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Effect of Alkyl Chain Unsaturation on Methyl Ester Thermo-Oxidative Decomposition and Residue Formation

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Abstract The formation of persistent residues by esters used in sheet metal-working lubricant formulations interferes with metal surface cleanliness and impairs the integrity of subsequent surface coatings. Understanding the thermal decomposition and residue formation properties of esters is therefore crucial to minimising residue formation during furnace-based cleaning and will aid in the improvement of coated metal products such as galvanised steel. The thermo-oxidative decomposition profiles of four different methyl esters were studied by Thermogravimetric Analysis (TGA) and Pressure Differential Scanning Calorimetry (PDSC). Chemical characterisation of residues remaining at different stages during the thermo-oxidative decomposition process was achieved by infrared spectroscopic analysis of TGA residue samples. Relationships between ester alkyl chain unsaturation levels and the amount/chemical nature of residue present at high temperature (500 °C) were assessed. In the presence of oxygen, polyunsaturated esters decomposed to leave significantly greater amounts of thermally-stable residue, comprising of metal carboxylate and non-volatile oxygenated compounds, than more saturated esters. Given that the formation of analogous residues by more complex esters used in sheet metal-working lubricants may give rise to metal surface coating defects, the results of this study suggest that polyunsaturated esters should be avoided in lubricant formulations where preventing residue formation is of paramount importance.

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Introduction

Understanding and controlling the oxidation reactions of naturally occurring esters (fats and oils) is critical to the application of these materials within the food, coatings, automotive and metal processing industries. The products of ester oxidation impart a repugnant flavour and odour to food [1, 2] such that the stability of edible fats and oils towards oxidation affects food shelf life and processability [3, 4]. Similarly, crosslinking reactions undergone by unsaturated esters during oxidation are essential to the formation of durable paint and varnish films within the coatings industry [2, 5] but are detrimental in the automotive and metal fabrication industries; crosslinking reactions have been associated with the formation of deposits that give rise to wear and failure in mechanical systems [6–12] and downstream coating problems in sheet metal processing [13, 14]. Given the industrial significance of ester oxidation, particularly in relation to the use of esters as lubricants in high temperature applications where preventing the formation of thermally stable residues is critical, a fundamental understanding of the oxidation process and its dependency on conditions such as temperature and ester chemical structure is of utmost importance.

In basic research applications, the simplified chemical structure of fatty acid methyl esters makes them ideal for use in modelling the properties of more complex esters such as triglycerides [15]. Fatty acid methyl esters are

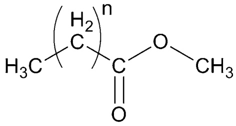


Fig. 1 Representation of a typical fatty acid methyl ester structure, where $n = 3$–21

typified by the structure given in Fig. 1 and are often given the notation Cx:y, where x is the number of carbon atoms in the ester alkyl chain (typically between 4 and 22) and y is the number of carbon–carbon double bonds (between 0 and 5) [2]. The oxidative stability of fatty acid methyl esters is of particular importance for biofuel applications and has been studied extensively by Dunn [16–19]. On a more fundamental level, the mechanisms involved in low temperature auto-oxidation of methyl oleate (C18:1), methyl linoleate (C18:2) and methyl linolenate (C18:3) have been comprehensively characterised by GCMS, FTIR and HPLC techniques [20, 21]. The process of auto-oxidation, described extensively in the literature for a variety of unsaturated esters, [1, 2, 4, 5, 21–23] can be summarised as: reaction initiation (usually catalysed by heat, light or transition metals); hydroperoxide (ROOH) formation involving molecular oxygen uptake and hydrogen atom abstraction from the hydrocarbon substrate; hydroperoxide decomposition to form a range of reactive radical species; polymerisation via radical addition to carbon–carbon double bonds (C=C), and radical side reactions to produce secondary oxidation products such as aldehydes, ketones, carboxylic acids and alcohols.

Thermal analysis techniques such as TGA and PDSC have proven to be invaluable in studying the thermal decomposition of a variety of synthetic [9, 10], semi-synthetic [9] and naturally occurring [1, 3, 4, 16, 22–24] tri-esters under oxidising conditions. However, the use of such techniques to study long chain fatty acids or their mono-esters has primarily been reported at temperatures below 200 °C [17, 18, 25] and under nitrogen [23, 26]. Although Litwinienko et al. [15, 27, 28] studied the oxidation of saturated and unsaturated fatty acid derivatives quite extensively, their work focussed on the kinetics of the initial stages of oxidation, as opposed to residue formation, and they employed atmospheric pressure DSC at temperatures below 300 °C. Dufaure et al. [29] used simultaneous TGA/DTA to study the thermo-oxidative decomposition of a series of mono-esters and ethers at temperatures up to 600 °C, however their focus was on thermal and thermo-oxidative stability and not on residue formation. Therefore, our understanding of the high temperature oxidation processes of fatty acid methyl esters, and how these processes lead to the formation of thermally-stable residues, is limited.

In this study, the effect of alkyl chain unsaturation levels on the thermo-oxidative decomposition and residue formation properties of a model system consisting of methyl stearate, methyl oleate, methyl linoleate and methyl linolenate has been investigated using TGA and PDSC. Attenuated Total Reflectance FTIR (ATR) has been applied to characterise the chemical structure of residues remaining at different stages throughout the thermo-oxidative decomposition process. The amounts of residue, and residue formation processes, undergone by each methyl ester are assessed independently, avoiding complexities associated with higher esters [8, 15].

Materials and Methods

Methyl Esters

Methyl stearate, methyl oleate, methyl linoleate and methyl linolenate (Nu-Check Prep Inc., Elysian, Minnesota) were of >99% purity and were stored in the dark under nitrogen to minimise oxidation.

