

Comparative Oxidative Stability of Fatty Acid Alkyl Esters by Accelerated Methods

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Abstract Several fatty acid alkyl esters were subjected to accelerated methods of oxidation, including EN 14112 (Rancimat method) and pressurized differential scanning calorimetry (PDSC). Structural trends elucidated from both methods that improved oxidative stability included decreasing the number of double bonds, introduction of *trans* as opposed to *cis* unsaturation, location of unsaturation closer to the ester head group, and elimination of hydroxyl groups. Also noticed with EN 14112 was an improvement in oxidative stability when a larger ester head group was utilized. Methyl esters that contained ten or less carbons in the fatty acid backbone were unacceptable for analysis at 110 °C (EN 14112) due to excessive sample evaporation. With respect to PDSC, a correlation was noticed in which the oxidation onset temperature (OT) of saturated fatty esters increased with decreasing molecular weight (R^2 0.7328). In the case of the monounsaturates, a very strong inverse correlation was detected between molecular weight and OT (R^2 0.9988), which was in agreement with EN 14112. Lastly, a strong direct correlation (R^2 0.8759) was elucidated between OT and oil stability index (OSI, EN 14112, 80 °C). The

correlation was not as strong (R^2 0.5852) between OSI obtained at 110 °C and OT.

Keywords Biodiesel · Differential scanning calorimetry · EN 14112 · Fatty acid methyl ester · Fatty acid ethyl ester · Induction period · Oxidation · Rancimat

Introduction

Biodiesel, an alternative fuel prepared by transesterification of vegetable oils or animal fats, is susceptible to autoxidation. The rate of autoxidation (Fig. 1) is dependant on the number and location of methylene-interrupted double bonds contained within fatty acid methyl or ethyl esters (FAME or FAEE) that comprise biodiesel. Polyunsaturated materials are particularly vulnerable to autoxidation, as evidenced by the relative rates of oxidation of the unsaturates: 1 for ethyl oleate, 41 for ethyl linoleate, and 98 for ethyl linolenate [1]. The American (ASTM D6751 [2]) and European biodiesel standards (EN 14214 [3]) contain an oxidative stability specification whereby biodiesel must resist oxidation for at least 3 (ASTM D6751) or 6 h (EN 14214) according to the Rancimat method (EN 14112, 110 °C) [4]. Not only will oxidized biodiesel fail oxidative stability requirements, but oxidative degradation negatively impacts acid value and kinematic viscosity [5–7], both of which are specified in ASTM D6751 and EN 14214 (Table 1).

Measurement of oxidative stability can be accomplished with accelerated methods whereby various experimental parameters are influenced to yield results in a reasonable period of time. Such parameters may include elevated temperature, pressure, and/or flow rate of air (oxygen) through the sample, among others. Accelerated methods

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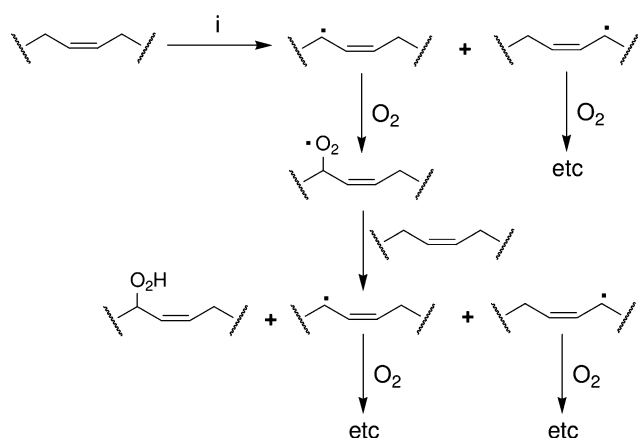


Fig. 1 Simplified pathway of initial lipid autoxidation (*i* initiator)

Table 1 Biodiesel specifications negatively impacted by autoxidation

	Test method	Units	ASTM D 6751	EN 14214
Oxidative stability, 110 °C	EN 14112	h	3.0 min	6.0 min
Acid value	ASTM D664 EN 14104	mg KOH/g	0.50 max	0.50 max
Kinematic viscosity, 40 °C	ASTM D445 EN ISO 310	mm ² /s	1.9–6.0	3.5–5.0

for determination of oxidative stability include, but are not limited to, the Rancimat method (EN 14112, [3]), AOCS official method Cd 12b-92 [8], and differential scanning calorimetry (DSC), which are summarized in Table 2.

