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A Comprehensive Evaluation of the Melting Points of Fatty Acids and Esters Determined by Differential Scanning Calorimetry

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Abstract The melting point is one of the most important physical properties of a chemical compound and it plays a significant role in determining possible applications. For fatty acid esters the melting point is essential for a variety of food and non-food applications, the latter including biodiesel and its cold-flow properties. In this work, the melting points of fatty acids and esters (methyl, ethyl, propyl, butyl) in the C_8–C_{24} range were determined by differential scanning calorimetry (DSC), many of which for the first time. Data for triacylglycerols as well as ricinoleic acid and its methyl and ethyl esters were also acquired. For some compounds whose melting points have been previously reported, data discrepancies exist and a comprehensive determination by DSC has not been available. Variations in the present data up to several °C compared to data in prior literature were observed. The melting points of some methyl-branched iso- and anteiso-acids and esters were also determined. Previously unreported systematic effects of compound structure on melting point are presented, including those for ω-9 monounsaturated fatty acids and esters as well as for methyl-branched iso and anteiso fatty acids and esters. The melting point of a pure fatty acid or ester as determined by DSC can vary up to approximately 1 °C. Other thermal data, including heat flow and melting onset temperatures are briefly discussed.

Keywords Fatty acids · Differential scanning calorimetry · Butyl esters · Ethyl esters · Melting point · Methyl esters · Propyl esters

Introduction

The melting point (MP) of a substance is one of its most important physical properties. It plays a major role in determining the suitability and applicability of a substance in countless food and non-food applications. Numerous structural factors influence the MP of an organic compound, including the molecular weight, the number and configuration of double bonds, triple bonds, branching, stereochemistry, and the presence of one or more polar groups such as OH, with interrelationships existing between these features for specific compounds or classes of compounds. These effects are also observed in long-chain fatty compounds.

Several reasons prompted the present investigation of the MP of fatty compounds. First, while MP data for many common fatty acids and esters are given in reference works [1–5] or primary literature [6–10], such data for many other similar compounds are not readily available. Especially data for compounds with MP at lower temperatures (below ambient) are often less readily available. Therefore, in this work additional MP data are provided that are not or not readily available in the existing literature including several new systematic structure-property effects. Furthermore, most MP data that are routinely used were determined with varying equipment before the advent or more widespread use of differential scanning calorimetry (DSC). Thus a

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second goal of this work is to provide compile and evaluate such information using DSC. It may be noted that photopyroelectric measurements of melting phenomena provide information complementary to DSC [11]. A third reason is that MP data compiled from the literature (Tables 1, 2) display discrepancies for many compounds, providing an incentive to determine more accurate values.

Previous work has shown that the melting and crystallization behavior of fatty acids and esters depend strongly on structural features such as chain length, position and configuration of double or triple bonds or functional groups, with some systematic effects of the structure on MP having been established. It was recognized early [12] that the MP of a saturated fatty acid with an odd number of carbon atoms is slightly lower than that of the even-numbered fatty acid with one less carbon atom, an observation confirmed by later studies cited above. Besides the aforementioned studies on common fatty acids and esters, other literature reports MP data with systematic influences for fatty acids and esters with a variety of structures, including octadecynoic [7, 13], pentadecynoic acids [13], methyl epoxyoctadecanoates [14], methyl-substituted octadecanoic acids [15], vinyl fatty acids [16], and wax esters [17]. Recently, melting data of some methyl and iso-propyl esters of branched (iso and anteiso) acids [18] and various oleates [19] were reported.

An increasingly common industrial application of fatty esters is biodiesel [20, 21], defined as the mono-alkyl esters of vegetable oils or animal fats. While biodiesel is generally technically competitive with conventional diesel fuel derived from petroleum (petrodiesel), it features advantages in terms of domestic production, renewability, reduction of most regulated exhaust emissions except nitrogen oxides, biodegradability, inherent lubricity, and safer handling due to higher flash point. Technical problems with biodiesel include nitrogen oxides exhaust emissions, oxidative stability and cold flow. The latter problem is exemplified by the relatively high cloud and pour points of biodiesel [22]. A major factor influencing this cold flow behavior is the high MP of saturated fatty esters found in biodiesel.

Data analyzed from DSC melting and cooling (freezing) curves were correlated with measured cold flow properties of biodiesel [23]. Both cloud point (CP) and low-temperature flow test (LTFT) data indicated good probabilities of correlating to melting curve peak maximum temperatures. Completion of melt temperatures from DSC melting curves were used to predict crystallization temperatures of FAME from conventional and low-palmitic acid soybean oil [24] and mono-alkyl esters from tallow and waste grease [25, 26].

Thus cold flow is a major factor when considering which fatty esters to enrich in biodiesel when "designing" an optimized biodiesel fuel composition. In recent work, it was discussed that esters of palmitoleic acid and decanoic acid may be candidate compounds for enrichment in biodiesel to help improve cold flow while not comprising other important fuel properties [27]. Biodiesel produced by transesterification of oils or fats with medium—(C_2 or C_4) or branched—chain alcohols, instead of the more commonly used methanol, generally has better cold flow properties [24–26, 28–30]. Thus, for determining optimum mono-alkyl fatty ester compositions and for modeling the cold flow behavior of mixtures of esters such as biodiesel, accurate and consistent MP data are critical, thus providing another reason for this study.

In light of the issues mentioned above, in this work the MP of fatty acids as well as a variety of methyl, ethyl and other alkyl esters, including fatty acids with methyl branching (iso and anteiso fatty acid chains) in the C_8–C_{24} range, which covers the most common fatty acids, were determined by DSC. The MP of numerous compounds previously not investigated for this property were determined. Systematic influences for ω-9 fatty acids and esters as well as methyl-branched iso acids and methyl esters are presented for the first time. The results are compared to literature data.

Experimental

Straight-chain fatty acids and esters were obtained from Nu Chek Prep (Elysian, MN). Branched fatty acids and esters were obtained from Sigma-Aldrich (Milwaukee, WI) or Matreya LLC (Pleasant Gap, PA). To ensure purity and nature of the samples, some samples were randomly checked by GC-MS and NMR (solvent $CDCl_3$; 500 MHz for ^{1}H-NMR, 125 MHz for ^{13}C-NMR). All samples were found to be of advertised purities or higher (>98–99%). NMR also served structure verification purposes, including the double bond position for unsaturated fatty acids and esters. The position and separation of the olefinic carbon signals in ^{13}C-NMR of monounsaturated fatty acid chains depends on the proximity of the double bond to the terminal ester or methyl group [31]. Thus, for a double bond "migrating" from the 5- to the 15-position in the monounsaturated samples investigated here, a decrease in the difference of the signals of the olefinic carbons from 2.9 ppm (C20:1 Δ5) to 0.03 ppm (C22:1 Δ13) to 0 ppm (C23:1 Δ14 and C24:1 Δ15) was observed.