ATR FTIR

ATR spectra of neat (room temperature) and partially thermo-oxidatively decomposed methyl esters were collected using a Nicolet Nexus 8700 FT-IR Spectrophotometer (Thermo Electron Corporation) fitted with a ‘Smart Orbit’ ATR accessory containing a diamond crystal internal reflection element. Spectra were collected over the range 4000–500 cm^{-1} at a resolution of 4 cm^{-1}. A minimum of 64 scans were acquired and averaged to give each sample spectrum. A background spectrum of an empty standard aluminium DSC pan (TA Instruments) was acquired and subtracted from each sample spectrum. Spectral processing and analysis was performed using OMNIC version 7.1 software (Thermo Electron Corporation).

Room temperature ester samples were prepared by weighing 1.0 ± 0.1 mg of the desired methyl ester into an aluminium pan. The pan sides were then cut, enabling the pan to be flattened out for ATR analysis. Thermo-oxidatively decomposed methyl ester samples were prepared by TGA as opposed to PDSC to enable rapid analysis following sample decomposition, minimising chemical changes in the sample between preparation and analysis. The thermo-oxidatively decomposed samples were prepared by heating to a series of temperatures in the range 100–500 °C. Samples were typically prepared at 100, 150, 200, 250, 300, 350, 400 and 500 °C; other temperatures were used when complex chemical changes were taking place over narrow temperature ranges. Fresh quantities of ester were used in the creation of each sample. Following TGA treatment, the aluminium pan was flattened out for ATR analysis. Analyses were performed in duplicate to confirm reproducibility.

TGA

A TGA 2950 Thermogravimetric Analyzer (TA Instruments) was used for all TG analyses. The instrumental temperature calibration was performed using the Curie temperatures of nickel and alumel standard reference materials (TA Instruments). Methyl ester samples were analysed in triplicate under continuous heating conditions (10 °C min^{-1}) between room temperature and 600 °C under a flow of high purity oxygen gas at 50 ml min^{-1}. Samples were weighed into standard aluminium pans, placed onto platinum crucibles and loaded onto the TGA balance for analysis. A small amount of sample (1.0 ± 0.1 mg) was used to ensure maximum ester exposure to the aluminium pan surface and the surrounding oxygen atmosphere. Data were analysed using Universal Analysis 2000 v3.3B software (TA Instruments) and the typical parameters measured are shown for methyl linoleate in Fig. 2a. Onset temperatures of mass loss (T_{onset}) were determined by extrapolation from the mass loss (TG) curve; peak temperatures (T_{max}) were determined at maxima in the first derivative of mass loss with respect to temperature (DTG) curve; shoulder temperatures (T_{max}) were estimated at points of inflection in the DTG curve; percentage of mass losses were determined from the TG curve for each peak or shoulder observed, and the percentage of residue was measured from the TG curve at 500 °C.

PDSC

A DSC 2920 (TA Instruments) fitted with a high pressure cell was used for all PDSC analyses. The experimental parameters used by Zhang et al. [6, 7] were optimised for methyl ester analysis, taking into account the findings of Sharma et al. [12] Accordingly, constant-volume conditions and a high purity oxygen pressure of 3792 kPa were used to reduce sample volatilisation, maximise oxygen

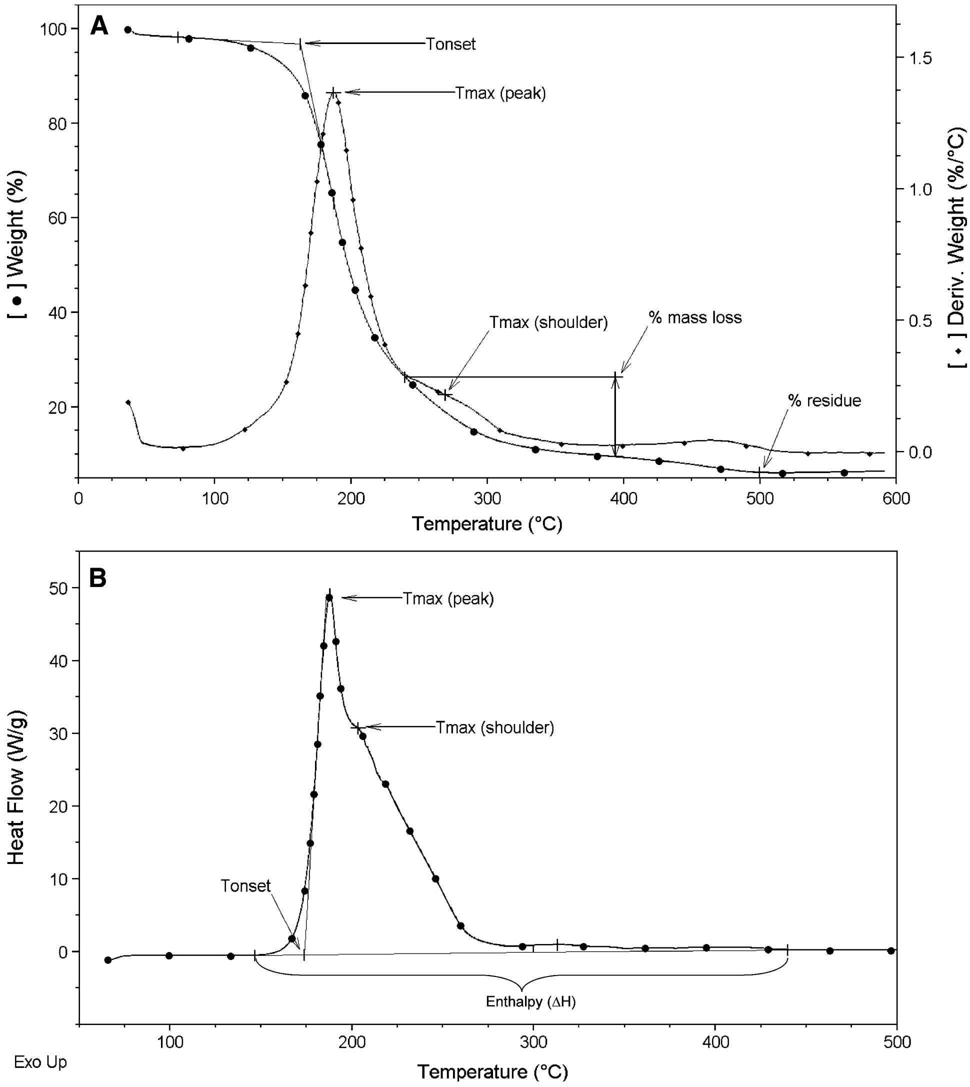


Fig. 2 Representative TGA (**a**) and PDSC (**b**) decomposition profiles obtained for methyl linoleate and methyl oleate respectively, indicating the various parameters measured in this study

