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Metal/bromide autoxidation of triglycerides for the preparation of FAMES to improve the cold-flow characteristics of biodiesel

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ABSTRACT

Triglyceride autoxidation using a homogeneous Co/Mn/Zr/bromide catalyst in acetic acid (93%) of low grade tallow, canola oil or soy bean oil in a batch reactor at 150 °C for 2 h, produced lower molecular weight products relative to the fatty acids of the starting triglycerides. For the autoxidation of tallow the main products after esterification were monoesters $\text{Me}(\text{CH}_2)_m\text{C}(\text{O})\text{OMe}$ ($m = 5-12$) and diesters $\text{MeOC}(\text{O})(\text{CH}_2)_n\text{C}(\text{O})\text{OMe}$, ($n = 7-12$). Oxidation of the saturated fatty acids in triglycerides was confirmed and modelled using methyl palmitate. Post-treatment esterification of tallow autoxidation products to produce biodiesel (BD) esters resulted in improved cold temperature properties by a mean of 13.0 °C, *i.e.* a mean cloud point (CP) 1.0 °C (*cf.* unmodified tallow biodiesel: CP 14 °C).

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1. Introduction

The production of biodiesel (BD) by transesterification of triglycerides with alcohols to generate fatty acid alkyl esters [1–5], *i.e.* fatty acid methyl esters (FAMES) in the case of methanol, is an established route in the area of renewable fuels. Typically, the feedstock triglycerides are found in food crops (first-generation biofuels). However, as an increasing plant oil demand for first-generation biofuels leads to land use issues (rainforest *vs.* oil palm plantations, fuel *vs.* food dilemma, *etc.*), it is prudent to investigate existing waste oils as a source from which to produce BD, particularly the use of low-grade waste, *e.g.* tallow and related residues, which are high in saturated fats [6–9].

Low grade tallow products, used vegetable oils and grease trap wastes provide an ideal feedstock for a sustainable, local production of a renewable fuel from a low-value source. However, a significant issue is the difficulty in obtaining BD with a low cloud point (CP), *i.e.* the on-set of crystallisation, when derived from such low grade sources, as triglycerides from these sources generally exhibit a greater degree of saturation and oxidation than plant

oils (*e.g.* soy- or canola-based)ⁱ and yield BDs with a CP of around 14 °C—Falling well outside the useable range [2,10,11]. Cold flow properties (freezing-, cloud- and gel-points) of BD are of crucial importance for its successful application. Given the feedstock constraints mentioned above, it is of considerable interest to produce low melting fatty acid esters from low grade sources [10–15].

In this contribution we set out to develop a new methodology to obtain low CPs for tallow-derived BDs, based on an autoxidation approach reported by Partenheimer [16], in which catalyst mixtures of cobalt (II) and manganese (II) acetates and zirconium (IV) chloride and sodium bromide in aqueous acetic acid oxidised a variety of hydrocarbon polymers in 70 bar of air at 150–180 °C, yielding predominantly dicarboxylic acids. Partenheimer has also shown that this catalyst system can oxidise lignin model compounds, and lignin samples [17,18].

Thus our concept is to produce mono- and diacids with shorter chain-lengths than those of the fatty acids of the triglyceride feedstock, and to subsequently esterify these shorter chain-length acids to yield the corresponding mono- and diesters. These should now have a comparatively lower CP than that obtainable *via* a straight triglyceride transesterification of the unmodified feedstock. Our

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ⁱ Canola is a trademarked quality description of low erucic acid ((*Z*)-docos-13-enoic acid) rapeseed variants. The erucic acid content of Canola oils for food use is generally less than 1%.

approach has several potential advantages in that air is used as an oxidant and the catalysts and solvents employed are relatively non-hazardous and inexpensive.

Accordingly, we report here the batch autoxidation of the triglyceride BD feedstocks tallow, canola oil and soy bean oil with air in the presence of metal/bromide catalysts, and an assessment of the modified cold flow properties of the FAMES derived from this process.

2. Experimental

2.1. Materials

Cobalt (II) acetate, manganese (II) acetate, zirconium (IV) chloride, potassium bromide, methyl palmitate, methyl stearate, anhydrous sodium sulfate, sodium chloride, silica gel, *n*-hexane, sulfuric acid, sodium hydrogen carbonate, diethyl ether, and glacial acetic acid (Sigma-Aldrich) were used as received. HPLC grade *n*-hexane, 2-propanol and methanol (Labscan) were filtered through a PTFE filter prior to use. Domestic, food grade tallow (Allowrie beef dripping), soy bean and canola oil (Crisco) were used as purchased. Dimethyl butandioate, dimethyl pentandioate, dimethyl hexandioate and dimethyl octandioate were obtained from Fluka. Methyl butanoate, methyl pentanoate, methyl hexanoate, methyl heptanoate, methyl octanoate, methyl nonanoate, methyl hexadecanoate, methyl octadecanoate, dimethyl heptandioate and dimethyl nonandioate were purchased from Sigma-Aldrich. All esters were used as received.