Differential scanning calorimetry analysis is based on determining heat flow through a sample by simultaneous measurements through a sample pan and an empty reference pan. Hermetically sealed aluminum pans were used for the present analyses. A computer-controlled DSC model Q2000 (TA Instruments, Wilmington, DE) was used

Table 1 Literature data for melting points (°C) of saturated straight-chain fatty acids and esters investigated here

Chain	Acid	Methyl ester	Ethyl ester	Propyl ester	Butyl ester	Triacylglycerol
8:0	16.5 [1, 3]; 16.3 [2] 16, 16.5 [4] 16 [5]	−40 [1–3] −37.27 [5]	−43.1 [1–3] −43.1 [5]	−46.2 [1–3] −45 [3]	−42.9 [1–3] −43 [3]	
9:0	12.2 [1], 12.3 [2], 12.4 [3] 12.5, 15 [4] 12.52 [5]	−35 [4]	−36.7 [1–3] −44.5 [4] −36.7 [5]		−38 [2, 3] −38 [4]	
10:0	31.5 fr [1]; 31.9 [2], 31.4 [3] 31.6, 31.5 [4] 31.39 [5], 31.0 [5]	−18 [1–3] −13.34 [5]	−20 [1–3] −19.9 [5]			32 [3] 32 [4]
11:0	28.6 [1–3] 29.3, 28.2–28.6 [4] 28.20 [5]		−16 [1], −15 [2, 3] −15 [5]			31.2 [4]
12:0	44 [1], 43.2 [2], 43.8 [3] 44.8, 44 [4] 44.1 [5], 44.2 [5]	5.2 FP [1], 5.2 [2, 3] 5 [4] 4.80 [5]	−1.8 FP [1], −10 [2, 3] −15.5 [5]		−7 [4]	46.4 [1]
13:0	41.5 [2, 3] 41.8, 44.5–45.5 [4] 41.76 FP [5]	6.5 [2, 3] 6.5 [4] 5.5 [5]	−4.8 [5]			44.5 [4]
14:0	58 [1], 53.9 [2], 54.2 [3] 54.4, 54 [4] 57.4 [5], 54.25 [5]	19 [1–3] 18.5 [4] 17.86 [5] 18.8–19.1 [9]	12–13 [1], 12.3 [2, 3] 12.3 [4] 11 [5] 12.6–13.0 [9]	9.4–10.0 [9]	6.2–7.0 [9]	56.5 [2], 58.5 [3] 58.5 [4]
15:0	53–54 [1], 52.3 [2, 3] 52.5, 53 [4] 52.40 [5]	18.5 [1–3] 18.5 [4] 18.5 [5] 19.2–19.4 [9]	14 [4] 11.5 [5] 12.7–13.2 [9]	11.9–12.1 [9]	6.8–7.1 [9]	
16:0	63 [1], 63.1 [2], 62.5 [3] 62.9, 63–64 [4] 62.8–63.0 [5]	30 [1–3] 30.5 [4] 29.5 [5] 30.0–30.3 [9]	α: 24 β: 19.3 [1], 24 [2, 3] 19.3 [4] 23.2 [5] 24.3–24.8 [9]	20.4 [1, 2] 20.9–21.9 [9]	16.9 [1–3] 16.8–17.1 [9]	66.4 [1], 66.5 [2.3] 66.4 [4]
17:0	62–63 [1], 61.3 [2, 3] 61.3, 62–63 [4] 60.85 [5]	30 [1–3] 30 [4] 29 [5] 29.7–30.2 [9]	28 [1, 2] 25.2 [5] 25.0–25.4 [9]	24.2–24.7 [7, 9]	20.4–21.0 [9]	64 [4]
18:0	71.2 [1], 68.8 [2], 69.3 [3] 70.1, 69.7 [4] 68.9 [5], 69.5 [5]	39.1 [1–3] 39.1 [4] 37.85 [5]	31–33 [1], 33 [2] 33.4 [4] 33.5 [5]	28.9 [1, 2] 28.6 [4] 30.8–31.4 [7]	27.5 [1, 2], 27[3] 27.5 [4] 26.6–27.2 [7]	73 [1] 73.5 [4]
19:0	69.4 [1–3] 69.4, 68.7 [4] 68.6 [5]	41.3 [n] 38.9 [4] 39.5–40.5 [5] 38.7–39.0 [9]	37–38 [5] 35.7–36.2 [9]	33.0–33.9 [7]	29.2–31.4 [7]	71 [4]

Table 1 continued

Chain	Acid	Methyl ester	Ethyl ester	Propyl ester	Butyl ester	Triacylglycerol
20:0	77 [1], 76.5 [2, 3]	54.5 [1–3]	50 [1, 2]	38.3–39.0 [7]	36.6–36.8 [7]	78 [4]
	76.1, 77 [4]	45.8–46.3 [4]	41.4–42 [4]			
	73.35 [5]	45.8 [5]	40.54 [5]			
		45.8–46.3 [9]	41.4–42.0 [9]			
21:0	75.2, 73–74 [3]	48–50 [3]	45 [4]	42.4–43.1 [6]	40.1–40.4 [6]	75.9 [4]
	74.3 [4]	48–49 [4]	44.3–44.5 [8]			
		46.7–47.0 [8]				
22:0	80 [1], 81 [2], 81.5 [3]	54 [1–3]	50 [1, 2]	45.7–46.2 [7]	43.8–44.1 [7]	82.5 [3]
	80, 81–82 [4]	54 [4]	50 [4]			
	79.95 [5]	53.2 [5]	48.25 [5]			
		52.2–52.8 [9]	47.8–48.5 [9]			
23:0	79.6, 79.1 [4]	55.6 [1]	52–53 [5]	48.4–49.2 [7]	47.3–47.5 [9]	
	79.1 [5]	53.4 [4]	50.8–51.2 [9]			
		55–56 [5]				
		53.3–53.5 [9]				
24:0	87.5 [2, 3]	59.5–60 [4]	56–57 [4]	51.8–52.3 [7]	50.6–50.8 [9]	86 [4]
	84.2, 87.5–88 [4]	57.8 [5]	54.35 [5]			
	84.15 [5]	57.8–58.3 [9]	54.2–54.5 [9]			

FP freezing point

for determining the melting phase transitions of experimental samples. The system consisted of a measurement cell fitted with a refrigerated cooling system and a model 5000 PC-based controller for conducting experiments and analyzing the resulting scans. Reference and sample pans were placed in precise positions within the cell by an autosampler. The sample purge gas was dry nitrogen at 50.00 mL/min.

Melting phase transitions were analyzed by the procedure given in American Oil Chemists' Society (AOCS) method Cj 1-94 [32]. The three-step temperature program consisted of: (1) heating the sample to the starting temperature and holding it isothermally for 10 min to ensure complete transition into the liquid phase; (2) cooling rapidly to form a solid phase and holding for 30 min; and (3) heating at 5 °C/min back across the melting region to the final temperature.

While DSC instruments are commonly calibrated with indium, the performance of the instrument at temperatures below the MP of indium (156.79 °C; enthalpy of melting = 28.66 J/g) was checked with additional materials due to the lower MP of fatty esters. Thus benzil, a common MP standard, and water were selected as compounds for comparison. The peak melting temperature values for benzil and water (distilled) were 94.37 (average of three determinations; standard deviation 0.08) and −0.04 °C (three determinations, standard deviation 0.34), respectively. A literature value for the MP of benzil is 94.87 °C [3].

For each DSC peak, an onset, peak and completion temperature (T_{on}, T_{peak}, T_{com}, respectively) can be determined directly from the scan by use of the system software. As discussed below, T_{peak} is given in the tables as MP. Typical scans are shown in Figs. 1 and 2.