concentration and favour residue-forming reactions. The instrumental cell constant and temperature calibration were determined using indium standard reference material. Methyl ester samples were analysed in triplicate under continuous heating conditions (10 °C min^{-1}) between room temperature and 500 °C. About 1.0 ± 0.1 mg of ester was weighed into a standard aluminium pan and placed onto the PDSC cell platform. The cell was then purged to establish an oxygen atmosphere before being sealed and pressurised. Data were analysed using Universal Analysis 2000 v3.3B software (TA Instruments) and the typical parameters measured are shown for methyl oleate in Fig. 2b. Onset temperatures of oxidation (T_{onset}) were determined by extrapolation from the heat flow curve baseline; peak temperatures (T_{max}) were determined at maxima in the heat flow curve; shoulder temperatures (T_{max}) were estimated at points of inflection in the heat flow curve; enthalpies were determined by integration of the total area under the exothermic region of the heat flow curve using a linear baseline, and the 'perpendicular drop' analysis tool was then used to apportion enthalpy values to each distinguishable exotherm.

Statistical Analysis

In order to evaluate if the PDSC and TGA parameter values relative to the different methyl esters were significantly different, one-way analysis of variance assays (ANOVA) were applied when comparing three or more values, and independent samples *t*-tests were applied when comparing two values. Data processing was performed using SPSS Statistics 17.0 software (SPSS Inc.). All comparisons are made against methyl stearate, except for the following: T_{max} event 2 and percentage of mass loss event 2 by TGA (comparisons made to methyl oleate); T_{max} event 3 and percentage of mass loss event 3 by TGA, and T_{max} exotherm 2 and ΔH exotherm 2 by PDSC (comparisons made to methyl linoleate).

Results and Discussion

Thermo-Oxidative Decomposition Profile by TGA

TGA was used to study the thermo-oxidative decomposition characteristics, including oxidative stability and residue formation properties, of the four methyl esters. Figure 3 compares the first derivative of mass loss with respect to temperature (DTG) curves obtained by analysing each methyl ester under oxygen. A summary of the extrapolated onset points (T_{onset}), peak and shoulder temperatures (T_{max}) and the associated mass losses is presented in Table 1. Significance level values (*p*-values) determined from ANOVA (T_{onset}, T_{max} event 1, percentage of mass loss event 1, T_{max} event 2, percentage of mass loss event 2) and *t*-tests (T_{max} event 3, percentage of mass loss event 3) are also indicated.

The methyl stearate thermo-oxidative mass loss process proceeds via a single step and essentially the entire sample is volatilised at 220 °C, with negligible residue remaining at 500 °C. In contrast, the decomposition processes for methyl oleate, methyl linoleate and methyl linolenate involve multiple overlapping mass loss events and volatile products are evolved over the entire temperature range of decomposition. No significant (i.e. >0.5%) amounts of thermally stable residue remain at 500 °C for the methyl oleate, methyl linoleate and methyl linolenate samples.

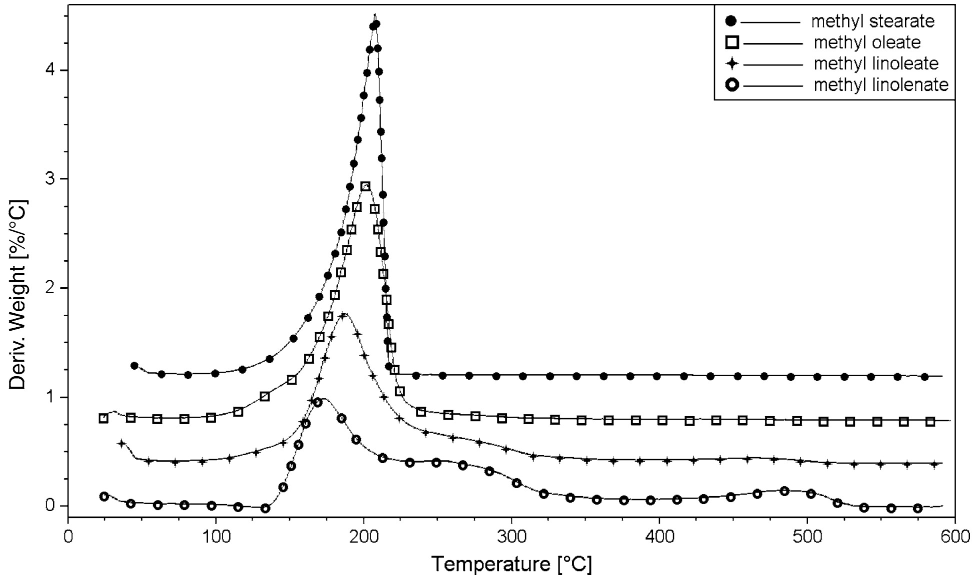


Fig. 3 Overlay showing the TGA decomposition profiles (DTG curves) of methyl stearate, methyl oleate, methyl linoleate and methyl linolenate