2.2. Instrumentation

A Shimadzu Gas Chromatograph (GC-17A) equipped with a FID detector and a polyethylene glycol column (BP21, 30 m length, 0.25 mm ID) was used for the quantification of reaction products. Initially the column was kept at 80 °C for 2 min and heated to 240 °C over 8 min and maintained at 240 °C for another 10 min. The ester products were calibrated from prepared standards containing known amounts of esters with a known amount of mesitylene as an external standard. Calibration curves were drawn as (concentration of esters)/(concentration of external standard) on the X-axis and (area of the ester peak)/(area of external standard peak) on the Y-axis. We have assumed that the FID response per carbon atom is the same for those FAMES for which standards were unavailable commercially, *i.e.* methyl decanoate, methyl undecanoate, ethyl dodecanoate, methyl tridecanoate, methyl tetradecanoate, methyl pentadecanoate, dimethyl decandioate, dimethyl undecandioate, dimethyl dodecandioate, dimethyl tridecandioate, dimethyl tetradecandioate, dimethyl pentadecandioate and dimethyl hexadecandioate.

A Shimadzu GC/MS (QP 2010 using a fused silica Rtx-5Sil MS column, 30 m length, 0.25 mm ID) was used to identify the reaction products. Initially the column was kept at 50 °C for 3 min and then heated at a rate of 15 °C/min to 300 °C and kept at 300 °C for 5 min. Volatile acids were measured with and without silylation. Compounds were identified using the NIST database and by comparison to the standards prepared.

Differential scanning calorimetry (DSC) was performed using a TA Instruments modulated differential scanning calorimeter (MDSC) 2920 equipped with the Liquid Nitrogen Cooling Accessory (LNCA). Samples were measured at a cooling rate of 1 °C/min from 40 to –30 °C.

High Performance Liquid Chromatography (HPLC) analyses were used to determine the lack or presence of triglycerides and diglycerides. The analyses were carried out with a Shimadzu Prominence HPLC system with a SPD-M20A diode array detector

($\lambda = 205 \text{ nm}$), using a Phenomenex Luna 5 μm C18(2) 100 Å column (250 \times 4.6 mm, 5 μm). The mobile phase was a mixture of (A) methanol, and (B) 2-propanol/hexane (5:4) (HPLC grade), with the following operating method: (1) an initial mixture consisting of A:B = 100:0 was ramped to A:B = 50:50 for 15 min; (2) then ramped to A:B = 0:100 for 5 min and was maintained at A:B = 0:100 for 5 min; (3) the mixture was then allowed to equilibrate to the initial ratio A:B = 100:0 within 5 min and then run for a further 5 min before the next analysis was performed. Sample injections were of 20 μL , and a total flow rate of 1 mL/min was employed.

2.3. Oxidation reactions

All substrates were oxidised using an Anton Parr 600 mL capacity reactor (Method 1). Some experiments with tallow were also conducted with a modified procedure referred to as Method 2 (Parr Instruments Co. 250 mL capacity reactor). Where not specified, reactant amounts were scaled accordingly to the vessel size.

In a typical experiment (Method 1) the catalyst mixture was prepared by dissolving cobalt (II) acetate (1.11 g, 4.47 mmol), manganese (II) acetate (1.10 g, 4.47 mmol), zirconium (IV) chloride (33 mg, 0.14 mmol) and potassium bromide (1.06 g, 8.94 mmol) in glacial acetic acid (150.0 g, 2.50 mol) and distilled water (12.0 g, 0.66 mol). This mixture was transferred into a stainless steel high-pressure reactor (Parr, 600 mL capacity, Hastalloy C) to which the triglyceride fat or oil (8.0 g, approximately 9 mmol, composition dependent) or the methyl hexadecanoate (8.0 g, 29.6 mmol) were added. The reactor was then sealed, pre-pressurised to 40 bar (or 50 bar, Method 2) with compressed air and then heated to 150 °C while being stirred by means of an integral PTFE blade mixer rotating at 500 rpm. Once the temperature reached 150 °C, the pressure was adjusted to 70 bar with additional air (if required). The time required to reach 150 °C was approximately 30 min. The system was maintained at the reaction temperature for 2 h and then allowed to cool to room temperature (typically around 30 min) and depressurised.

2.4. Work-up—Methyl hexadecanoate

Refer to Fig. 1. The liquid products typically appeared as a dark brown mono-phasic solution. Initially, volatile components were isolated from the product liquid under reduced pressure on a Schlenk line (Step 1) and analysed by GC/MS. This product isolation was achieved using two cold traps arranged in series: trap one was at –78 °C (dry ice and acetone) and trap two was at –196 °C (liquid nitrogen). The resultant product liquid was viscous with the formation of some precipitates. Acetic acid (20 mL) was added to achieve a homogenous solution. Subsequently, it was dried using silica gel (10 g) and anhydrous Na_2SO_4 (20–30 g) (Step 2). The drying agents were removed by filtration. The residue was extracted further with diethyl ether and *n*-hexane (20 mL each). Esterification (2–6 h) of the combined organic fractions proceeded smoothly in excess methanol with concentrated sulfuric acid as catalyst (3 mol%, calculated based on the conservative assumption that all of the substrate was acetic acid). The esterified mixture was neutralised by the addition of solid NaHCO_3 , and the mixture subsequently filtered (Step 3). To remove any methyl acetate (originating from the esterification of acetic acid), the filtered mixture was subjected to reduced pressure on a rotary evaporator (Step 4: final volume approx. 15 mL). To purify the esters (Step 5), crude esters were washed with brine (3 \times 10 mL), stirred overnight with anhydrous Na_2SO_4 to remove water, filtered and the dried product evacuated for 90 min on a Schlenk line before conducting cloud and gel point tests.