Previous literature [9–21] on the oxidative stability of oleochemicals utilizing DSC studied a variety of vegetable oils and biodiesel, along with selected fatty acids and their corresponding ethyl esters. However, individual FAME were not investigated. Other reports [21–28] on the oil stability index (OSI) of various fatty acid alkyl esters (including

biodiesel) and vegetable oils were accomplished following AOCS official method Cd 12b-92 at a variety of block temperatures (50–110 °C), but these studies did not include a number of FAME commonly found in biodiesel, nor were EN 14112 or DSC methods utilized. A more recent report [29] on the OSI of selected FAME and FAEE employed both EN 14112 and AOCS official method Cd 12b-92 at 110 °C, but once again did not include a number of FAME commonly found in biodiesel, nor were the effects of chain length, double bond location or orientation investigated.

The aim of the current study was to measure and compare the oxidative stability of FAME typically found in biodiesel (Table 3) by accelerated methods such as EN 14112 and pressurized DSC (PDSC). Of particular interest were the effects of chain length, type of ester head group, and double bond content, orientation, and location on oxidative stability. The Rancimat method (EN 14112) was selected because it is specified in ASTM D6751 and EN 14214. Although PDSC is not specified in ASTM D6751 or EN 14214, it is rapid, requires very little sample (<5 mg) and provides good precision for measurement of oxidative degradation [9, 10]. Also of interest were potential correlations between methods and the influence of other factors on the oxidative stability of FAME and FAEE, such as molecular weight and boiling point.

Materials and Methods

Materials

The following alkyl esters were purchased from Nu-Chek Prep, Inc. (Elysian, MN) and used as received soon after arrival: methyl hexanoate (**1**, 99 + %, methyl caproate), methyl octanoate (**2**, 99 + %, methyl caprylate), methyl decanoate (**3**, 99 + %, methyl caprate), methyl dodecanoate (**4**, 99 + %, methyl laurate), methyl tetradecanoate (**5**, 99 + %, methyl myristate), methyl hexadecanoate (**6**, 99 + %, methyl palmitate), methyl 9Z-hexadecenoate (**7**, methyl palmitoleate), methyl octadecanoate (**8**, 99 + %, methyl stearate).

Table 2 Comparison of EN 14112, AOCS official method Cd 12b-92 and PDSC accelerated oxidation methods

Method	EN 14112 OSI	AOCS Cd 12b-92 OSI	PDSC OT
Pressure	Atmospheric	Atmospheric	200 psi
Temperature	110 °C	110 °C	50–350 °C
Temp. ramp rate	NA	NA	10 °C/min
Air flow rate	10 L/h	10 L/h	NA
Property monitored by instrument	Conductivity of H ₂ O (μS/cm)	Conductivity of H ₂ O (μS/cm)	Heat flow (W/g)
Parameter reported	Time (h)	Time (h)	Temp (°C)
Sample size	3.0 g	5.0 g	2 μL
ASTM D 6751 limit	>3 h	NA	NA
EN 14214 limit	>6 h	NA	NA

NA not applicable

Table 3 Fatty acid composition [36] (wt.%) of several vegetable oils

	RSO	SFO	PO	SBO	CCO	COO	CTO	CKO	BSO
6:0					1.3				
8:0					12.2			0.6	6
10:0					8.0			91.6	4
12:0			0.2		48.8	0.1		1.5	45
14:0		0.1	1.1		14.8	0.2	0.8	0.6	17
16:0	3.6	3.6	44.1	11	6.9	13.0	27.3	1.3	9
18:0	1.5	4.9	4.4	4	2.0	2.5	2.0		3
20:0		0.4	0.2	1	0.1	0.5	0.3		
22:0		1.2							
16:1		0.1	0.2	0.5			0.8		
18:1	61.6	80.6	39.0	22	4.5	30.5	18.3	1.1	13
18:2	21.7	8.4	10.6	53	1.4	52.0	50.5	3.1	2
18:3	9.6	0.1	0.3	7.5		1.0			
20:1	1.4	0.3		1.0		0.2			
22:1	0.2								