Table 1 Summary of TGA data obtained for the four methyl esters

Ester	T_{onset} [°C]	O_2 uptake [%]	T_{max} event 1 [°C]	Mass loss event 1 [%]	T_{max} event 2 [°C]	Mass loss event 2 [%]	T_{max} event 3 [°C]	Mass loss event 3 [%]
Methyl stearate (C18:0)	176 ± 1.2	–	207 ± 1.1	100 ± 0.0058	–	–	–	–
Methyl oleate (C18:1)	167 ± 0.39*	–	202 ± 0.70	96.0 ± 0.27	259 ± 0.37	3.97 ± 0.40	–	–
Methyl linoleate (C18:2)	159 ± 1.3*	–	186 ± 1.5*	76.0 ± 2.4*	260 ± 3.4	17.8 ± 1.0*	463 ± 0.60	3.31 ± 0.10
Methyl linolenate (C18:3)	154 ± 0.62*	0.165 ± 0.0046	172 ± 2.3*	54.2 ± 0.94*	254 ± 2.6	34.2 ± 1.1*	485 ± 6.1	12.4 ± 1.1**

Mean values ± the standard error of the mean are shown

* *p*-value < 0.01, indicating a significant difference between values at a 99% confidence interval

** *p*-value < 0.05, indicating a significant difference between values at a 95% confidence interval

Table 1 shows that increasing the level of oil unsaturation shifts the oil mass loss onset point to a lower temperature and that the observed differences in T_{onset} for each of the four methyl esters are significantly different. The decrease in T_{onset} is in accordance with the findings of Sathivel et al. [23], who observed that the onset temperature of mass loss under nitrogen followed the progression C18:0 > C18:1 > C18:2. This trend was attributed to a decrease in the heat resistance of C18 fatty acids with increasing unsaturation levels. Under an oxidising atmosphere it can be expected that the decrease in onset temperature with increasing oil unsaturation is due to a combination of the decreased heat resistance of unsaturated oils together with the greater susceptibility of these oils to oxidation.

In contrast to the literature [1, 4, 23], here methyl linolenate is the only unsaturated sample for which the thermo-oxidative decomposition process is initiated by oxygen uptake as no mass increase is observed for either methyl oleate or methyl linoleate. Under the ramped heating conditions employed, and given the limited ester exposure to the metal catalyst (the aluminium pan surface), the oxidation initiation step is likely to be slow, limiting the radical species available for reaction with molecular oxygen [2, 30]. In addition, highly unsaturated esters are considerably more susceptible to hydrogen abstraction than their more saturated counterparts [5, 24]. Therefore, whilst methyl linolenate undergoes a discernable mass increase of ~0.2% associated with oxygen uptake, the oxygen uptake of methyl linoleate and oleate may be shifted to increasingly higher temperatures and masked by simultaneous mass loss processes such as sample evaporation.

The decomposition of methyl oleate involves two mass loss events, whilst the methyl linoleate and methyl linolenate decomposition patterns are more complex, comprising of at least three mass loss events (see Table 1). Statistical analysis of the T_{max} and percentage of mass loss results for these additional mass loss events shows that whilst the T_{max} values for event 2 (observed for methyl oleate, methyl linoleate and methyl linolenate) and event 3 (observed only for methyl linoleate and methyl linolenate) are the same, suggesting that these events may represent similar oxidative decomposition processes, the percentage of mass lost during these events varies depending on ester chemical structure. Furthermore, evaluation of the T_{max} and the percentage of mass loss results for event 1 shows that values differ depending on whether the methyl ester is saturated, mono-unsaturated or poly-unsaturated. These observations confirm that the presence and level of unsaturation within the methyl ester alkyl chain significantly affects the thermo-oxidative decomposition process.

The temperature at which thermo-oxidative decomposition is complete is highly dependent on the presence of C=C bonds. Whilst methyl stearate fully decomposes by 220 °C, the decomposition of methyl oleate, methyl linoleate and methyl linolenate is not complete until 320, 500 and 525 °C respectively. The significantly higher decomposition end temperatures observed for methyl linoleate and methyl linolenate, together with the observation of an additional mass loss event (event 3), may result from polyunsaturation in these esters; the presence of multiple C=C bonds in the alkyl chains of methyl linoleate and methyl linolenate means that inter- and intra-molecular crosslinking can occur more readily than in methyl oleate or methyl stearate, facilitating the formation of densely crosslinked deposits. Event 3 may involve the decomposition of these deposits, given that crosslinking is well-known to afford a higher thermal stability [31].

Thermo-Oxidative Decomposition Profile by PDSC

PDSC is a complimentary technique to TGA for studying the thermo-oxidative decomposition properties of materials. The PDSC technique measures heat flow in and out of the sample of interest as a function of temperature and can therefore be used to identify physical and chemical changes that do not result in mass loss (i.e. are unmeasurable by TGA). Figure 4 shows an overlay of the heat flow vs temperature plots obtained by constant-volume PDSC analysis of the methyl esters. The extrapolated onset points (T_{onset}), peak and shoulder temperatures (T_{max}) and enthalpies are given in Table 2, together with significance level values (*p*-values) from ANOVA (T_{onset}, T_{max} exotherm 1, ΔH exotherm 1, T_{max} tail-like region, ΔH tail-like region) and *t*-tests (T_{max} exotherm 2, ΔH exotherm 2).

Statistical analysis of the PDSC results shows that the T_{onset} and exotherm 1 T_{max} results follow the same trend observed by TGA; the PDSC T_{onset} is significantly different for all four methyl esters, whilst T_{max} for exotherm 1 differs depending on whether the ester is saturated, mono-unsaturated or poly-unsaturated, confirming the important role of ester unsaturation levels in governing the oxidative decomposition process. The thermo-oxidative decomposition of methyl stearate is preceded by an endotherm at 179 °C (Fig. 4 inset) that is due to a small amount of sample evaporation despite the high test pressure employed [22]. This endotherm is followed immediately by a sharp exotherm at 222 °C that contributes to 97.0% of the total heat flow and indicates ester oxidation. Finally, a broad, tail-like region (Fig. 4 inset) accounting for only 3.00% of the total heat flow occurs at 314 °C. This region comprises of multiple overlapping exothermic and endothermic transitions; processes such as reaction initiation and the evaporation of volatiles give rise to endotherms, whilst combustion and thermal cracking of residual carbonaceous material correspond to exotherms [6]. The evolution of volatile products during the thermo-oxidative decomposition of methyl stearate therefore involves numerous interdependent processes and reactions that occur up to high temperatures (>500 °C). Although this finding contradicts the observations made by TGA, which show that the majority of methyl stearate is volatilised at 220 °C, it is consistent with the high oxygen pressure employed during PDSC testing.