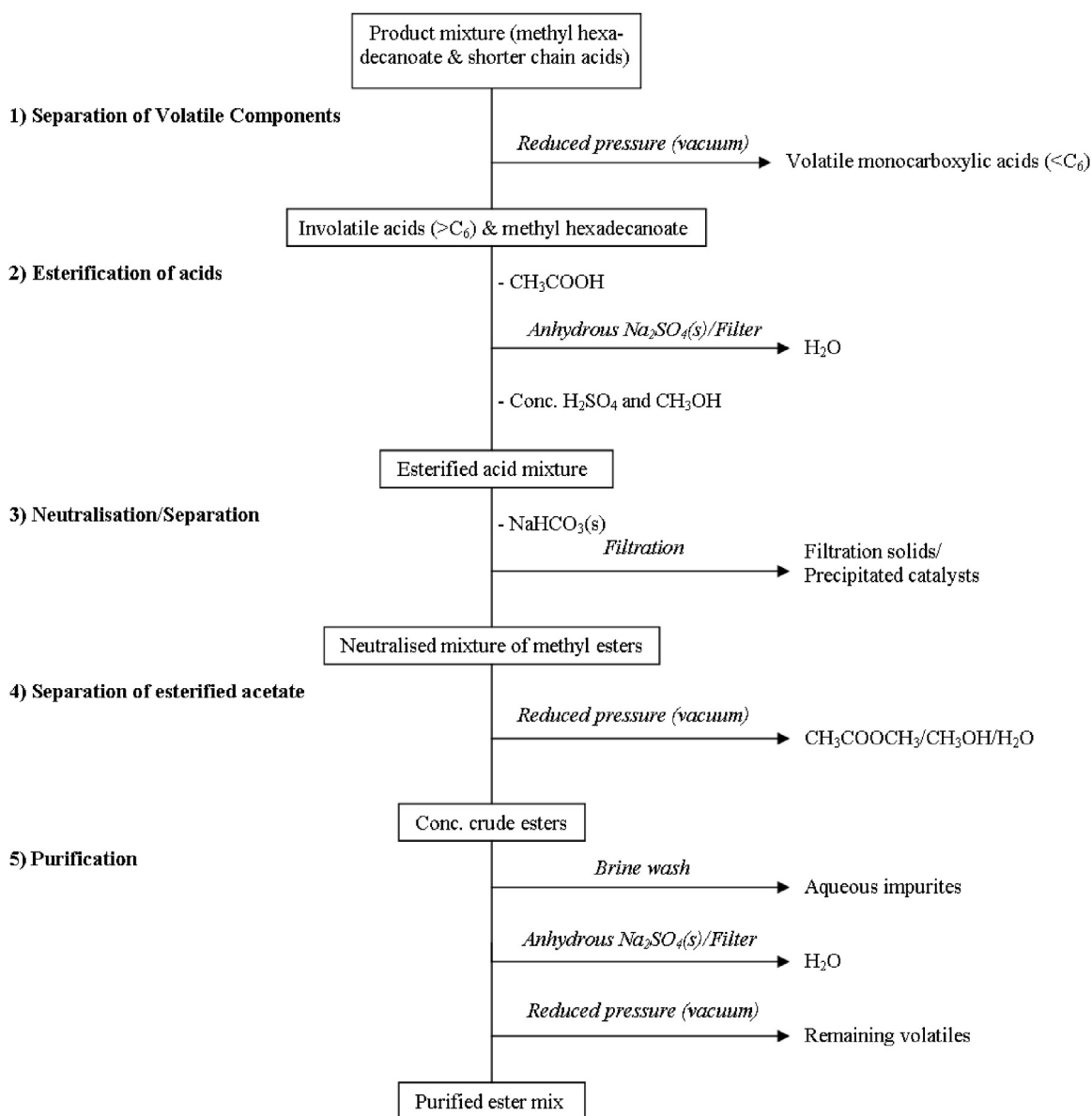


Fig. 1. General purification procedure.

2.5. Work-up—Tallow oxidation products

The work-up protocol for tallow oxidation was based on that used for methyl hexadecanoate oxidation with minor differences. Prior to the esterification of acids (Step 2), the drop-wise addition of concentrated sulfuric acid was used to adjust the pH to <math><2.5</math> (from pH 4) and any precipitated solids were removed by filtration. The precipitate was not analysed as it was assumed to consist of sulfated autoxidation catalyst. In the purification of crude esters (Step 5), a saturated NaHCO₃ solution (5 mL) wash preceded the brine wash (10 mL). This was repeated three times.

2.6. Cloud- and gel-point measurements

Since insufficient volumes of products were produced in this study to determine cloud points (CPs) by a standard method *i.e.* ASTM D2500–11 (CP test of the American Society for Testing and Materials which requires 40 mL) [19,20], the approximate CP was determined by periodic visual observation of samples contained in glass vials immersed in a refrigerated bath, the temperature of

which was progressively lowered (CPs determined in the ASTM method are also based on visual observations of the forming wax crystals) [21]. Due to this constraint, in order to report conservative values only, at all times the highest temperature at which the sample appeared to turn cloudy—'cloud point' or 'CP'—was recorded. Several of the experiments were also analysed by differential scanning calorimetry (DSC) to supplement the visual measurements.