RSO (low erucic acid) rapeseed oil, SFO (high oleic acid) sunflower oil, PO palm oil, SBO soybean oil, CCO coconut oil, COO corn oil, CTO cottonseed oil, CKO *Cuphea koehneana* seed oil, BSO Babassu seed oil

methyl stearate), ethyl octadecanoate (**9**, 99 + %, ethyl stearate), methyl 12-hydroxyoctadecanoate (**10**, 99 + %, methyl 12-hydroxystearate), methyl 6Z-octadecenoate (**11**, 99 + %, methyl petroselinic acid), methyl 9Z-octadecenoate (**12**, 99 + %, methyl oleate), ethyl 9Z-octadecenoate (**13**, 99 + %, ethyl oleate), methyl 9E-octadecenoate (**14**, 99 + %, methyl elaidate), methyl 9Z,12-hydroxyoctadecenoate (**15**, 99 + %, methyl ricinoleate), methyl 9Z,12Z-octadecadienoate (**16**, 99 + %, methyl linoleate), ethyl 9Z,12Z-octadecadienoate (**17**, 99 + %, ethyl linoleate), methyl 9E,12E-octadecadienoate (**18**, 99 + %, methyl linoelaidate), methyl 9Z,12Z,15Z-octadecatrienoate (**19**, 99 + %, methyl linolenate), ethyl 9Z,12Z,15Z-octadecatrienoate (**20**, 99 + %, ethyl linolenate), methyl eicosanoate (**21**, 99 + %, methyl arachidate), methyl 11Z-eicosanoate (**22**, 99 + %, methyl gondoate), methyl tricosanoate (**23**, 99 + %, methyl behenate), and methyl 13Z-tricosanoate (**24**, 99 + %, methyl erucate). The samples were stored at -15 °C until needed to mitigate unwanted autoxidation. Soybean oil methyl esters (SME) were obtained from Ag Environmental Products, LLC (Omaha, NE) and were found to contain by GC (wt.%) 10.5% **6**, 4.1% **8**, 22.5% **12**, 1.6% methyl 11Z-octadecenoate, 53.6% **16**, and 7.7% **19**, along with a trace amount (in summation less than 1%) of other methyl esters.

EN 14112

OSI (h) was measured following EN 14112 [3] at 110 and 80 °C utilizing a Metrohm (Herisau, Switzerland) model

743 Rancimat instrument provided by Brinkmann Instruments, Inc. (Westbury, NY). The flow rate of air through 3 ± 0.01 g of sample was 10 L/h. The block temperature was set to 110 or 80 °C with correction factors (ΔT) of 1.5 and 0.9 °C, respectively. The conductivity measuring vessel contained 50 ± 0.1 mL of deionized water. Each sample was run in triplicate and mean values are reported (Tables 4, 5, 6). OSI was mathematically determined as the inflection point of a computer-generated plot of conductivity ($\mu\text{S}/\text{cm}$) of deionized water versus time (h).

Pressurized Differential Scanning Calorimetry

Oxidation onset temperature (OT, °C) was determined using a DSC 2910 thermal analyzer from TA Instruments (Newcastle, DE). Typically, a 2 μL sample, resulting in a film thickness of <1 mm, was placed in an aluminum pan hermetically sealed with a pinhole lid and oxidized with pressurized (1378.95 kPa; 200 psi) dry air (Gateway Air-gas, St. Louis, MO) in the module with a heating rate of 10 °C/min from 50 to 350 °C. A computer-generated plot of heat flow (W/g) versus temperature was used to graphically determine OT. Each sample was run in triplicate and average values rounded to the nearest tenth of a degree are reported (Table 4).

Results and Discussion

Oil Stability Index

The American (ASTM D6751) and European Union (EN 14214) biodiesel standards contain oxidative stability specifications utilizing the Rancimat (EN 14112) method. Consequently, this method was chosen for investigation of the oxidative stability of FAME in the current study. The Rancimat (EN 14112) method specifies that samples are to be analyzed at 110 °C (block temperature) with an air flow rate of 10 L/h through the sample. However, these parameters do not approximate conditions which are likely to be encountered during typical storage of biodiesel. Under the conditions of the standard EN 14112 method, unsaturated compounds generally undergo oxidative degradation in a relatively short (<3 h) period of time [23, 26, 28, 29, and results reported herein]. Therefore, block temperatures of 80 and 110 °C were selected for investigation. Earlier reports [21, 22] demonstrated that variances in OSI tended to increase with increased OSI values. Accordingly, experiments conducted in the present study were terminated at 40 h.