Introducing a centre of unsaturation into the ester alkyl chain, as per the case for methyl oleate, generates notable differences in the PDSC profile. The onset temperature for methyl oleate thermo-oxidative decomposition is approximately 30 °C lower than that observed for methyl stearate and no sample evaporation is evident. Like methyl stearate, methyl oleate decomposes via two dominant exothermic events, however the first of these (at 188 °C) is a broad envelope containing at least three overlapping exotherms that indicate multiple oxidation processes. Overlapping of exothermic events during the oxidation of oleic acid derivatives was also reported by Litwinienko et al. [28] and

Fig. 4 Overlay showing PDSC decomposition profiles obtained for methyl stearate, methyl oleate, methyl linoleate and methyl linolenate

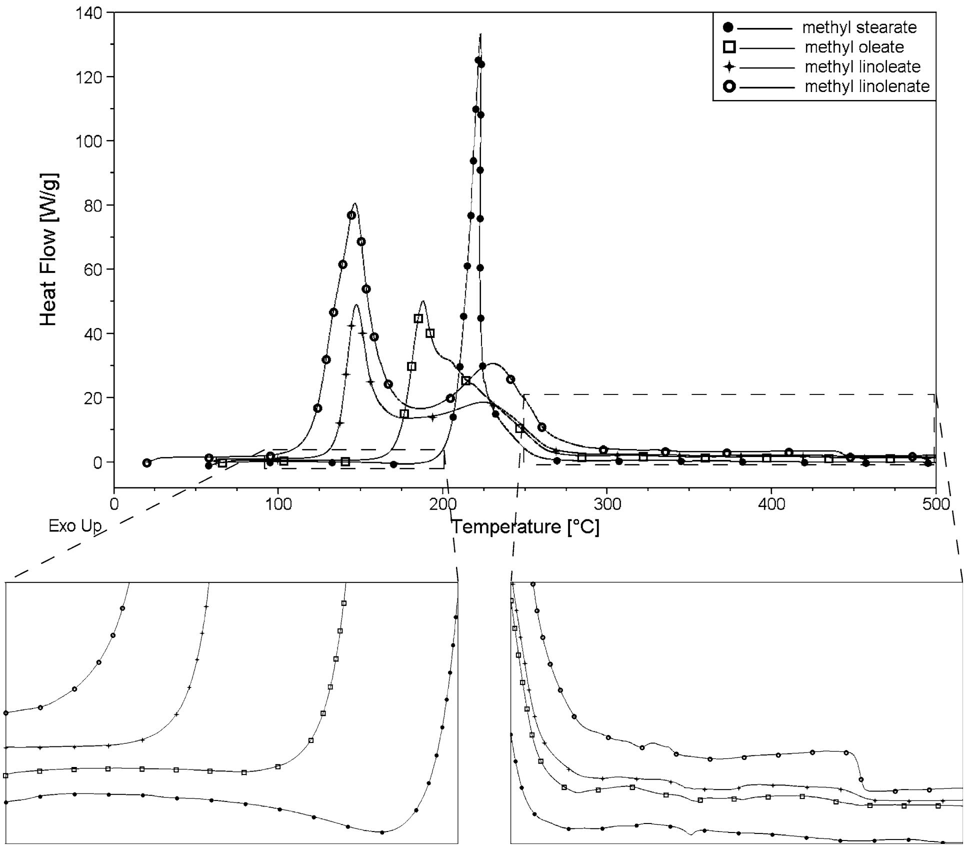


Table 2 Summary of PDSC data obtained for the four methyl esters

Ester	T_{max} endotherm 1 [°C]	ΔH endotherm 1 [J g^{-1}]	T_{onset} [°C]	T_{max} exotherm 1 [°C]	ΔH exotherm 1 [J g^{-1}]	T_{max} exotherm 2 [°C]	ΔH exotherm 2 [J g^{-1}]	T_{max} tail-like region [°C]	ΔH tail-like region [J g^{-1}]
Methyl stearate (C18:0)	179 ± 0.54	137 ± 3.0	207 ± 0.65	222 ± 1.7	9020 ± 130	–	–	314 ± 5.6	282 ± 19
Methyl oleate (C18:1)	–	–	174 ± 0.055*	188 ± 0.19*,[a]	12000 ± 680	–	–	319 ± 3.5	419 ± 55
Methyl linoleate (C18:2)	–	–	136 ± 0.24*	148 ± 0.11*	6080 ± 28	226 ± 0.41	7030 ± 170	310 ± 0.50	511 ± 50***
Methyl linolenate (C18:3)	–	–	121 ± 0.37*	147 ± 0.031*	14600 ± 1200**	230 ± 0.87	10500 ± 520**	328 ± 5.5	1050 ± 12*

Mean values ± the standard error of the mean are shown

* *p*-value < 0.01, indicating a significant difference between values at a 99% confidence interval

** *p*-value < 0.05, indicating a significant difference between values at a 95% confidence interval

*** *p*-value < 0.1, indicating a significant difference between values at a 90% confidence interval

[a] Exotherm 1 for methyl oleate comprises approximately three overlapping exotherms at 188 °C, 202 °C and 221 °C

was attributed to the kinetic similarity between initial and subsequent oxidation processes in monounsaturated compounds. However, Litwinienko et al. used atmospheric pressure DSC and only described two distinguishable exothermic events below 300 °C. The detection of a third exothermic event in the present work may result from the greater oxygen:ester ratio employed during PDSC testing accelerating oxidative processes [17].