3. Results and discussion

3.1. Work-up rationale

Minor variations in the work-up procedures were used for improved manipulation and workability of the samples, although these are not expected to affect the results. For example, in the esterification stage (Step 2), to ensure the pH was low enough for esterification, the pH was reduced beforehand. This produced a precipitate, which was presumed to be sulfated autoxidation catalyst. As the focus was to achieve improved BD with low freezing points, these solids were not analysed further. To determine

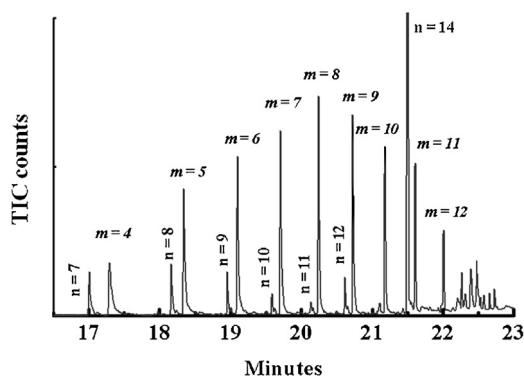


Fig. 2. Partial GC/MS chromatograms of ester mixture from autoxidation of methyl hexadecanoate showing monoesters $\text{Me}(\text{CH}_2)_n\text{C}(\text{O})\text{OMe}$ and diesters $\text{MeOC}(\text{O})(\text{CH}_2)_m\text{C}(\text{O})\text{OMe}$. Other less abundant products were detected outside the elution range shown.

the time required for complete esterification, reactions were conducted with various reaction times (2–6 h). GC analyses indicated the absence of identifiable carboxylic acids, and that virtually complete esterification with methanol occurred within 2 h under the conditions used. Measurements of samples from one of the reactions by HPLC (UV detection at 205 nm) showed the absence of triglyceride or diglyceride fragments.

In the purification stage (Step 5), to rule out a contribution to the cloud/gel point depression by any or all of, e.g. acetic acid and methanol, the product was washed with saturated aqueous NaHCO_3 solution.

To obtain meaningful measurements of cloud and gel points, it was necessary to ensure the removal of shorter chain esters that

were too volatile for BD use. Hence, the samples were evacuated for 90 min on a Schlenk line before conducting any cloud and gel point tests. Qualitative analysis by GC/MS demonstrated that this procedure was sufficient to completely remove methyl acetate and all, but a trace amount, of methyl pentanoate (b.p. 126.5°C) from the samples. The final product was a room temperature-mobile liquid.

3.2. Methyl palmitate oxidation

To verify that saturated fatty acid chains can be oxidised via Partenheimer's autoxidation method and to better understand the reactions involved, we examined the oxidation of the saturated fatty acid ester, methyl hexadecanoate (methyl palmitate), $\text{H}_3\text{C}(\text{CH}_2)_{14}\text{C}(\text{O})\text{OCH}_3$. Due to the wide variety of products and subsequent unfeasibility of full quantification, the aim was to provide a qualitative description of the products. A partial GC/MS is shown in Fig. 2. Autoxidation of methyl hexadecanoate, followed by esterification of the products with methanol yielded, as main products (by GC/MS and GC/FID) diesters $\text{MeOC}(\text{O})(\text{CH}_2)_m\text{C}(\text{O})\text{OMe}$ ($m = 5–12$). Smaller quantities of monoesters $\text{Me}(\text{CH}_2)_n\text{C}(\text{O})\text{OMe}$ where $n = 7–12$ and diesters where $m = 4$ and 13 were also formed. Traces of monoesters where $n = 4–6$ and 13 and diesters where $m = 2$ and 3 were also observed. Propanoic (the most abundant), butanoic and pentanoic acids were detected among the most volatile components of the post reaction liquids. The GC/MS chromatogram of Fig. 2 also shows that not all of the methyl hexadecanoate ($n = 14$) was autoxidised, but conversion to all oxidation products was 93% as quantified by GC-FID from the acetic acid solution removed from the reactor using mesitylene as an external standard.

Similarly to the results reported for polyethylene autoxidation [16] the products of methyl palmitate oxidation are dominated by