Results and Discussion

In this work, the MP of saturated and unsaturated fatty acids and esters with chain lengths C_8–C_{24} were determined by DSC using AOCS method Cj 1-94. The examined chain length range covers most fatty acids as they occur naturally in vegetable oils or animal fats. Several methyl-branched saturated acids of the iso (branching at C_{n-1} in the chain) and anteiso (branching at C_{n-2}) types were also studied. Typical DSC heating scans are shown in Figs. 1 and 2. Tables 1, 2 and 3 contain literature data on the MP of compounds investigated here while Tables 4, 5, 6, and 7 present data determined during the course of this work. Table 4 presents the MP of saturated fatty acids, methyl esters, ethyl esters as well as some propyl and butyl esters for this range of fatty acid chain lengths. Table 5 lists the same information for a variety of olefinic fatty acids and esters with chain lengths C_{11}–C_{24}. Table 6 gives this information for some methyl-branched (mainly iso and anteiso) acids and esters with a total of C_{11}–C_{20} including the methyl branch. The MP of triacylglycerols

Table 2 Literature data for melting points (°C) of unsaturated fatty acids and esters investigated here

Chain	Acid	Methyl ester	Ethyl ester	Propyl ester	Butyl ester	Triacylglycerol
C11:1 Δ10	24.5 [2, 3]	−27.5 [2, 3]	−38 [2, 3]			
	24.5 [4]	−27.5 FP [4]	−37.5 [5]			
	24–24.5 [5]	−27.5 [5]				
C14:1 Δ9*c*	−4 [2]					
	−4.5 [4]					
	−4.5 to −4 [5]					
C16:1 Δ9*c*	−0.1 [2], 0.5 [3]	<15 [5]	<15 [5]			
	0.5 [4]					
	−1.0 [5]					
C16:1 Δ9*t*	32, 32–33 [4]					
C18:1 Δ6*c*	29.8 [3], 29, 31, 33 [4]					28 [4]
	31 [10]					
	28–29 [6], 29 [8]					
	28.6 [5]					
C18:1 Δ6*t*	52.7–53.4, 54–59 [4]					52 [4]
	53 [10]					
	53-54 [6], 54 [8]					
	53.6 [5]					
C18:1 Δ9*c*	16.3 [1], 13.4 [2, 3]	−19.9 [1–3]	<−15 [5]		−26.4 [1–3]	−5.5 [1], −32 [2], −4 [3]
	12 (lab), 16 (stab), 16.2 [4]	−19.6 to −19.9 [5]			−26.4 [4]	5 [4]
	13.2 [5]					
	13 [10]					
	10–11 [6], 11 [8]					
C18:1 Δ9*t*	45 [1–3]	13.5 [3]	5.8 [3]	−12.5 [4]	10.6 [4]	
	45.5, 45–45.5 [4]	13–13.5 [4]	5.1 [4]			
	43.68 [5]	<15 [5]				
	44 [10]					
	44.5–45.5 [6], 45 [8]					
C18:1 Δ11*c*	15.5, 14.5–15.5 [4]					
	13–14 [5]					
	15 [10]					
	12.5–13.5 [6], 13 [8]					
C18:1 Δ11*t*	44 [2, 3]					
	44.1, 43.5–44.1 [4]					
	43.5–44.5 [5]					
	44 [10]					
	43.5–44.5 [6], 44 [8]					
C18:1 Δ9*c*,12*c*	−5 [1]	−35 [1, 3]	<15 [5]			−11 [4]
	−5 [2]	<15 [5]				
	−5 [10]					
	−5.2 to −5.0 [5]					
C18:1 Δ9*c*, 12*c*, 15*c*	−11.3 [1]	−45.5 [3]				
	−11 [2]	<15 [5]				
	−11 [10]					
	−11.3 to −11 [5]					
C20:1 Δ5*c*	27, 26–27 [4]					
C20:1 5*t*	52.5–54 [4]					
C20:1 Δ9*c*	23–23.5 [4]					

Table 2 continued

Chain	Acid	Methyl ester	Ethyl ester	Propyl ester	Butyl ester	Triacylglycerol
C20:1 Δ9*t*	54 [4]					
C20:1 Δ11*c*	24 [2, 3]	−45 [4]				
	25, 24–25 [4]	−15 [5]				
	22 [5]					
C20:1 Δ11*t*	49–51 [4]					
	53–54 [5]					
C22:1 Δ13*c*	33–34 [1], 33.5 [2], 34.7 [3]		2–3 94 [5]			32 [4]
	33.5 (−51, −7, 2, 14) [4]					
	33.5 [5]					
C22:1 Δ13*t*	61.5 [1], 61.9 [2, 3]	34–35 [4]	30.5 [4]			58 [4]
	61.5 [4]	34–35 [5]	30–30.5 [5]			
	60 [5]					
C24:1 Δ15*c*	39–39.5 [5]					
	45–41 [4]					

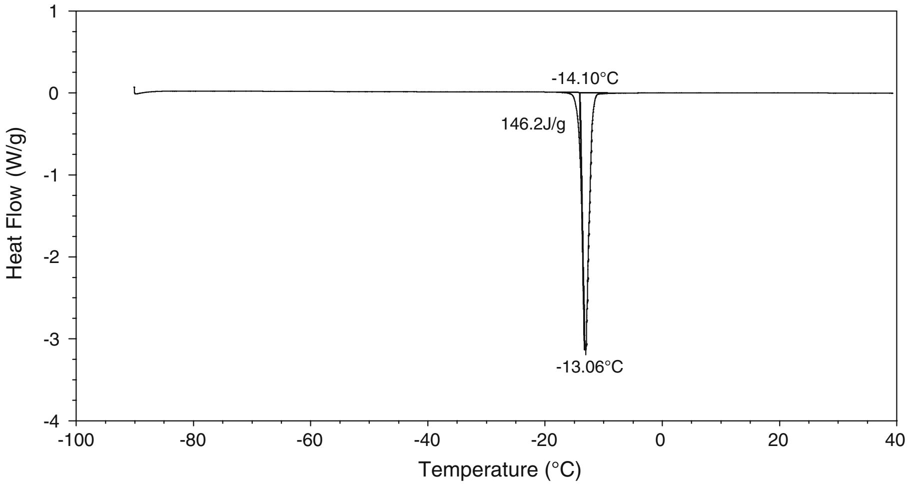

Fig. 1 DSC heating scan of methyl decanoate (data included in calculation in Table 5)

(triglycerides) of fatty acids with chain lengths C_8–C_{24} are contained in Table 7. Figs. 3, 4 and 5 are visualizations of the data in Tables 4, 5, 6 and 7.

Procedure

For sake of brevity and reasons given below, only the values of T_{peak} are given in Tables 4, 5, 6 and 7. Although generally an increase in heat flow was observable for increased chain lengths, heat flow varied considerably and was probably affected by how the sample itself was distributed within the pan. Therefore, no heat flow data are given. The variability of heat flow was confirmed by analyzing some samples sequentially five times. The heat flow decreased considerably within such a sequence, being only a fraction of the initial value when the fifth run was conducted.