The trend towards lower onset temperature and increased complexity of thermo-oxidative decomposition with increasing ester unsaturation is continued for methyl linoleate and methyl linolenate. These esters show decomposition onset temperatures of only 136 °C (methyl linoleate) and 121 °C (methyl linolenate) and both decompose via three, as opposed to two, exothermic events. The first event occurs at approximately 148 °C, accounts for 44.7% (methyl linoleate) and 55.8% (methyl linolenate) of the total heat flow and represents the initial process of auto-oxidation [28]. The increase in the proportion of the total heat flow signal attributed to event 1 observed with increasing alkyl chain poly-unsaturation levels is in good agreement with the literature [28] and is significant at the 0.01 level. The third net exothermic event is the 'tail like' region common to all of the esters and described above for methyl stearate. Although T_{max} for this region is statistically similar for all four methyl esters, the total enthalpy associated with this region is significantly different for the poly-unsaturated esters, indicating that oxidative decomposition of thermally-stable products formed by these esters evolves greater amounts of energy. Similarly, although exotherm 2 occurs at similar temperatures for both methyl linoleate (226 °C) and methyl linolenate (230 °C), it accounts for significantly different proportions of the total heat flow (51.6% for methyl linoleate; 40.2% methyl linolenate). Interestingly, the temperature at which exotherm 2 occurs in the poly-unsaturated methyl esters is similar to that of the third overlapping exotherm in the methyl oleate thermogram (at 220 °C), suggesting that it may represent similar processes in all three esters. The 202 °C exotherm in the methyl oleate PDSC results has no counterpart in the methyl linoleate and methyl linolenate results, either because the reactions giving rise to this event do not occur, or because they are obscured by surrounding exotherms.

A comparison between the mean TGA and PDSC onset points for the four esters (Fig. 5) shows that while the onset point by TGA decreases marginally with increasing oil unsaturation, the onset point obtained by PDSC decreases quite dramatically. For methyl stearate the onset point by PDSC is considerably greater than by TGA, however for methyl oleate the two onset temperatures are comparatively similar and for methyl linoleate, the TGA onset temperature exceeds the onset temperature measured

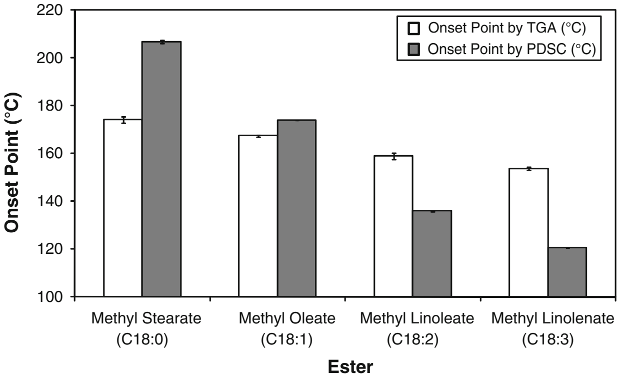


Fig. 5 Comparison between mass loss (TGA) and oxidation (PDSC) onset temperatures for methyl stearate, methyl oleate, methyl linoleate and methyl linolenate. The error bars represent the standard error of the mean

by PDSC. In fact, for methyl linoleate, approximately 4260 J g^{-1} of heat flow occurs before the TGA onset point of 159 °C. These observations suggest that highly unsaturated esters undergo exothermic reactions at low temperatures (such as crosslinking to form high molecular weight polymeric deposits) that do not result in the production of volatile material. Such reactions are of particular interest as they contribute to thermally-stable residue formation.

Residue Evaluation by the Percentage of B/A Ratio Technique

According to Zhang et al. [6, 7], the tendency for the esters to form thermally stable deposits can be measured by calculating the percentage of *B*/*A* ratio:

$$\%B/A\ \text{Ratio} = \frac{B}{A} \times 100 \tag{1}$$

B is known as the secondary decomposition region and represents the percentage of sample mass lost between 240–500 °C (TGA) or the total heat flow associated with events occurring between 300 and 500 °C (PDSC). A is known as the primary decomposition region and represents the percentage of sample mass lost between room temperature and 240 °C (TGA) or the total heat flow associated with events occurring between room temperature and 300 °C (PDSC). The temperature regions over which '*A*' and '*B*' are calculated are defined such that processes predominantly leading to the formation of thermally stable deposits (oxidation, crosslinking) are included within '*A*' while those processes which destroy deposits (combustion and thermal cracking of high molecular weight material) are included within '*B*'. It should be noted that sample evaporation is also included within '*A*' despite the fact that it does not lead to the formation of deposits.

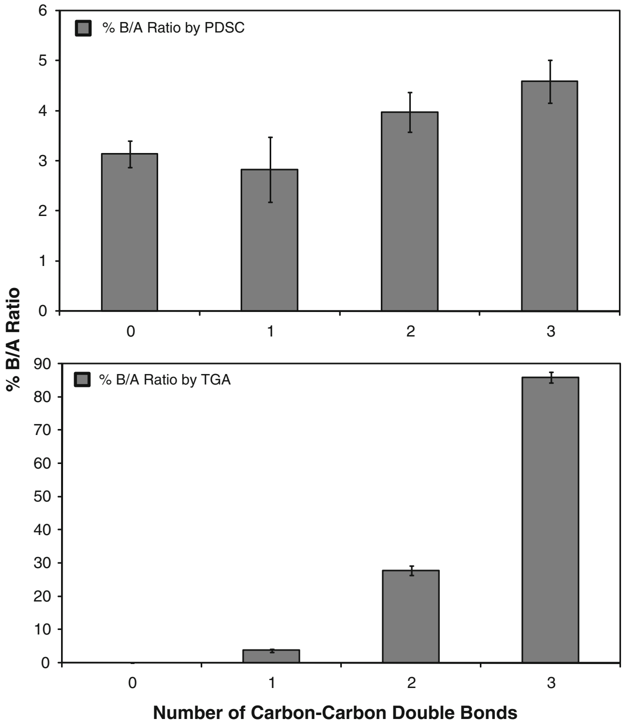


Fig. 6 Mean percentage of B/A ratio versus the number of ester alkyl chain carbon–carbon double bonds. The error bars represent the standard error of the mean