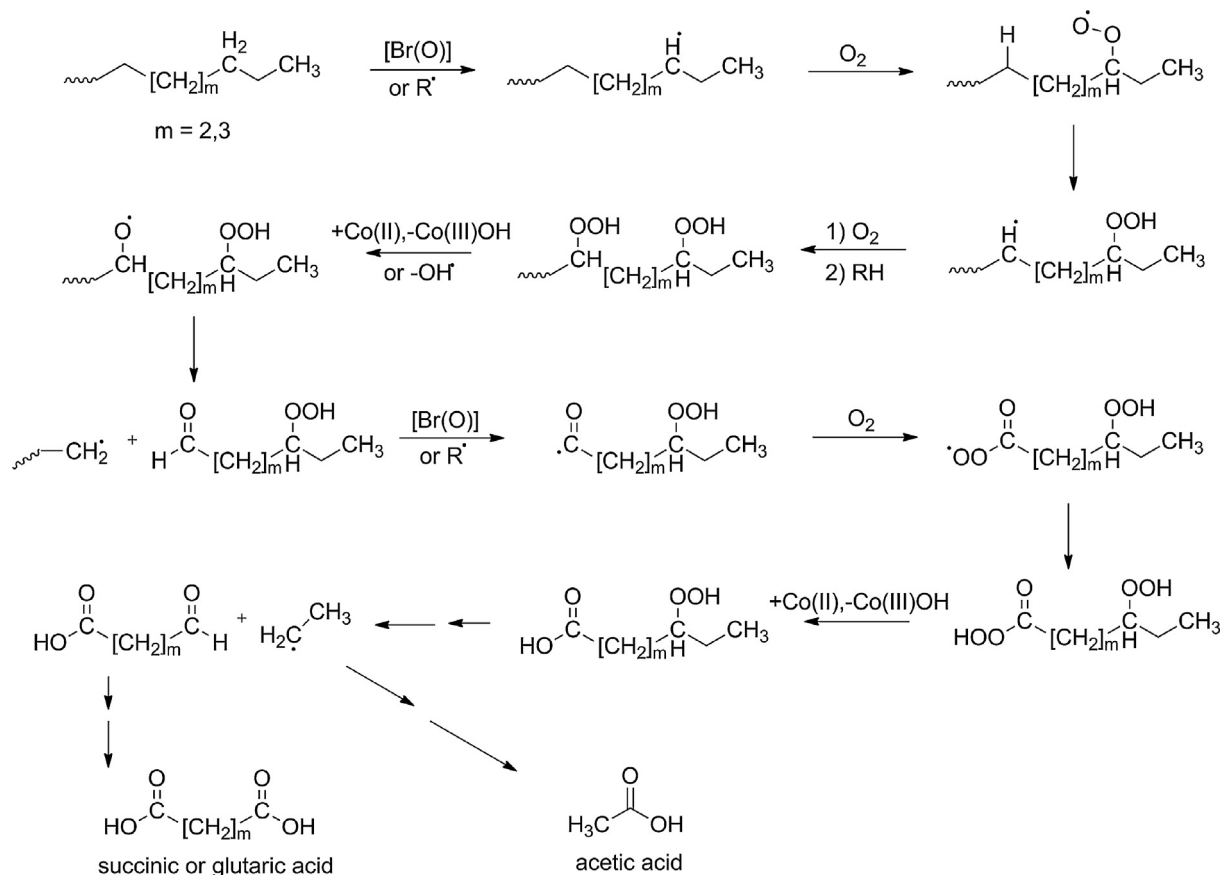


Fig. 3. Partenheimer's proposed mechanism of diacid formation from polyethylene [16].

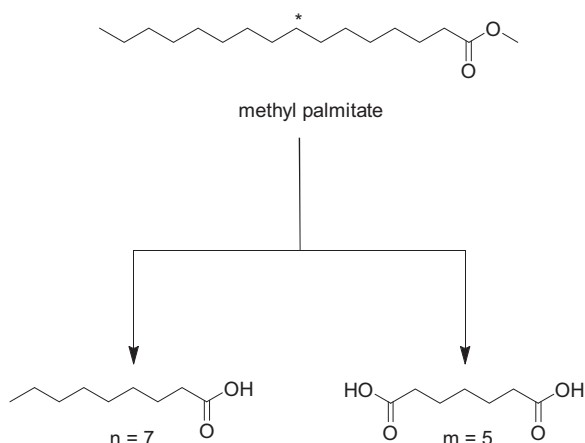


Fig. 4. Proposed product formation route of saturated fatty acid ester chains. * denotes a possible site for hydrogen abstraction and subsequent autoxidation.

diacids (here, detected as their diesters). The distribution of chain lengths, however, is significantly different in the present case. The most abundant products in the distribution of diacids ($m=7-9$) correspond to compounds substantially higher in mass than those found to dominate in polyethylene autoxidation ($m=2-4$), notwithstanding that the latter oxidation was carried out at higher pressures and with a different oxygen:substrate ratio.

Partenheimer suggested that the mechanism of polyethylene oxidation (Fig. 3) was similar to that involved in the thermal autoxidation of hexadecane [22]. Such mechanisms involve initial radical formation either by hydrogen atom abstraction from a methylene or methyne group or carboxyl radical formation [23]. The tertiary C–H bonds of the methyne groups formed during the polymerisation of ethylene [24], are favoured as the initial points of attack for oxidation mechanisms involving hydrogen abstraction, because the resulting radicals are more stable than those formed from methylene groups. Partenheimer noted that although the C–H bonds at the branching points formed during ethylene polymerisation were most favoured for initial attack during oxidation, the overall high yields of short chain diacids ($\text{HOOC}(\text{CH}_2)_m\text{COOH}$, where $m=2-4$) indicated that the linear backbone was also oxidised in his experiments. A possible mechanism for the oxidation of the linear backbone was proposed by Partenheimer, involving a cyclic transition state that originates from a dihydroperoxide via a ‘backbiting’ process. This involved reversible intramolecular hydrogen atom abstraction of the initially formed peroxy radical. Presumably cyclic transition states, where $m=2-4$ were energetically favoured; leading, in the case of polyethylene oxidation, to the observed distribution of products dominated by dicarboxylic acids $\text{HOOC}(\text{CH}_2)_m\text{COOH}$. A similar mechanism, also involving a cyclic transition state, but starting with a carboxyl radical, has been suggested to explain the distribution of products from the photo- and thermo-degradation of LDPE [23].