Melting onset and completion can also be determined by DSC and these parameters are usually reported when AOCS method Cj 1-94 is applied to analyze oils and fats. However, these temperatures, rather the differences between melting peak maxima and onset and completion temperatures, also depend on the amount of sample, so that the melting onset and completion temperatures are not given here. The values for T_{peak} appear to be less influenced by this aspect. Generally, the difference between melting onset temperature and peak temperature (given as MP) was greater (range of 1.5–3 °C) than that between peak temperature and melting completion temperature (range 0.5–1.5 °C). The peak melting temperature is given as MP in Tables 4, 5, 6 and 7. It may be noted that, for example, the peak melting temperature given for water and benzil (see "Experimental" section) is the closest of all

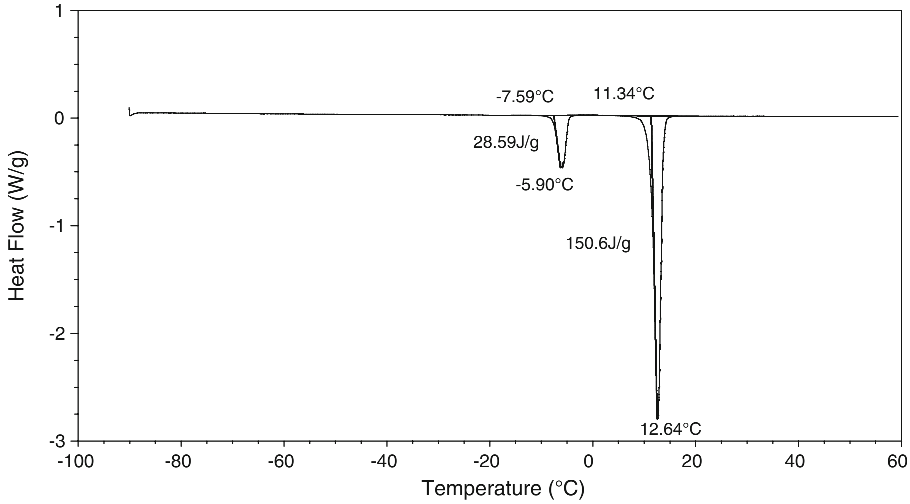

Fig. 2 DSC heating scan of oleic acid (data included in calculation in Table 5)

Table 3 Literature data for melting points (°C) of branched fatty acids and esters investigated here

Branched (iso)[a]	Acid	Methyl ester
10-Me C11	41.2 [4]	
	41.2 [5]	
12-Me C14	53 [4]	2.7 [18]
	50.5–51 [5]	
13-Me C14	52.5–53 [4]	
14-Me C15	61.8–62.4 [4]	16.5 [18]
	61.8–62.4 [5]	
15-Me C16	60.3–60.5 [4]	18.3–18.9 [4]
16-Me C17	68.8–69.7 [5]	25.7 [18]
17-Me C18	67.3–67.8 [4]	26/27.5 [4]
	67.3–67.8 [5]	26–28 [5]
	66.5–67 [15]	
18-Me C19	75.3 [5]	
Branched (anteiso)		
10–Me C12		−31.8 [18]
12-Me C14		−10.9 [18]
13-Me C15	65–66 [5]	
14-Me C16	(*S*): 39.5–40, 39–40 [4]	3.8 [18]

[a] For example, the acid termed 10-Me C11 is 10-methyl undecanoic acid with 11 carbons in the chain but possessing a total of 12 carbon atoms when counting the branching at C11

three temperatures (onset, peak, melting) to its known MP, providing a justification for using only this value.

Variations in the DSC-based MP determinations of up to approximately ±1 °C were observed. The MP points of all samples were thus determined at least in triplicate. The resulting standard deviation (SD) for a sample is given in parentheses in Tables 4, 5, 6 and 7.

The DSC scans of some compounds investigated here are more complex than only exhibiting one peak corresponding to the MP. Investigating the polymorphism of all materials exhibiting such behavior is beyond the scope of this work. In order to record any such observations, peaks indicating polymorphism are indicated in Tables 4 and 5 by peak maxima given in italics. The MP given correspond to the stable modification of the compounds investigated here. Note that in case of discrepancies with literature values, the MP determined here are usually either slightly lower than the previous literature values or tend towards the lower end of reported values.

Comparison to Prior Data

The data in Tables 1, 2 and 3 show that in many cases the MP data in the literature agree well with data observed here. However, in some cases significant differences can be observed. Furthermore, there are numerous cases in which prior literature data vary, so that the present data can be used to verify or confirm more accurate data.

Results for several compounds deviated considerably from reported literature data. The MP was −2 °C in the present work for ethyl dodecanoate compared with lower literature values of −10 and −15 °C (Table 1). Likewise, the MP of propyl heptadecanoate was 22.3 °C compared with 24.2-24.7 °C in the literature. Similar observations were made for comparison of results with literature values in Table 2 with corresponding data for alkyl oleates. Propyl oleate has MP = −30.5 versus −27.2 °C from the literature (Table 2); butyl oleate has MP = −34.8 versus −26.4 to −31.7 °C (Table 2); and butyl elaidate has MP = 0.2 versus 10.6 °C. The MP of methyl linoleate was −43.1 °C in the present work though some scans showed a minor peak near −37.8 °C, compared with a value of −35 °C from the literature. Methyl *cis*-11-eicosenoate had an MP = −7.8 °C for the present work, a value that was considerably higher than −45 °C as reported in the literature.

Table 4 Melting points (°C) of saturated fatty acids and esters determined in the present work

Chain	Acid	Methyl ester	Ethyl ester	Propyl ester	Butyl ester
8:0	15.41 (0.18)	−37.43 (0.26)	−44.74 (0.14)	−45.68 (0.32)	−43.33 (0.06)
9:0	11.28 (0.50), *−9.31 (0.19)*	−34.99 (0.53)	−43.56 (0.22)	−41.81 (0.13)	−43.10 (0.10)
10:0	30.80 (0.31)	−13.48 (0.52)	−20.44 (0.42)	−21.84 (0.19)	−22.96 (0.21)
11:0	27.32 (0.05), *17.42 (0.26)*	−12.17 (0.33)	−19.43 (0.41)	−19.70 (0.08)	−23.69 (0.14)
12:0	43.29 (0.34), *42.96 (0.03)*	4.30 (0.54)	−1.78 (0.24)	−4.35 (0.19)	−6.53 (0.19), *−7.42 (0.09)*
13:0	41.37 (0.20), *34.64 (0.46)*	5.17 (0.35)	−2.07 (0.22)		−8.48 (0.25)
14:0	53.47 (0.31), *50.52 (0.16)*	18.09 (0.42)	12.52 (0.60)	9.24 (0.37)	5.57 (0.12)
15:0	52.15 (0.17), *46.00 (0.35)*	18.47 (0.50)	11.81 (0.29)		6.26 (0.06), *3.82 (0.31)*
16:0	62.20 (0.19)	28.48 (0.44)	23.23 (0.42)	20.27 (0.23)	16.07 (0.26)
17:0	60.85 (0.34), *57.27 (0.15)*	28.58 (0.06), *25.85 (0.37)*	24.70 (0.32), *19.92 (0.41)*	22.32 (17.81)	19.68 (0.20), *9.18 (0.23)*
18:0	69.29 (0.19)	37.66 (0.25)	32.98 (0.33), *30.43 (0.33)*	28.10 (0.30), *24.93 (0.81)*	25.63 (0.18), *10.51 (0.11)*, *14.09 (0.14)*
19:0	67.76 (0.27), *66.53 (0.23)*	38.03 (0.31), *31.89 (0.13)*	35.28 (0.41), *27.30 (0.53)*	32.94 (0.24), *25.36 (0.15)*	30.71 (0.03), *15.84 (0.06)*, *18.87 (0.10)*
20:0	74.76 (0.27)	46.43 (0.38)	41.33 (0.66)	37.15 (0.07), *31.99 (0.09)*	35.14 (0.07), *20.27 (0.02)*, *23.60 (0.23)*
21:0	73.69 (0.34)	47.58 (0.34)	43.66 (0.37), *36.30 (0.28)*		
22:0	79.54 (0.34)	53.22 (0.26)	48.64 (0.25)	45.29 (0.17)	
23:0	78.74 (0.26)	53.38 (0.45)	51.22 (0.73)		
24:0	83.82 (0.42)	58.61 (0.71)	55.92 (0.16)	52.32 (0.44), *51.17 (1.22)*	

Standard deviations in parentheses. Secondary peaks likely indicating additional phase transitions are italicized