Compounds that are otherwise similar but contain a greater number of methylene-interrupted double bonds undergo oxidative degradation at faster rates [1, 27, 29,

Table 4 Molecular weight (MW), oil stability index (OSI, h), and oxidation onset temperature (OT, °C) of fatty acid alkyl esters

	Trivial name	Double bond location (s)	MW g/mol	EN 14112		PDSC OT ^b (°C)
				OSI ^a 80 °C (h)	OSI ^a 110 °C (h)	
1	Methyl caproate	–	130.19	>40	n.d. ^c	211.0
2	Methyl caprylate	–	158.24	>40	n.d.	208.1
3	Methyl caprate	–	186.29	>40	n.d.	202.5
4	Methyl laurate	–	214.34	>40	>40	198.5
5	Methyl myristate	–	242.40	>40	>40	198.5
6	Methyl palmitate	–	270.45	>40	>40	198.4
7	Methyl palmitoleate	9Z	268.44	14.3 ± 0.2	2.1	172.9
8	Methyl stearate	–	298.50	>40	>40	197.2
9	Ethyl stearate	–	312.54	>40	>40	195.9
10	Methyl 12-hydroxystearate	–	314.50	>40	>40	208.4
11	Methyl petroselinic acid	6Z	296.49	15.9 ± 0.2	3.5	181.0
12	Methyl oleate	9Z	296.49	15.1 ± 0.2	2.5	174.9
13	Ethyl oleate	9Z	310.52	15.7 ± 0.2	3.5	176.8
14	Methyl elaidate	9E	296.49	>40	7.7 ± 0.2	182.8
15	Methyl ricinoleate	9Z	312.49	5.8	1.6	170.2
16	Methyl linoleate	9Z, 12Z	294.48	3.4	1.0	142.6
17	Ethyl linoleate	9Z, 12Z	308.50	3.5	1.1	142.2
18	Methyl linoelaidate	9E, 12E	294.48	4.4 ± 0.2	1.2	146.2
19	Methyl linolenic acid	9Z, 12Z, 15Z	292.46	0.4	0.2	129.8
20	Ethyl linolenic acid	9Z, 12Z, 15Z	306.48	0.4	0.2	129.2
21	Methyl arachidic acid	–	326.56	>40	>40	195.4
22	Methyl gondoic acid	11Z	324.54	>40	2.9	176.9
23	Methyl behenic acid	–	354.61	>40	>40	198.9
24	Methyl erucic acid	13Z	352.59	>40	2.8	179.2

^a Standard deviation (σ) ± 0.1 h ($n = 3$) unless otherwise noted

^b Average σ ± 0.3 °C ($n = 3$)

^c *n.d.* not determined due to sample loss during experimentation

Table 5 Sample loss during EN 14112 evaluation (110 °C) of methyl caproate (**1**), caprylate (**2**), caprate (**3**), and laurate (**4**)

	bp ^a (°C)	Mass remaining at 0 h (g)	Mass at 3 h (g)	Mass at 6 h (g)	Mass at 24 h (g)
1	151	3.00	1.87 (62%) ^b	0.96 (32%)	0.05 (2%)
2	193	3.00	2.71 (90%)	2.42 (81%)	0.83 (28%)
3	223	3.00	2.73 (91%)	2.50 (83%)	1.66 (55%)
4	267	3.00	2.84 (95%)	2.72 (91%)	1.94 (65%)

^a Boiling points (bp) are from [34] with the exception of **4**, which was from [35]

^b Percentage of original mass remaining ($n = 3$, average σ ± 0.04 g)

30], which is confirmed in the present study through comparison of the OSI values (Table 4) of methyl stearate (**8**), methyl oleate (**12**), methyl linoleate (**16**), and methyl linolenate (**19**). There is a strong inverse relationship between the number of double bonds contained in a series

of compounds and the resultant OSI values. For instance, for the series **12**, **16**, and **19**, R^2 values of 0.8955 and 0.9700 were obtained for block temperatures of 80 and 110 °C, respectively (graphs not shown). Compounds that do not contain double bonds, such as **8**, have not undergone oxidative degradation by 40 h at either 80 or 110 °C. Applying these results to biodiesel, one may expect superior oxidative stability from biodiesel fuels that were prepared from feedstocks relatively high in saturated fatty acid content and/or relatively low in polyunsaturated fatty acid content. For example, palm oil methyl esters are known to be considerably more stable to oxidation than soybean oil methyl esters according to EN 14112 [31, 32].