The difference in the product distributions between the oxidations of polyethylene and methyl palmitate suggests the dihydroperoxide ‘backbiting’ mechanism (Fig. 3) implicated as a possible reaction path in the polyethylene autoxidation is not the dominant mechanism under the conditions of our experiments. It seems likely in the absence of methyne C–H groups, the preferred sites for initial hydrogen abstraction are the methylene groups toward the centre of the chain, (and that the resulting acid may undergo further attack in a similar manner) with the overall effect of producing a series of diacids (Fig. 4). This is consistent with the observations that the higher abundance acids and diacids observed are m and $n=6-9$ as opposed to chain-end oxidation events (e.g. m , $n=4$ or 12). The rationale is that the formed radical is most

stabilised near the centre of the chain, leading to the observed product distributions.

3.3. Oxidation of canola, soy oil, and tallow triglycerides

The triglycerides of tallow, soy and canola oils represent a significant increase in substrate complexity over that of methyl palmitate. In addition to the glycerol backbone, they possess varying degrees of unsaturation. Table S1 lists the products identified in the ester mixtures derived from the autoxidation and esterification of these materials, carried out under the same conditions as used for methyl hexadecanoate. The most abundant compounds were quantified by GC/FID analysis, however the complexity of the product mixture meant that complete quantification was not possible.

The yields in Table S1 are shown as mass concentration (g/g) of substrate and molar concentration (mol/mol) of fatty acid, making the simplifying assumptions that (3 mol fatty acids = 1 mol triglycerides) and that the triglyceride molecular weight is that of triolein, i.e. 885 g/mol. The complexity of the oxidation reactions and of the substrates used precludes any detailed commentary on the reaction mechanisms taking place, therefore this discussion is confined to general features of the reactions studied, but the reaction products observed are consistent with the mechanistic discussions of the methyl palmitate reactions (*vide supra*) and the presence of additional paths involving the unsaturated moieties.

For simplicity, it is assumed that the fats and oils are composed entirely of triglycerides with a fatty acid distribution as shown in Table S2, consistent with accepted literature [2].

The dominant products as g/g substrate from the autoxidation–esterification of canola oil are dimethyl nonandioate ($m=7$) at 0.216 g/g and methyl nonanoate ($n=7$) at 0.118 g/g. This suggests that C=C cleavage is a significant reaction pathway. These compounds are expected derivatives of the products of such oxidative cleavage from oleic acid (64.40 wt% by composition from Table S2). Since HPLC measurements were showing the absence of glycerides, it is further inferred that under the acidic reaction conditions the ester bonds of the glycerides are completely hydrolysed. Interestingly, only trace amounts of glycerol were detected among the products across the triglyceride sources, suggesting that glycerol had also been oxidised.

The autoxidation products for soy oil are mainly a result of alkene cleavage reactions. In addition to oleic acid (22.80 wt%) products, linoleic acid (53.70 wt%) yields dimethyl nonandioate ($m=7$), methyl hexanoate ($n=4$) and dimethyl malonate ($m=1$) due to the position of the C=C bond (at 9 and 12 positions). As soy oil mostly consists of linoleic groups, the most abundant product quantified was methyl hexanoate ($n=4$) at 0.205 g/g followed by dimethyl nonandioate ($m=7$) 0.118 g/g which is consistent with C=C cleavage products.

Alkene cleavage has been reported for metal/bromide autoxidation reactions. Cleavage of 1-octene to heptanoic acid and formic acid, along with the formation of 5-acetylpentanoic acid, was reported by Jason and Fields, using a Co/Mn/Br catalyst in acetic acid at 170 °C with an air flow at 28 bar pressure [25]. More commonly, however, allylic oxidation or acetoxylation of the carbon atom(s) in an α -position to the double bond has been reported [26]. The metal/bromide autoxidation of hydrocarbon compounds is generally regarded as operating by means of a free radical chain mechanism [26]. Alkene cleavage is also well known in ozonolysis. This is typically achieved by bubbling through a methanolic solution of the alkene at low temperatures (–78 °C) with ozone. Following a reductive work-up, cleaved products result amongst others in aldehydes, ketones, alcohols or carboxylic acids [27].