Table 5 Melting points (°C) of unsaturated fatty acids and esters determined in the present work

Chain	Acid	Methyl ester	Ethyl ester	Propyl ester	Butyl ester
11:1 Δ10	23.91 (0.14)	−24.63 (0.23)	−32.24 (0.31)		
14:1 Δ9*c*	−3.91 (1.17)	−52.26 (0.82)	−65.35 (0.38)		−66.19 (0.07)
16:1 Δ9*c*	1.22 (0.46), *−23.77 (2.69)*	−34.10 (0.26), *−43.53 (0.14)*	−36.65 (0.29)		−52.61 (0.36), −54.10 (0.14)
16:1 Δ9*t*	32.22 (0.33)	−2.99 (0.39)	−10.99 (0.29)		−12.83 (0.16)
17:1 Δ10 *c*	15.05 (0.19), −0.62	−16.02 (0.26)	−20.02 (0.32), −21.94 (0.41)		−24.35 (0.12)
18:1 Δ6 *c*	29.11 (0.14)	−0.97 (0.26)	−7.74 (0.49)		
18:1 Δ6 *t*	52.38 (0.22)	19.16 (0.20)	9.45 (0.30)		−11.35 (0.14)
18:1 Δ9 *c*	12.82 (0.15), *−5.59 (0.30)*	−20.21 (0.51)	−20.32 (0.36)	−30.50 (0.34)	−34.76 (0.43)
18:1 Δ9 *t*	43.35 (0.24)	9.94 (0.24)	4.17 (0.36)		−0.03 (0.60)
18:1 Δ11 *c*	15.40 (0.29)	−24.29 (0.72)	−36.49 (0.68)		
18:1 Δ11 *t*	43.37 (0.65)	9.94 (0.24)	4.10 (0.32)		−0.23 (0.03), −0.55
18:2 Δ9*c*, Δ12*c*	−7.15 (0.69)	−43.09 (0.71), *−37.77 (0.02)*	−56.72 (0.57), *−58.80 (1.23)*		−51.50 (0.63)
18:3 Δ9*c*, Δ12*c*, Δ15*c*	−11.58[a]		−61.71[a]	−57.63[a]	−58.61[a]
19:1 Δ10*c*	22.47 (0.29)	−2.33 (0.49)	−7.51 (0.36)		
20:1 Δ5*c*	26.61 (0.57) (4.92)	2.39 (0.20), *−45.52 (0.21)*	−8.57 (0.45), *−46.95 (0.51)*, *−18.92 (0.44)*		
20:1 Δ8*c*	35.13 (0.26) (*34.09*)	9.11 (0.43)	3.14 (0.75)		
20:1 Δ11*c*	23.37 (0.14) (*−4.68*),	−7.79 (0.34)	−8.80 (0.26)		−22.69
20:1 Δ11*t*	51.94 (0.31)	20.76 (0.41)	14.11 (0.43)		
21:1 Δ12	32.96 (0.14)	8.47 (0.15)	5.63 (0.32), *3.00 (0.06)*		
22:1 Δ13*c*	32.18 (0.37), *7.69 (0.19)*, *29.16 (0.62)*	−3.05 (0.43)	−10.54 (0.22)		
22:1 Δ13*t*	59.16 (0.39)	29.36 (0.14)	24.50 (0.34)		
23:1 Δ14*c*	43.23 (0.11), *39.28 (0.23)*	18.22 (0.13)	13.27 (0.15)		
24:1 Δ15*c*	42.87 (0.27)	9.49 (0.28)	1.21 (0.42)		

Secondary peaks likely indicating additional phase transitions are italicized

[a] Single determination

Table 6 Melting points (°C) of some branched fatty acids and methyl esters determined in the present work

Chain	Acid	Methyl ester
Iso acids		
10-Methyl C11	40.28	−13.02
11-Methyl C12	40.57	−6.87
12-Methyl C13	53.13	3.48
13-Methyl C14	51.35	6.37
14-Methyl C15 (isopalmitic)	61.94	16.80
15-Methyl C16	59.78	17.55
16-Methyl C17 (isostearic)	69.23	26.82
17-Methyl C18	66.34	27.98
18-Methyl C19	74.68	
19-Methyl C20	72.51	36.43
Anteiso acids		
12-Methyl C14	24.05	−5.29
13-Methyl C15		−13.34
14-Methyl C16	37.10	7.62

The present data can also be employed to verify more accurate data reported in the literature. For example, ethyl nonanoate had a MP = −43.6 °C (Table 4) compared to values of −36.7 and −44.4 °C in Table 1. Other examples included methyl decanoate (MP = −13.5 herein vs. −18 to −13 °C in the literature), ethyl heptadecanoate (24.7 vs. 25–28 °C), methyl eicosanoate (MP = 46.4 vs. 46–54.5 °C), ethyl eicosanoate (MP = 41.3 vs. 41–50 °C), and tetracosanoic acid (83.8 vs. 84–88 °C). The common methyl palmitate had MP = 28.5 °C in comparison with values of 24 and 29.5–30.5 °C reported in the literature.

In the present work, the MP of oleic acid was determined to be around 12.8 °C. Literature values for the MP of oleic acid given in the literature varies in the range of 10–16 °C, probably due to different crystalline modifications, although one paper [33] reports 5 °C as the MP for oleic acid as determined by DSC, a result not in agreement with the present work or with other investigations reported in the literature. For the common ester methyl stearate, a MP of 37.7 °C (Table 4) was found, a value that generally agreed well with MP data given in the literature (37–39.1 °C).

Another work [18] provides MP for various oleate esters. In that reference, the peak melting temperature of methyl oleate is reported as −17.3 °C, which is several °C higher than the value reported here. The lowest melting reported was for isopropyl oleate around −33 °C. In contrast, analysis of DSC cooling curves for methyl oleate yielded crystallization onset (freezing point) temperatures = −17.5 °C [34] and −19.8 °C [35], values comparable to those in Tables 2 and 5.

Table 7 Melting points of some triacylglycerols determined in the present work (quadruplicate determinations; standard deviations in parentheses)

Chain	Melting point (°C)
Saturates	
8:0	9.44 (0.14)
9:0	9.46 (0.09)
10:0	30.37 (0.24)
11:0	27.98 (0.84)
12:0	46.29 (0.04)
13:0	44.60 (0.25)
14:0	57.35 (0.19)
15:0	55.46 (0.05)
16:0	65.45 (0.27)
17:0	64.11 (0.06)
18:0	72.67 (0.32)
19:0	71.31 (0.29)
20:0	77.67 (0.12)
21:0	76.36 (0.43)
22:0	82.50 (0.08)
23:0	81.85 (0.22)
Unsaturates	
16:1 Δ9*c*	−22.75; 25.68, −21.81; −27.75, −21.88 (two peaks)
18:1 Δ6*c*	26.24 (0.06)
18:1 Δ9*c*	3.98 (0.59)
18:1 Δ11*c*	1.04 (0.08)
18:2 Δ9*c*, Δ12*c*	−12.70 (0.35)
19:1 Δ10*c*	26.12 (0.05)
20:1 Δ11*c*	10.11 (0.10), 17.80 (0.14)
21:1 Δ12*c*	37.97 (0.08)
22:1 Δ13*c*	29.78 (0.23)
24:1 Δ15*c*	41.43 (0.09)

Another study [36] reported MP data for several pure FAME measured by an automated “mini-cloud point” test apparatus. Although this experimental procedure is better characterized as analysis of crystallization onset temperatures, data reported as MP for methyl myristate (17 °C) and stearate (37 °C) were within 1–2 °C of results reported in the present work. An earlier work [37] analyzed and reported T_{onset} and T_{peak} from DSC heating scans performed on methyl palmitate, stearate and oleate. Onset temperatures were 1.8–2.1 °C lower than measured peak maxima for these esters. Taking the MP at peak maximum temperature resulted in values for methyl palmitate, stearate and oleate (29.9, 39.0, −18.9 °C) that agreed well with results shown in Table 4.