The effect of double bond location on oxidative stability was investigated through comparison of the OSI values of methyl petroselinic acid (**11**, 6Z-monoene) and **12** (9Z-monoene). As seen from Table 4, **11** was more stable to oxidation than **12**, as evidenced by higher OSI values for

Table 6 Effect of adding methyl caproate (**1**), caprylate (**2**), caprate (**3**), and laurate (**4**) on the oil stability index (OSI, h, 110 °C) of soybean oil methyl esters

1 (wt.%)	2 (wt.%)	3 (wt.%)	4 (wt.%)	OSI ^a (110 °C, h)
0	0	0	0	6.6 (0.1)
5	0	0	0	6.4 (0.1)
0	5	0	0	6.6 (0.1)
0	0	5	0	6.6 (0.1)
0	0	0	5	6.8 (0.2)
10	0	0	0	6.0 (0.2)
0	10	0	0	6.0 (0.1)
0	0	10	0	6.2 (0.2)
0	0	0	10	6.7 (0.1)
20	0	0	0	5.2 (0.2)
0	20	0	0	5.4 (0.2)
0	0	20	0	5.5 (0.2)
0	0	0	20	6.6 (0.3)

^a Standard deviation indicated in parenthesis ($n = 3$)

11 at block temperatures of 80 and 110 °C. A possible explanation for this result may be the comparatively close proximity of the electron rich carboxylate moiety to unsaturation in **11**, which may introduce mild stereoelectronic repulsive effects during initial radical formation not present in the case of **12**. Applying these results to biodiesel, biodiesel fuels enriched in FAME with unsaturation located close to the ester head group would have superior oxidative stability (as measured by EN 14112) to those with 9-ene FAME, such as **12**, **16**, and **19**.

The influence of double bond orientation was ascertained through comparison of materials that contain *trans* double bonds [methyl elaidate (**14**) and methyl linoelaidate (**18**)] to the corresponding *cis* isomers (**12** and **16**). As seen from Table 4, **14** exhibited superior stability to oxidation (OSI: 7.7 and >40 h at 110 and 80 °C) in comparison to **12** (OSI: 2.5 and 15.1 h at 110 and 80 °C). Likewise, a similar observation was made between **18** and **16** at 80 °C (OSI: 4.4 vs. 3.4 h), but at 110 °C they were essentially indistinguishable. These results are not surprising, as it is known that *trans* isomers are generally thermodynamically more stable than the corresponding *cis* isomers. Applying these results to biodiesel, biodiesel fuels that contain at least some *trans* constituents would exhibit somewhat enhanced stability to oxidation according to EN 14112 than biodiesel fuels that contain a similar number of entirely *cis* double bonds. Although naturally occurring *trans* fatty acid-containing vegetable oils are rare, *trans* isomers can be chemically introduced through catalytic partial hydrogenation. Partially hydrogenated soybean oil methyl esters (7.7% *trans* FAME, 16.4% saturated FAME, 44.7% polyunsaturated FAME) yielded an OSI value of 6.2 h (110 °C, AOCS Cd 12b-92) versus 2.3 h for SME [33].

Due to the nature of AOCS official method Cd 12b-92 and EN 14112, a bias is introduced whereby compounds of higher molecular weight will appear to be more stable to oxidation than compounds of similar double bond and other functional group (such as ester) content but lower molecular weight. The parameters of the methods are the cause of this bias: a specified mass (3.0 g in the case of EN 14112) of material is required as opposed to a specified molar amount. This shortcoming has been discussed previously [27, 29]. Illustrative of this point is methyl palmitoleate (**7**, MW 268.44), methyl oleate (**12**, MW 296.49), and methyl gondoate (**22**, MW 324.54), which have similar double bond content but increasing OSI values (110 °C) of 2.1, 2.5, and 2.9 h (R^2 1.0000, graph not shown), respectively (Table 4). This trend was also evident when compared at 80 °C, which provided OSI values of 14.3, 15.1, and >40 h for **7**, **12**, and **22**. Concomitant with these results was variation in ester group among otherwise similar compounds. Ethyl oleate (**13**, MW 310.52) demonstrated greater oxidative stability than **12**, as evidenced by OSI values for **13** of 3.5 (110 °C) and 15.7 h (80 °C). The effect of ester head group on OSI was less pronounced for polyunsaturated compounds such as methyl and ethyl linoleates (**16** and **17**) and methyl and ethyl linolenates (**19** and **20**). The increased double bond content of these materials resulted in an accelerated rate of oxidation which essentially masked the aforementioned molecular weight effect on OSI.