In the case of the autoxidation of tallow, besides alkene cleavage products due to the substantial oleic acid composition (42.40%), products from the autoxidation of unsaturated palmitic (23.30%)

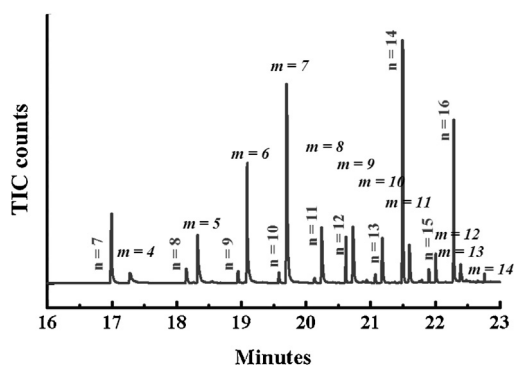


Fig. 5. Partial GC/MS chromatograms of ester mixture from autoxidation–esterification of tallow showing monoesters $\text{Me}(\text{CH}_2)_n\text{C}(\text{O})\text{OMe}$ and diesters $\text{MeOC}(\text{O})(\text{CH}_2)_m\text{C}(\text{O})\text{OMe}$. Other less abundant products were detected outside the elution range shown.

and stearic (19.40%) acids are expected. The GC/MS (Fig. 5) clearly shows peaks for dimethyl nonandioate ($m=7$) and the shorter diesters ($m=5$ and 6) similar to the product distribution of the autoxidation reaction of soy and canola oil. Additionally considerable amounts of the monoesters of palmitic ($n=14$) and stearic ($n=16$) acid can be detected, suggesting that the autoxidation reaction of saturated fatty acids is slower than that observed for unsaturated fatty acids. The remaining contributions stem from the oxidation of the saturated fatty acid chains (e.g. $m=14$) in a manner that resembles the autoxidation of methyl hexadecanoate. For example, dimethyl hexadecandioate is likely to have originated from the oxidation of stearic acid.

3.4. Low temperature properties

The low temperature properties of the autoxidised tallow, soy and canola BD and a comparison with regular tallow BD are shown in Table 1.

The cloud point of the tallow sample prepared from triglyceride substrates by transesterification using methanol and potassium hydroxide as catalyst is consistent with typical values reported in the literature [10]. A promising 1°C CP mean value was achieved through the autoxidation method. However, some variation in the CP and yields of tallow autoxidation–esterification products was observed. In some instances this was attributable to deliberate variations in the autoxidation conditions (e.g. method 1 or 2). In other instances the differences are believed to originate from the nature of the reaction: as the autoxidation is radical mediated, there is inherent variability in the product distribution. Table 2 indicates the CP values of each individual tallow autoxidation experiment. For those experiments conducted using method 1, the spread of CPs is large (5 to 1°C), although this still represents a very significant improvement over unmodified tallow BD (cf. 14°C) in each

Table 1
Summary of cloud point (CP) and differential scanning calorimetry (DSC) measurements.

	Cloud point ^a ($^\circ\text{C}$)	T_{co} ($^\circ\text{C}$)
Autoxidised soy BD	-13.0^{b}	n/a
Autoxidised canola BD	-13.0^{b}	n/a
Tallow BD	14.0	12.5
Autoxidised tallow BD	1.0	-1.5

Values are recorded to the nearest 0.5°C . T_{co} refers to the crystallisation onset temperature ($^\circ\text{C}$).

^a Values of CP are rounded to the nearest 0.5°C .

^b Estimated from a simulated mixture of esters according to Table S1.

Table 2
Cloud point (CP) and differential scanning calorimetry (DSC) measurements of individual tallow autoxidation experiments..

Experiment	Method	CP ($^\circ\text{C}$)	T_{co} ($^\circ\text{C}$)
1	1	1	0
2	1	5	4
3	1	3	3
4 ^a	2	-2	-2.5
5 ^a	2	-2^{b}	-12.5

Values are recorded to the nearest 0.5°C . T_{co} refers to the crystallisation onset temperature ($^\circ\text{C}$)

^a Autoxidation step was conducted for 4 h instead of 2 h.

^b A conservative value, the sample exhibited liquid properties towards -12.5°C .

case. Mixing samples of the esters obtained after autoxidation in the appropriate proportions as quantified in Table S1, allowed an estimate cloud point for autoxidised canola and soy BD (Table 1, column 2). Both representative samples of soy oil and canola indicated lowered CPs of -13°C , which again are substantial reductions relative to the original esters (canola: $0 \pm 3^\circ\text{C}$, soy oil: $1 \pm 2^\circ\text{C}$) [28,29]. Potentially, other triglyceride substrates, not limited to soy and