Saturated Unbranched Fatty Acid Chains

The data in Table 1 for saturated fatty acids confirm previous observations [9, 12] regarding alternating MP,

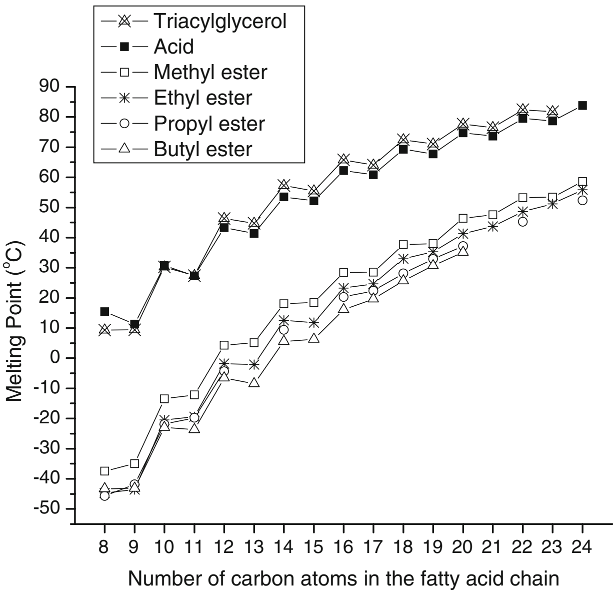

Fig. 3 Melting points [peak maximum (T_{peak})] of saturated fatty acids, esters, and their triacylglycerols

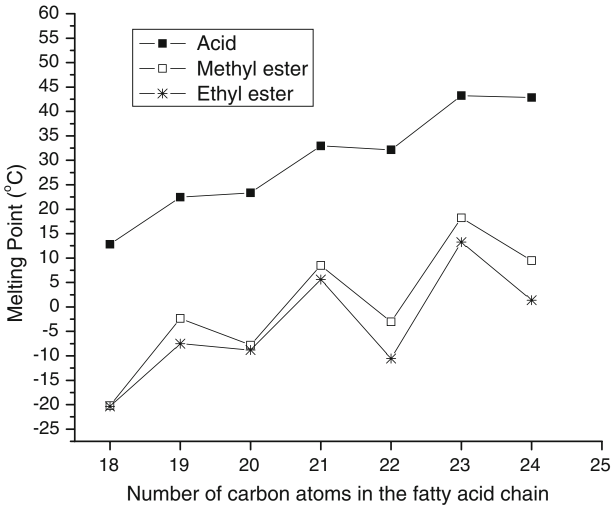

Fig. 4 Melting points (T_{peak}) of *cis* ω-9 monounsaturated fatty acids and esters

i.e., that the MP of an odd-numbered fatty acid is slightly lower than that of the preceding even-numbered fatty acid. However, differences of up to several °C compared to previous data were observed as discussed above. The increases in MP decrease with increasing chain length.

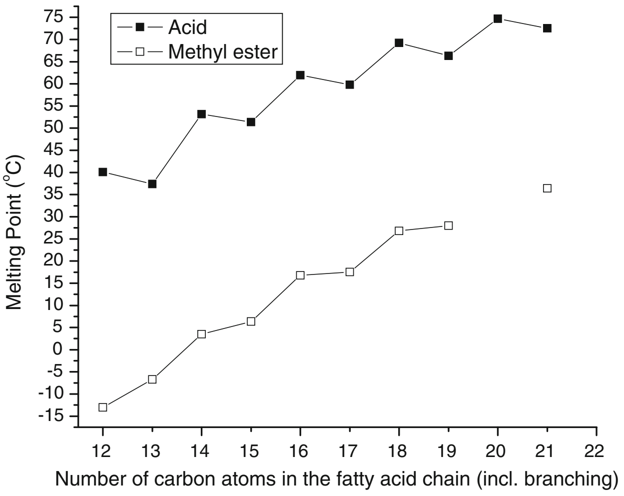

Fig. 5 Melting points (T_{peak}) of iso acids and their methyl esters. The number of carbon atoms includes those in the methyl branches

The observation regarding melting point alternation holds only partially for methyl and other esters and this effect diminishes with increasing chain length. The differences in the MP between odd-numbered and preceding even-numbered fatty acids decrease with increasing chain length for all types of esters studied here. For ethyl and higher esters, a steady increase without alternation is observed, the chain length at which this effect commences decreasing with the number of carbons in the ester moiety. In this case, the esters of odd-numbered fatty acids show only minor differences, often less than 1 °C, to those of the preceding even-numbered fatty esters. Furthermore, the MP differences between acids their corresponding esters decrease with increasing chain length.

Unsaturated Fatty Acid Chains

The introduction of one *cis* double bond in a fatty acid chain reduces the MP considerably compared to the saturated chain with the same number of carbon atoms. A *trans* double bond has comparatively little effect on the MP compared to the saturated chain with the same number of carbon atoms. This is a result of a *cis* double bond introducing a bend in the hydrocarbon chain while in the case of a *trans* double bond, the chain is propagated in a fashion close to that of the corresponding saturated species. This structural similarity of chains with *trans* double bonds to fully saturated chains is also expressed in other physical properties, such as viscosity [38].

The *cis* ω-9 fatty acids in the range of C_{18}–C_{24} show MP alternation reversed in comparison to the saturated fatty acid chains. For these fatty acids, the even-numbered *cis* ω-9 fatty acid possesses a slightly lower MP (or only slightly higher, see C_{20} vs. C_{19}) than the preceding odd-numbered fatty acid or the increase is very small (Table 5; Fig. 4). Another reversal is the strong alternation observed for the *cis* ω-9 methyl and ethyl esters in comparison to the acids. This effect is also shown by the difference in MP between the acids and the corresponding methyl esters. For the *cis* ω-9 chains with an even number of carbons, the difference in MP between the acid and the corresponding methyl ester is between 31 and 35 °C, while this difference is reduced to 24–25 °C for chains with an odd number of carbon atoms.

In other literature sources, for octadecenoic acids with *trans* configuration, exhibited zig-zag alternation for Δ5–Δ14 (MP of even-numbered acids higher, range 51–55 °C; odd-numbered acids 43–45 °C, with Δ5 at 46.5–47.5 °C [6]. Chains with *cis* configuration in the range of Δ5–Δ12 (even-numbered 23–29 °C; odd-numbered 10–13.5 °C) behaved similarly. The highest MP were found for the Δ3 acids (*cis* 49.5–50.5 °C, *trans* 64.5–65.5 °C), Δ16 acids (*cis* 53.5 °C, *trans* 65.5–66.5 °C) as well as the Δ17 acid (55.5–56.5 °C), with the Δ2-*cis* and Δ5-*trans* acids also showing high MP Δ57.5–58.5 and 58.5–59.5 °C, respectively). On the other hand, octadecynoic acids show little change in the range Δ5–Δ12, which are 45.5–52.5 °C [6]. Higher MP were reported for 4-octadecynoic acid (74–75 °C) and 2-octadecynoic acid (56–57 °C). Values related to those given in Ref. [6] are given in additional literature [10]. MP alternation was observed for odd-numbered (C15) acids with triple bonds [13], while for octadecynoic acids the MP vary significantly only towards the end of the chain [8, 13].