Relatively short chain saturated FAME, such as methyl hexanoate (**1**, methyl caproate), methyl octanoate (**2**, methyl caprylate) and methyl decanoate (**3**, methyl caprate) are found in coconut, cuphea and babassu oils (Table 2), among others. These materials (**1–3**) were stable to oxidation due to the absence of unsaturation, which was verified in Table 4 at 80 °C (OSI of **1–3**: >40 h). However, sample loss as a result of evaporation was noticed when OSI was determined at 110 °C for **1–3**, which yielded unexpectedly low and unreliable OSI values. Although **1–3** possess boiling points in excess of 110 °C [34, 35, Table 5], prolonged exposure to elevated temperature in combination with a constant flow of air through the sample during experimentation resulted in evaporation. To explore this phenomenon more carefully, **1–3** and methyl laurate (**4**) were re-evaluated at 110 °C with concomitant determination of sample loss at 3, 6, and 24 h. As can be seen from Table 5, only 62% (wt.%) of **1** remained after 3 h. The remainder of the sample evaporated into the conductivity measuring vessel. After 6 h, only 32% of **1**, 81% of **2**, and 83% of **3** remained in the tube containing the sample. After 24 h, nearly all of **1** (2% remaining) had evaporated, along with a majority of **2** (28%) and a significant percentage of **3** (55%). Only after 24 h did **4** exhibit substantial sample evaporation (65% remaining).

These results indicated that oxidative stability determined at 110 °C (AOCS or EN methods) of biodiesel containing **1–3** should be viewed with skepticism. Accordingly, soybean oil methyl esters (SME) were enriched in **1–4** at 5, 10, and 20 wt.% to ascertain the influence of these relatively volatile constituents on OSI at 110 °C of biodiesel. Soybean oil methyl esters were chosen because they do not naturally contain these constituents, so the effect(s) of adding **1–4** on oxidative stability could be clearly determined. As indicated in Table 6, addition of **1–4** did not influence OSI of SME at 5 wt.%. However, at 10 and especially 20 wt.% a deleterious effect on OSI was observed, as evidenced by the decreasing OSI values of SME enriched with methyl caproate at 0, 5, 10, and 20 wt.% (6.6, 6.4, 6.0, 5.2 h, respectively, Table 6). As anticipated, the negative impact on OSI of SME was greatest for the lowest molecular weight species (**1**), as indicated by the OSI values at 20 wt.% of **1** (5.2 h), **2** (5.4 h), **3** (5.5 h), and **4** (5.8 h).

Hydroxylated fatty acids occur naturally in castor and lesquerella oils. Ricinoleic acid (9Z-12-hydroxyoctadecanoic acid) constitutes roughly 80–90% of castor oil (*Ricinus communis*) and lequerolic acid (11Z-14-hydroxyeicosenoic acid), the C₂₀ homolog of ricinoleic acid, comprises about 50–70% of lesquerella oil (*Lesquerella fendleri*) [36]. Both methyl 12-hydroxystearate (**10**) and **8** (Table 4) yielded indistinguishable OSI results (>40 h) at both 80 and 110 °C, but methyl 9Z-12-hydroxyoctadecanoate (**15**, methyl ricinoleate) exhibited inferior stability to oxidation when compared to **12**. These results indicate that hydroxyl moieties in unsaturated FAME may impart mild pro-oxidant behavior to biodiesel.

Pressurized Differential Scanning Calorimetry

The OT (°C) is defined as the temperature at which a rapid increase in the rate of oxidation is observed [37], which is obtained from extrapolation of the tangent line drawn on the steepest slope of the reaction exotherm of a plot of heat flow versus temperature (Fig. 2). Higher OT values indicate greater stability to oxidation [37]. As with EN 14112, the parameters of the PDSC method do not approximate conditions encountered during typical storage of biodiesel. However, tests that do not employ accelerated oxidation conditions are unacceptably long to be of practical industrial value.

Results from PDSC analysis of **1–24** (Table 4) were generally in agreement with those obtained from EN 14112. Similar trends noticed from both methods included the effects of the number of double bonds, double bond orientation, and double bond position on stability to oxidation. In contrast to OSI, PDSC failed to provide a clear trend with regard to the effect of ester head group on