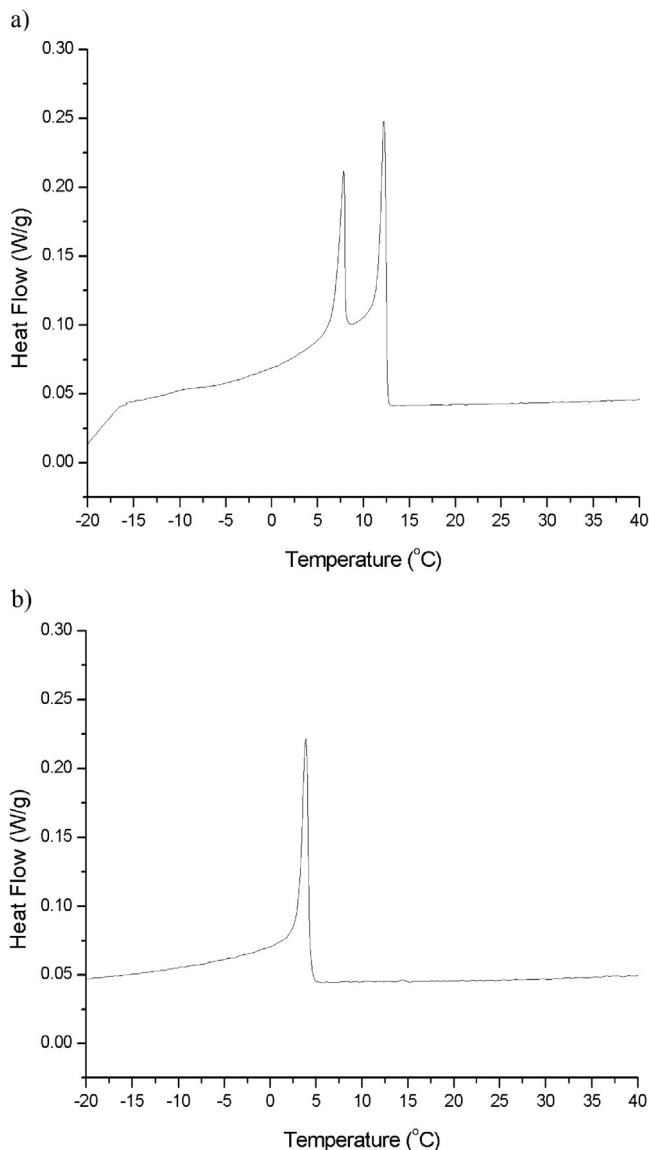


Fig. 6. Cooling DSC curves for (a) tallow BD ($T_{\text{co}}=14^\circ\text{C}$) and (b) autoxidation–esterification tallow BD ($T_{\text{co}}=5^\circ\text{C}$).

canola oil, could be used to produce BD with improved CPs over their unmodified esters.

3.5. Differential scanning calorimetry (DSC)

Even though the basis of the ASTM CP determination is also visual determination, differential scanning calorimetry (DSC) was conducted to augment and add further consistency to our observations. Cooling DSC curves for tallow BD and autoxidation tallow BD are shown in Fig. 6. The curves were recorded at a cooling rate of 1 °C/min. The crystallisation onset temperature T_{co} (Table 2) was recorded to the nearest 0.5 °C determined by the intersection of a tangent to the baseline and a tangent to the slope at the high temperature end of the endothermic peak. Under the conditions employed in this study, as a general rule, T_{co} corresponds reasonably well to the approximate CP (Table 2). As a matter of interest, two experiments were autoxidised for twice the duration (4 h vs. 2 h) and produced lower CP and T_{co} (experiments 4 and 5 in Table 2).

3.6. Viability and practicality

The ester mixture ultimately obtained from the tallow autoxidation–esterification is potentially useful as a fuel in its own right, however, by virtue of its composition it might not meet current BD standards in Australia or elsewhere. The main reasons for this would be that the shorter chain esters and possibly the shorter chain diesters would fall outside the flash point criteria specified for BD, so that the overall flash point of the BD is likely to be lower than permitted by the standards (minimum 120 °C) [30]. For this reason a likely application of the ester mix would be blending with petroleum diesel to give mixtures with lower cloud point than would result from blending with unmodified tallow BD. Alternatively, the ester mixtures could be blended with, e.g. unmodified tallow BD to produce a BD that meets relevant BD standards, but possesses a lower cloud point. In these scenarios it may prove cost-effective to treat the acids produced during the oxidation by esterification with ethanol instead of methanol. Methanol is usually the alcohol of choice for BD production, because of its lower cost, but additional cloud point depression is likely to be obtained for ethyl esters [28,31]. The use of ethanol may also lower the volatility of the ester mixture with a subsequent increase in flash point. However, these are commercial considerations directed by the regulatory framework of the time.

4. Conclusions

Homogeneous Co/Mn/Zr/bromide catalysed autoxidations in aqueous acetic acid at ca. 150 °C and 70 bar of air were conducted in a batch reactor using methyl palmitate, low grade tallow, canola oil and soy bean oil as substrates. It was found that under these reaction conditions the glyceride ester linkages will get hydrolysed and an oxidative cleavage of the fatty acid chains occurs. Preferably, the oxidative cleavage takes place at the double bonds of unsaturated fatty acids, but cleavage of saturated fatty acid chains can be also detected, as demonstrated for methyl palmitate as “model” substrate. After esterification of the autoxidised reaction mixture, the products formed were mainly (methyl-) diesters and monoesters with varying chain lengths: $\text{MeOC(O)(CH}_2)_m\text{C(O)OMe}$ where $m = 5–12$ and monoesters $\text{Me(CH}_2)_n\text{C(O)OMe}$ where $n = 7–12$ as noted by GC/FID. GC/MS and GC/FID analyses of methyl palmitate indicated that for saturated fatty acids the product distribution is best rationalised via a radical mechanism, involving initial hydrogen abstraction from the centre of the chains.

The autoxidised tallow, canola and soy bean oil BDs all have reduced CPs or T_{co} relative to BD from the unmodified oils as determined by visual observation and DSC measurements. The CP values corresponded reasonably well with those of T_{co} .

Further optimisation of reaction parameters (temperature, pressure, reaction time, etc.) is required but in principle, potentially other non-food and cost-effective (e.g. trap greases) feedstocks with a large saturated fat composition (and thus, inherently high CP), may be autoxidised in this manner. Depending on local fuel specifications, these autoxidised products may find use as an outright fuel or in blends to meet specific cold temperature property targets.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cattod.2014.02.041>.

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