2}$, $C_{18:3}$) had iodine values (IV) in the relatively narrow range 112–121. The OSI times for those mixtures were generally of the same magnitude, with the OSI times decreasing with increasing amounts of $C_{18:2}$ and $C_{18:3}$ methyl esters. Note that the increasing amounts of $C_{18:3}$ coincided with increasing amounts of the stable $C_{18:0}$. A mixture of 10% methyl linoleate with 90% methyl stearate (entry E in Table 2) had an OSI value of the same magnitude as that of neat methyl linoleate. Generally, the present results confirmed the observation that small amounts of more highly unsaturated fatty compounds containing bis-allylic carbons have a disproportionately strong effect on oxidative stability. This kind of observation was discussed in early studies on autoxidation of fatty compounds (30). The relation to the IV and an alternative to the IV are discussed below.

Influence of metals. Only methyl oleate was selected for investigating the influence of metals because the more highly unsaturated compounds already had low OSI times. The OSI values of 5 g methyl oleate at 90°C in the presence of elemental copper, iron, and nickel are given in Table 3. Copper had the strongest catalytic effect of the three metals investigated. Other researchers have observed that the PV of biodiesel samples increased more rapidly in a copper container than in a steel container although final values were very similar (6). Since OSI measures induction time, i.e., initial rates of oxidation as men-

tioned in the introduction, it likely compares with the initial stronger increase in PV noted for copper. Peroxides are the species initially formed during oxidation before breakdown and further rapid oxidation occur.

The effect of metal was catalytic, as small amounts of metal had nearly the same influence on OSI as larger amounts. However, the OSI values depended somewhat on the particle size. There may also have been an influence from varying thickness of oxide coatings. The effect of metals was similar to that of more highly unsaturated fatty compounds, although the influence of fatty compounds with bis-allylic carbons was of greater magnitude. The dependence of the OSI time on the kind of metal shows that long-term storage tests in different kinds of containers for assessing the influence of the container material on oxidative stability of biodiesel may be replaced by the significantly faster OSI test serving as an accelerated storage test.

Other methods for assessing oxidative stability of biodiesel have been investigated. The ASTM Method D 2274 (oxidation stability) was not applicable to biodiesel due to unsuitable filters (5). PV also may not be a suitable indicator of biodiesel oxidation because FA with higher unsaturation appear to produce hydroperoxides in lower yields as they are readily decomposed (especially in the presence of contaminating catalysts). As a result, analyses measuring hydroperoxides show decreasing rates with increasing numbers of double bonds (1). Furthermore, the PV increases to a maximum and then decreases as secondary products are formed (5,31,32). Recent studies (23–25,33) demonstrated that the oxidative stability of fatty materials, including long-chain monoalkyl esters, may be determined by pressurized-DSC (P-DSC). Temperature-ramping calorimetric analyses may be completed rapidly and require only very small sample quantities (typically less than 100 mg). Calorimetric analyses also may be used to determine activation energies and other kinetic parameters for the oxidation reaction, enabling modeling of the oxidation reaction (34–36). P-DSC methods for screening compounds as oxidation inhibitors for increasing the oxidative stability of methyl soyate were developed (23).

Relation to the IV. The IV is a structure-related index in FA chemistry that relates to the total number of double bonds in a fat or oil (or derivatives thereof). A major drawback of the IV is that it does not distinguish the structural differences in fatty compounds such as nature (position in the chain, etc.) and amount of olefinic carbons. It treats all double bonds, or rather, in the case of oxidation of fatty compounds, allylic and bis-allylic carbons, as being equally reactive. The IV also has developed into a fuel quality parameter, as it has been included in some biodiesel standards, particularly in Europe. A recent study (37) showed that the IV is insufficiently precise to justify its inclusion in technical issues such as biodiesel standards. In that study, the development of alternatives to the IV, termed "allylic position equivalents (APE)" and "bis-allylic position equivalents (BAPE)," were suggested to correlate better with oxidative stability. The APE and BAPE values of the mixtures are included in Table 2. The calculation of APE and BAPE values is given in the literature (37).

The IV did not correlate well with oxidative stability. For the mixtures A–D given in Table 2, the OSI time decreased with increasing concentration of methyl linolenate although the IV is in a relatively narrow range of 112–121. Methyl linoleate, which has an IV = 172.4 and an OSI value of 1.2 h at 90°C (Table 1), imparts a low OSI value of 3.65 h to a 90:10 mixture of methyl stearate and methyl linoleate (mixture E in Table 2), which has an IV = 17.2. For comparison purposes, methyl oleate with IV = 85.6 has a higher OSI time of 10.70 h at 90°C. The lack of correlation between oxidative stability as well as other properties of biodiesel and IV value had been noted previously by other researchers (10,38). However, the alternative concept of APE and BAPE is based on the relative rates of oxidation of these positions in unsaturated FA as well as their amounts (37) and gives more useful results. The BAPE value is the more significant for oxidation of unsaturated fatty compounds due to the significantly higher relative rate of oxidation of bis-allylic CH_2 positions (37, and references therein). Regression of the BAPE values and the OSI times in Table 2 gave the following correlation:

$$OSI = 3.91 - 0.045 \times BAPE \qquad [3]$$

with $R^2 = 0.983$. This approach, however, does not consider the contribution of the oxidation of the allylic positions. Further research appears necessary to quantify the contribution of the allylic positions relative to the more oxidation-prone bis-allylic positions.

The lack of correlation between IV and oxidative stability is also demonstrated by the studies on varying amounts of compound or M.W. discussed above. Since oxidative stability depends more on the nature of double bonds in a molecule and less on M.W., then the IV, which depends on M.W. and on the number but not nature of double bonds, cannot be a predictor of oxidative stability.

In summary, reduction of highly unsaturated components likely will enhance oxidative stability more than preventing exposure to metals. Of the three metals investigated, copper appears to have the strongest catalytic effect. Oxidative stability is also affected by the molar concentration of double bonds in fatty compounds. An alternative to the IV, bis-allylic position equivalents and allylic position equivalents, appears more suitable for assessing oxidative stability. Last, oleic and linoleic acids had decreased oxidative stability compared with their alkyl esters. Commercial vegetable oil alkyl esters from the same lot stored at the same location under the same conditions (including history and material of the storage tanks) in two storage tanks may oxidize at similar but not identical rates.

ACKNOWLEDGMENT

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