Since castor oil has been suggested as a potential feedstock of biodiesel, although issues such as oxidative stability, viscosity and cetane number are problematic [27], the behavior of ricinoleic acid as well as of its methyl and ethyl esters were investigated. Ricinoleic acid displayed a complex melting curve with major peaks around 6 and 15 °C. It appears to warrant further investigation beyond the scope of this work. Methyl ricinoleate exhibited an MP of −5.08 °C (SD = 0.73) and ethyl ricinoleate of −17.16 °C (SD = 1.00). The *trans* isomers (ricinelaidic acid and its esters) displayed MP around 49.25 °C (acid), 27.65 °C (methyl ester), and 24.87 °C (ethyl ester), with ricinelaidic acid not displaying the complex behavior observed in ricinoleic acid.

Methyl-Branched Fatty Acids Chains

The iso acids (acids with a methyl branch at the penultimate carbon in the chain) show zig-zag alternation of their MP similar to the saturated straight-chain fatty acids. The maxima can be depicted either for the total number of carbon atoms in which case the even-numbered fatty acids possess the higher MP (Fig. 5) or for the number of carbon atoms in the chain not taking the methyl branch into account, in which case the odd-numbered chains would exhibit the higher MP. No zig-zag alternation is observed for the corresponding methyl esters, in which case the MP increase continuously, although the differences in the increase between even and odd number of carbons decrease with increasing chain length. Furthermore, the MP differences between the acids and the corresponding methyl esters decrease with chain length. For example, the difference for the even-numbered chains decrease from about 53 °C for a total of 12 carbon atoms to about 44 °C for 18 carbon atoms, while for odd-numbered chains, the differences decrease from about 44 °C to about 36 °C for a total number of 13 or 21 carbon atoms, respectively.

The MP differences between acids and their methyl esters are greater for the methyl-branched iso acids than for the straight-chain counterparts. For example, the MP difference between stearic acid and methyl stearate is about 31.7 °C while that of isostearic acid and methyl isostearate is approximately 42.4 °C. These differences increase with decreasing fatty acid chain length. Thus, the difference between lauric acid and methyl laurate is approximately 38.8 °C while the difference between isolauric acid and methyl isolaurate is about 53.1 °C. The difference is also greater for iso acids and their methyl esters than for anteiso acids and their methyl esters.

Few anteiso acids and esters were available. However, the data for the three methyl esters show a strong MP minimum for a total of 16 carbons, implying that minima are found for even-numbered carbons of anteiso methyl esters when including the methyl branch. Generally the MP of the anteiso acids and esters are significantly below those of the iso acids and esters, showing the significance of the location of branching. The MP of two other anteiso fatty acid methyl esters are given in the literature (Table 3), [18].

Generally, for methyl-substituted octadecanoic acids, the MP reaches a minimum when the methyl group is located at C_{11}, with the MP rising if the methyl group “migrates” towards either end of the chain [15]. The MP of the methyl esters of anteiso acids show a behavior similar to that of esters of straight-chain fatty acids, however, more strongly so. This behavior also contrasts with that of the methyl esters of *iso* acids.

For epoxyoctadecanoic acids with *cis* configuration, a plateau was observed at C_8–C_{10}, with alternation broken at C_9 (m.p. 56–57 °C), and a minimum observed at C_{11} (41.5–44 °C), the reasons for which are unknown [14]. For *trans*-epoxyoctadecanoic acids, no alternation was observed, rather a well in the range of 51–55 °C exists with increases when the epoxy group moves towards either end of the chain. Therefore, the higher MP for a given position of the epoxy group varies between *cis* and *trans* configuration. Vinyl fatty acids showed similar behavior in that the even-numbered acids showed higher MP than the following odd-numbered acid [16]. For higher diesters of dicarboxylic acids, the odd-numbered acid has a higher melting point than the preceding even-numbered acid [17].

Application to Biodiesel

As mentioned in the introduction, one of the major technical issues facing biodiesel is its low-temperature properties. Minor components such as monoacylglycerols

(MAG) of saturated fatty acids (MP > 70 °C) or steryl glucosides (MP > 240 °C) may precipitate and settle at the bottom of storage tanks during cold weather, leading to clogged diesel filters and causing problems in vehicle fuel tanks [39, 40]. Saturated MAG and diacylglycerols increased CP of soybean oil FAME at concentrations as low as 0.1-0.6 wt% [40–42]. In contrast, the presence of only 10-90 ppm free (non-acylated) steryl glucosides may cause haziness in biodiesel at room temperatures [43].

The very high MP of the fatty ester components of biodiesel, such as methyl palmitate and methyl stearate, may directly influence cloud point, cold filter plugging point and other cold flow properties. Palm oil FAME consists of up to 48 wt% methyl palmitate [44] and has relatively high CP = 16 °C and CFPP = 12 °C [45]. In comparison, low erucic (<5%) rapeseed oil FAME has only 6-10% methyl palmitate + methyl stearate [20] and much lower CP = −3 °C and CFPP = −9 °C [45].

Esters such as iso-propyl or iso-butyl (ethyl esters sometimes have CP very close to corresponding methyl esters) possess lower MP than methyl esters. While this approach deals with modifying the ester moiety by using a different alcohol, another possibility is to utilize different fatty acids. Thus, it was shown that methyl decanoate or methyl palmitoleate (or other esters of decanoic or palmitoleic acid) would be suitable major components of biodiesel [27]. Acquisition of accurate MP data may be combined with thermodynamic models reported in earlier studies [36, 37] to help confirm the cold flow properties of various mixtures of fatty acid alkyl esters. Such models may also be utilized to account for the effects of trace concentrations of saturated MAG or free sterol glucosides.

Triacylglycerols

For sake of completeness of study, triacylglycerols were also studied. Literature data on triacylglycerols is included in Tables 1 and 2, while results from the present study are given in Table 7. These compounds have been studied previously for their polymorphism [46–48]. The MP given in the present work correspond to the most stable *β*-crystalline form of triacylglycerols. Note that the MP of triacylglycerols of saturated fatty acids show a behavior similar to that of methyl esters, i.e., the triacylglycerol of a fatty acid with an odd number of carbons has a slightly lower MP than of the preceding triacylglycerol of fatty acid chain with one less carbon, an observation also noted in references cited above.