Figure 6 shows a plot of the percentage of *B*/*A* ratio, calculated from PDSC and TGA thermograms using Eq. 1, against the number of C=C bonds in the ester alkyl chain. The TGA percentage of *B*/*A* ratio increase in an exponential fashion with respect to increasing alkyl chain unsaturation. This is in good agreement with the differences in residue thermal stability described above; polyunsaturated methyl esters form residues that persist until high temperatures, giving rise to a significant mass loss over the '*B*' region. The corresponding increase in the PDSC percentage of *B*/*A* ratio is only small; enthalpies associated with events in both the primary and secondary regions increase with increasing unsaturation. Consequently, alkyl chain unsaturation levels have a greater effect on the *amount* of thermally stable material that is decomposed at higher temperatures as opposed to the energy evolved by decomposing this material. This indicates that the use of more highly saturated esters is preferable in applications where minimising residue formation in imperative.

Infrared Spectroscopic Characterisation of Thermo-Oxidative Decomposition Reactions

ATR spectroscopy was used to elucidate the chemical composition of residues remaining at different stages during the thermo-oxidative decomposition of each of the methyl esters. The room temperature ATR spectra collected for the four methyl ester samples are similar and a representative spectrum for methyl linoleate is shown in Fig. 7. The spectrum of methyl stearate contains no peaks above 3000 cm^{-1} or between 1680 and 1600 cm^{-1}, indicating the absence of C=C bonds. The methyl oleate spectrum contains a characteristic unsaturated C–H stretching band at 3004 cm^{-1} arising from the single C=C bond in its alkyl chain. Analogous bands for methyl linoleate and methyl linolenate occur at slightly higher wavenumber (3009 cm^{-1} and 3010 cm^{-1} respectively). All four esters show the distinctive ester C=O stretching band at approximately 1740 cm^{-1}, however the precise position of this band is sensitive to the chemical environment of the carbonyl group [32]. The esters can therefore be readily distinguished by the characteristics of the C=O stretching band at 1740 cm^{-1} and the unsaturated C–H stretching band just above 3000 cm^{-1}. These bands can be monitored during ester thermo-oxidative decomposition to detect the reaction of C=C bonds and the formation of radical recombination and secondary oxidation products [5, 8].

Figure 8 shows ATR spectra obtained for thermo-oxidatively decomposed methyl stearate, methyl oleate and methyl linoleate in the temperature range 100–350 °C in the C=O (1820–1550 cm^{-1}, Fig. 8a) and C–H (3550–2780 cm^{-1}, Fig. 8b) and O–H (3700–3000 cm^{-1}, Fig. 8c) stretching regions. The spectra acquired for methyl linolenate are analogous to those of methyl linoleate.

For methyl stearate, a gradual decrease in spectral intensity is observed until 200 °C, indicating that sample evaporation dominates the low-temperature mass loss process. Between 175 °C and 200 °C, shifts in the CH$_2$ and C=O stretching bands to higher wavenumber suggest degradation of the ester hydrocarbon chain and at 220 °C, bands at 1723 and 3400 cm^{-1} appear, revealing decomposition of methyl stearate into its carboxylic acid and alcoholic components respectively. These compounds are subsequently volatilised and decomposition of the sample is complete at temperatures above 240 °C.