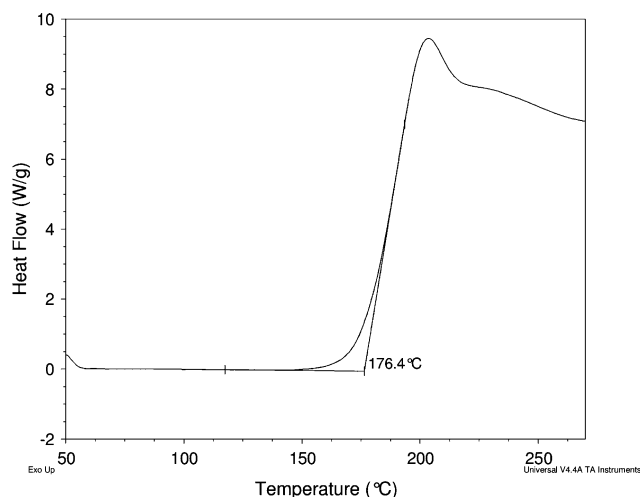


Fig. 2 Typical PDSC exotherm for ethyl oleate (**13**). The OT in this case was 176.4 °C

oxidative stability. In fact, the effect of ester head group was minimal. For example, methyl esters **8** (OT 197.2 °C), **16** (OT 142.6 °C), and **19** (OT 129.8 °C) were more stable to oxidation than the corresponding ethyl esters (**9**, OT 195.9 °C; **17**, OT 142.2 °C; **20**, OT 129.2 °C). However, in the case of the oleates, the ethyl ester (**13**, OT 176.8 °C) was more stable than the methyl ester (**12**, OT 174.9 °C).

A statistically significant inverse relationship (R^2 0.7328, Fig. 3) was elucidated between OT and molecular weight in the case of the saturated esters (**1–6**, **8**, **9**, **21**, **23**). In the case of the mono-unsaturated methyl esters (**7**, **12**, **22**, **24**) a statistically significant direct relationship (R^2 0.9988, Fig. 4) was discovered, which was in accordance with the OSI results obtained from EN 14112. The opposite trends noticed for oxidation of the saturated and unsaturated esters can be attributed to molecular weight effects. The PDSC method, like EN 14112, utilizes the same mass of material for every experiment. As with the OSI results, compounds with a similar number of double bonds but

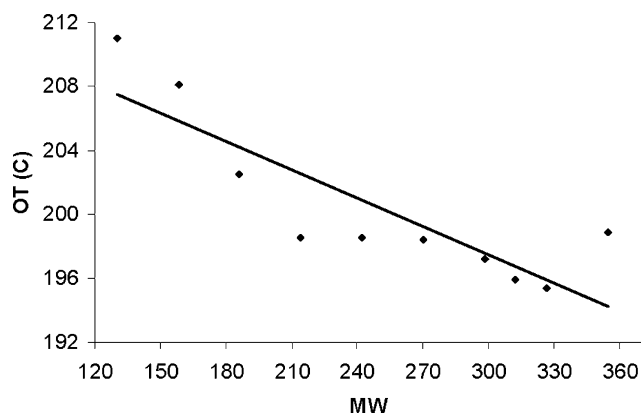


Fig. 3 Correlation (R^2 0.7328) between molecular weight (MW, g/mol) of saturated fatty acid alkyl esters and OT (°C)

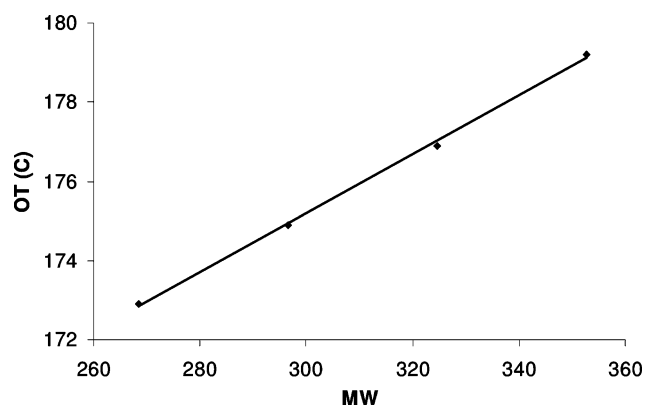


Fig. 4 Correlation (R^2 0.9988) between molecular weight (MW, g/mol) of monounsaturated FAME and OT ($^{\circ}\text{C}$)

greater molecular weight yielded higher OT values. In the case of the saturated esters, the mechanistic pathway for oxidative degradation is considerably slower and may occur at any point along the fatty acid backbone with the exception of the terminal methyl group. A sample of molecules of lower molecular weight contains more unreactive terminal methyl groups than a sample of higher molecular weight. The general rule is that the ease of oxidation of C–H bonds follow the order: $-\text{CH}_3$ (most stable) $>$ $-\text{CH}_2-$ \gg $\text{CH}-$ (most reactive).