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References

1. Weast RC (1985) Handbook of chemistry and physics, 66th edn. CRC Press, Boca Raton
2. Lide DR (1999) Handbook of chemistry and physics, 80th edn. CRC Press, Boca Raton
3. Lide DR (2007) Handbook of chemistry and physics, 88th edn. CRC Press, Boca Raton, FL
4. Gunstone FD, Harwood JL, Dijkstra AJ (eds) (2007) The lipid handbook, 3rd edn. CRC Press, Boca Raton
5. Doss MP (1952) Properties of the principal fats, fatty oils, waxes, fatty acids and their salts. Texas, New York
6. Gunstone FD, Ismail IA (1967) Fatty acids part 14. The conversion of the cis octadecenoic acids to their trans isomers. Chem Phys Lipids 1:264–269
7. Schlenk W Jr (1969) Long-chain carboxylic esters: melting points, rules for occurrence of vertical type crystals, and atomic distances in long spacings (Langkettige Carbonsäureester: Schmelzpunkte, Regeln für das Auftreten des Vertikaltyps der Kristallstruktur, Inkremente des grossen Netzebenenabstandes). Liebigs Ann Chem 727:1–9
8. Barve JA, Gunstone FD (1971) Fatty acids, part 33. The synthesis of all the octadecynoic acids and all the trans-octadecenoic acids. Chem Phys Lipids 7:311–323
9. Marosi L, Schlenk W Jr (1973) Melting points in homologous series of long-chain compounds (Schmelzpunkte in einigen homologen Reihen langkettiger Verbindungen). Liebigs Ann Chem 4:584–598
10. Jalal IM, Zografi G, Rakshit AK, Gunstone FD (1982) Thermal analysis of fatty acids. Chem Phys Lipids 31:395–404
11. Dadarlat D, Bicanic D, Gibkes J, Kloek W, van den Dries I, Gerkema E (1996) Study of melting processes in fatty acids and oil mixtures: a comparison of photopyroelectric (PPE) and differential scanning calorimetry (DSC). Chem Phys Lipids 82:15–23
12. Levene PA, West CJ (1914) Purification and melting points of saturated aliphatic acids. J Biol Chem 18:463–467
13. Howton DR (1970) Empirical melting point-structure relationships in the normal acetylenic carboxylic acids. J Chem Soc B 18:4–188
14. Gunstone FD, Jacobsberg FR (1972) Fatty acids, part 35. The preparation and properties of the complete series of methyl epoxyoctadecanoates. Chem Phys Lipids 9:26–34
15. Weitzel G, Wojahn J (1951) Biochemical branched-chain carboxylic acids. VI. Preparation of the racemic monomethylstearic acids. Hoppe-Seyler's Z Physiol Chem 287:296–310
16. Seher A (1956) Synthesis and properties of vinyl fatty acids. (Synthese und Eigenschaften von Vinyl-Fettsäuren). Fette Seifen Anstrichmittel 58:1077–1080
17. Iyengar BTR, Schlenk H (1969) Melting points of synthetic wax esters. Lipids 4:28–30
18. Yao L, Hammond EG (2006) Isolation and melting properties of branched-chain esters from lanolin. J Am Oil Chem Soc 83:547–552
19. Yao L, Hammond E, Wang T (2008) Melting points and viscosities of fatty acid esters that are potential targets for engineered oilseed. J Am Oil Chem Soc 85:77–82
20. Knothe G, Van Gerpen J, Krahl J (eds) (2005) The biodiesel handbook. AOCS Press, Champaign
21. Mittelbach M, Remschmidt C (2004) Biodiesel—the comprehensive handbook publ. M Mittelbach, Graz
22. Dunn RO, Bagby MO (1995) Low-temperature properties of triglyceride-based diesel fuels: transesterified methyl esters and petroleum middle distillate/ester blends. J Am Oil Chem Soc 72:895–904

23. Dunn RO (1999) Thermal analysis of alternative diesel fuels from vegetable oils. J Am Oil Chem Soc 76:109–115
24. Lee I, Johnson LA, Hammond EG (1995) Use of branched-chain esters to reduce the crystallization temperature of biodiesel. J Am Oil Chem Soc 72:1155–1160
25. Foglia TA, Nelson LA, Dunn RO, Marmer WN (1997) Low-temperature properties of alkyl esters of tallow and grease. J Am Oil Chem Soc 74:951–955
26. Wu W-H, Foglia TA, Marmer WN, Dunn RO, Goering CE, Briggs TE (1998) Low temperature property and engine performance evaluation of ethyl and isopropyl esters of tallow and grease. J Am Oil Chem Soc 75:1173–1178
27. Knothe G (2008) “Designer” biodiesel: optimizing fatty ester composition to improve fuel properties. Energy Fuels 22:1358–1364
28. Warabi Y, Kusdiana D, Saka S (2004) Biodiesel from vegetable oil by various supercritical alcohols. Appl Biochem Biotechnol 113–116:793–801
29. Zhang Y, Van Gerpen JH (1996) Combustion analysis of esters of soybean oil in a diesel engine. SAE Spec Publ SP-1160 (performance of alternative fuels for SI and CI engines). Society of Automotive Engineers, Warrendale, paper no. 960765
30. Lang X, Dalai AK, Bakhshi NN, Reaney MJ, Hertz PB (2001) Preparation and characterization of bio-diesels from various bio-oils. Bioresour Technol 80:53–62
31. Knothe G, Bagby MO (1995) ^{13}C NMR spectroscopy of unsaturated long chain compounds: an evaluation of the unsaturated carbon signals as rational functions. J Chem Soc Perkin Trans 2:615–620
32. American Oil Chemists’ Society, method Cj 1-94. AOCS, Champaign
33. Cedeño FO, Prieto MM, Espina A, García JR (2001) Measurements of temperature and melting heat of some pure fatty acids and their binary and ternary mixtures by differential scanning calorimetry. Thermochim Acta 369:39–50
34. Soriano NU Jr, Migo VP, Sato K, Matsumura M (2005) Crystallization behavior of neat biodiesel and biodiesel treated with ozonized vegetable oil. Eur J Lipid Sci Technol 107:689–695
35. de Rodrigues JA Jr, de Cardoso FP, Lachter ER, Estevão LRM, Lima E, Nascimento RSV (2006) Correlating chemical structure and physical properties of vegetable oil esters. J Am Oil Chem Soc 83:353–357
36. Imahara H, Minami E, Saka S (2006) Thermodynamic study on cloud point of biodiesel with its fatty acid composition. Fuel 85:1666–1670
37. Dunn RO (2008) Crystallization behavior of fatty acid methyl esters. J Am Oil Chem Soc 85:961–972
38. Knothe G, Steidley KR (2005) Kinematic viscosity of biodiesel fuel components and related compounds. Influence of compound structure and comparison to petrodiesel fuel components. Fuel 84:1059–1065
39. Kotrba R (2006) Bound by determination. Biodiesel Mag 3:42–50
40. Van Gerpen JH, Hammond EG, Johnson LA, Marley SJ, Yu L, Lee I, Monyem A (1996) Determining the influence of contaminants on biodiesel properties. In: Report prepared for the Iowa Soybean Promotion Board. http://www.biodiesel.org/resources/reportsdatabase/reports/gen/19960731_gen014.pdf (accessed 11/21/2008)
41. Pfalzgraf L, Lee I, Foster J, Poppe G (2007) Effect of minor components in soy biodiesel on cloud point and filterability inform supplement no. 4: biorenewable resources. AOCS Press, Champaign, pp 17–21
42. Yu L, Lee I, Hammond EG, Johnson LA, Van Gerpen JH (1998) The influence of trace components on the melting point of methyl soyate. J Am Oil Chem Soc 75:1821–1824
43. Lee I, Pfalzgraf LM, Poppe GB, Powers E, Haines T (2007) The role of sterol glucosides on filter plugging. Biodiesel Mag 4:105–112
44. Benjumea P, Agudelo J, Agudelo A (2008) Basic properties of palm oil based biodiesel–diesel blends. Fuel 87:2069–2073
45. Rashid U, Anwar F (2008) Production of biodiesel through optimized alkaline-catalyzed transesterification of rapeseed oil. Fuel 87:265–273
46. Lutton ES, Fehl AJ (1970) The polymorphism of odd and even saturated single acid triglycerides, C_8–C_{22}. Lipids 5:90–99
47. Hagemann JW, Tallent WH, Kolb KE (1972) Differential scanning calorimetry of single acid triglycerides: effect of chain length and unsaturation. J Am Oil Chem Soc 49:118–123
48. Hagemann JW, Tallent WH, Barve JA, Ismail IA, Gunstone GD (1975) Polymorphism in single-acid triglycerides of positional and geometric isomers of octadecenoic acid. J Am Oil Chem Soc 52:204–207