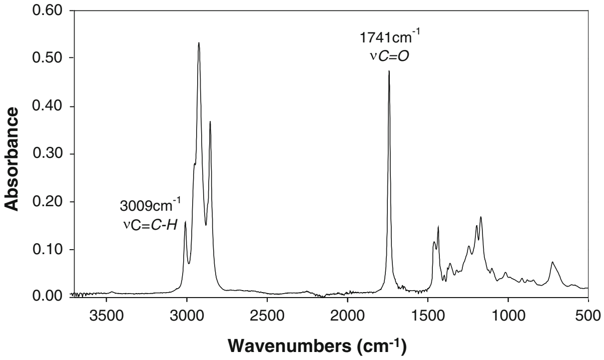


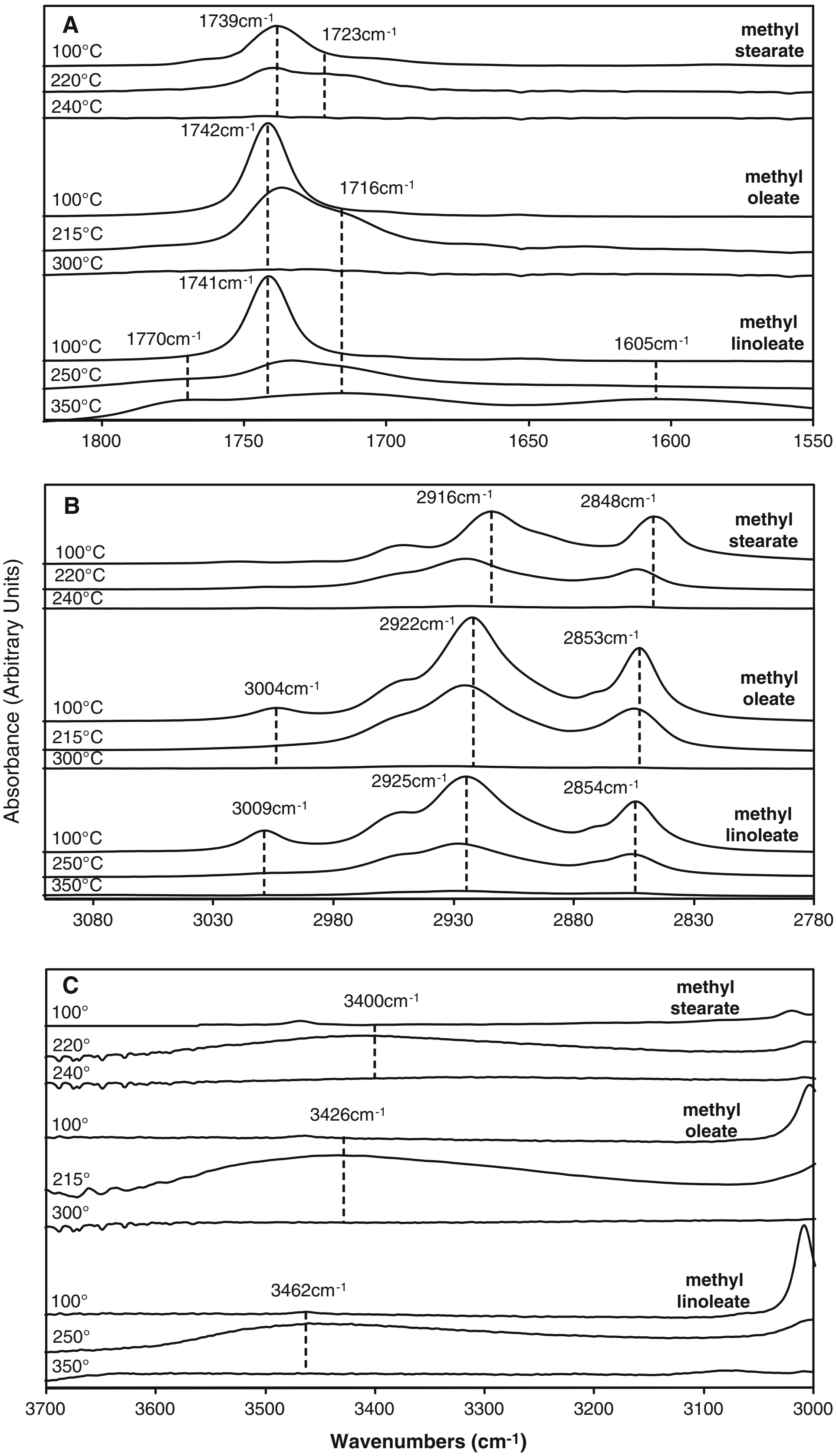
Fig. 7 Infrared spectrum of methyl linoleate acquired at room temperature

The methyl oleate ATR results evidence an entirely different decomposition process; minimal sample evaporation is apparent at low temperatures and at 200 °C, a broad OH stretching band at 3426 cm^{-1} is evolved, corresponding to sample oxidation via hydroperoxide formation [5]. An increase in intensity of this band at 215 °C, together with significant broadening of the C=O stretching band at 1742 cm^{-1} and the evolution of bands at lower wavenumber (1716 cm^{-1}), infers the formation of secondary oxidation species such as aldehydes, ketones and acids [5, 8]. Oxidative decomposition is also noticeable by changes in the C–H stretching region. A shift in the C–H stretching bands at 2853 cm^{-1} and 2922 cm^{-1} to higher wavenumber confirms the formation of volatiles, whilst the decreasing intensity of the band at 3004 cm^{-1} indicates that reactions involving C=C bonds in the oleate alkyl chain are occurring. A decrease in spectrum intensity between 250 °C and 300 °C infers the volatilisation of residues and the decomposition process for methyl oleate is complete by 350 °C, with no significant residues remaining at higher temperatures.

At temperatures below 250 °C, the thermo-oxidative decomposition processes undergone by methyl linoleate and linolenate are analogous to those of methyl oleate, although the observed changes occur at lower temperatures due to increased susceptibility to oxidation. At temperatures above 250 °C, the decomposition processes undergone by methyl linoleate are more complex than those observed for methyl stearate and methyl oleate. Broad bands at 1770 cm^{-1} and 1716 cm^{-1} appear at 300 °C and increase in intensity up until 350 °C, suggesting the formation of C–O–C and C–O–O–C linkages via processes such as radical recombination [5]. A band at 1605 cm^{-1}, characteristic of metal carboxylates, also becomes apparent at 350 °C and represents the reaction of carbonyl compounds such as acids with the aluminium pan surface. The formation of these complexes was not observed for methyl stearate or methyl oleate as a result of the complete volatilisation of these esters by 350 °C. The combustion of hydrocarbon-based material is not complete until 400 °C for methyl linoleate, confirming observations made by TGA and PDSC and the significant thermal stability of the residues formed. The carboxylate and oxygenated carbonaceous materials persist up to 500 °C and contribute to the high levels of residue present at temperatures of 500 °C and above.

In summary, the results of this study highlight the value of using ATR FTIR in conjunction with TGA and PDSC thermal analysis techniques to evaluate the thermo-oxidative decomposition and residue formation properties of methyl esters. Observations made using these techniques indicate that highly unsaturated esters, modelled in the present study through the use of methyl linoleate and linolenate, thermally decompose in the presence of oxygen to

Fig. 8 Infrared spectra of thermo-oxidatively decomposed methyl stearate, methyl oleate and methyl linoleate samples in the region 1820–1550 cm^{-1} (**a**), 3550–2780 cm^{-1} (**b**) and 3700–3000 cm^{-1} (**c**)



form significant amounts of carboxylate and oxygenated carbonaceous residues which persist to temperatures above 500 °C. The use of highly unsaturated esters in sheet metal-working lubricants should be therefore be avoided to reduce the formation of decomposition residues where furnace-based cleaning methods are employed. In contrast, saturated and mono-unsaturated esters decompose comparatively cleanly such that the use of these esters in sheet metal-working lubricants may aid in maintaining good metal surface cleanliness by minimising the formation of thermo-oxidative decomposition residues.

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