Another area in which disparate results were obtained with PDSC was the effect of hydroxyl group on stability to oxidation. In the case of methyl 12-hydroxystearate (**10**, OT 208.4 $^{\circ}\text{C}$) a higher OT was obtained than for methyl stearate (**8**, OT 197.2 $^{\circ}\text{C}$). This result is not comparable to the aforementioned OSI data, since both **8** and **10** yielded OSI values in excess of 40 h. With regard to the unsaturated alcohols, the reverse trend was noticed: methyl (**12**, OT 174.9 $^{\circ}\text{C}$) and ethyl (**13**, OT 176.8 $^{\circ}\text{C}$) oleates exhibited higher OT values than methyl ricinoleate (**15**, OT 170.2 $^{\circ}\text{C}$). This result is in agreement with the OSI data, which indicated that the presence of the hydroxyl group may result in a mild pro-oxidant effect.

Relationship between Methods

A plot of OSI at 80 $^{\circ}\text{C}$ of esters that exhibited OSI values less than 40 h (**7**, **11–13**, **15–20**) versus OT yielded a statistically significant direct relationship (R^2 0.8759, Fig. 5) in which samples with higher OSI values also yielded higher OT values. A plot of OSI at 110 $^{\circ}\text{C}$ of esters that yielded OSI values of less than 40 h (**7**, **11–20**, **22**, **24**) versus OT yielded a similar trend, but the relationship was not as strong (R^2 0.5852, Fig. 6). This was likely due to the compression of OSI data at higher block temperatures. For instance, **16** and **18** only differed by 0.2 h at a block temperature of 110 $^{\circ}\text{C}$, but the difference was 1.0 at 80 $^{\circ}\text{C}$.

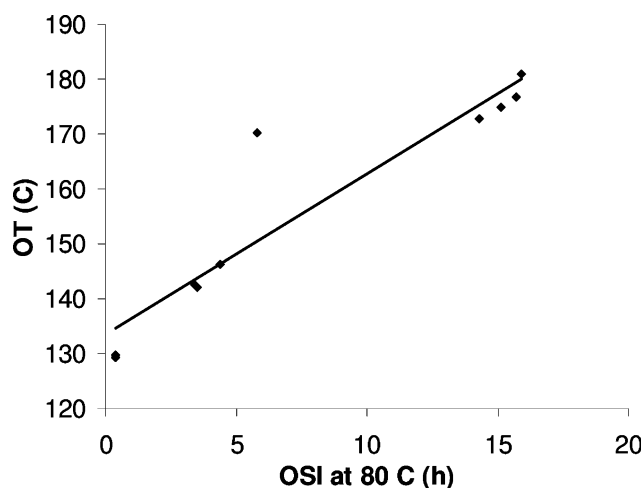


Fig. 5 Correlation (R^2 0.8759) between OSI (h, 80 $^{\circ}\text{C}$) and OT ($^{\circ}\text{C}$) of fatty acid alkyl esters that exhibited OSI values of less than 40 h. The outlier peak corresponds to methyl ricinoleate (**15**)

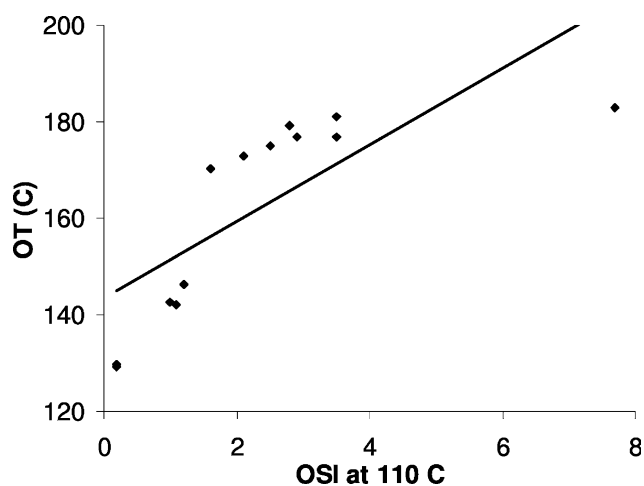


Fig. 6 Correlation (R^2 0.5852) between OSI (h, 110 $^{\circ}\text{C}$) and OT ($^{\circ}\text{C}$) of fatty acid alkyl esters that exhibited OSI values of less than 40 h

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