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Comparisons of Biodiesel Produced from Unrefined Oils of Different Peanut Cultivars

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Abstract Biodiesels were prepared according to standard procedures from unrefined oils of eight commercially available peanut cultivars and compared for differences in physical properties important to fuel performance. Dynamic viscosity, kinematic viscosity and density were measured from 100 to 15 °C, and differences ($p < 0.05$) in these physical properties occurred more frequently at lower temperatures when comparing the different cultivars. Unlike data for the oil feedstocks, no meaningful correlations among biodiesel fatty acid profiles and either fuel viscosity or density were observed. Low temperature crystallization of the peanut biodiesels was measured via differential scanning calorimetry. Increased concentrations of long chain saturated fatty acid methyl esters (FAME) were associated with an increased propensity for low temperature crystallization, and the single FAME category most associated with low temperature crystallization was C:24. Tempering at 10 °C followed by analysis of the soluble fractions (winterization), improved crystallization properties and confirmed the importance that long chain saturated FAMEs play in the final functionality of peanut biodiesel. Peanut data is also compared to data for canola and soy biodiesels, as these feedstocks are more common worldwide for biodiesel production. Overall, this work suggests that minimizing the concentration of long chain saturated FAMEs within peanut biodiesel, either through processing and/or breeding efforts would improve the low temperature performance of peanut biodiesel.

Keywords Biodiesel · Crystallization · Viscosity

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Introduction

Biodiesel is an alternative fuel that is appropriate for use in unmodified, standard diesel engines. Biodiesel production typically involves the transesterification of a triglyceride feedstock with methanol or other short-chained alcohols [1, 2]. The term biodiesel refers to the alkyl esters of fatty acids produced during this chemical reaction, with glycerin being the primary byproduct. Biodiesel can be used alone, or more commonly it is blended with petroleum based diesel.

Biodiesel has a number of important benefits which include: (1) the fuel is renewable, (2) the fuel burns cleaner in most major emission categories, (3) biodiesel is compatible with current fuel infrastructure, (4) the addition of biodiesel improves lubricity of diesel blends, (5) the use of biodiesel reduces petroleum dependence while potentially promoting domestic jobs [1, 3]. The primary concern of biodiesel producers has been a stable supply of low-cost oil feedstocks that yield a quality biodiesel product competitive in price with petroleum diesel fuels.

Refined peanut oil produced from large-scale seed oil crushing operations currently commands a high value within the edible market due to its excellent functionality as cooking oil. This price makes traditional peanut oil economically unattractive for biodiesel production. However, there is ongoing collaborative research among the

USDA ARS National Peanut Research Lab, the USDA ARS Market Quality and Handling Research Unit and the University of Georgia to develop unrefined peanut oil as an on-farm or small-scale biodiesel feedstock. Essentially, farmers would be able to grow, harvest, crush, and transesterify peanut oil into a usable fuel source to offset petroleum consumption. Accordingly, the primary goal of this work was to evaluate the quality of biodiesel produced from unrefined peanut oil that had been collected from multiple common cultivars.

This research is related to earlier studies in which unrefined peanut oils from these same cultivars were evaluated for variation in important physical properties such as viscosity, density and propensity of the oils to crystallize at low temperatures [4, 5]. Significant variation was noted among these parameters with differences generally being well explained by the differing fatty acid profiles (FAP) of these peanut oils. As such, the current research allows for a unique opportunity to directly compare oil feedstock quality factors with the corresponding biodiesel quality factors.

Materials and Methods

Materials

Peanut cultivars and the method of oil removal have been described previously [4]. Briefly, peanut pods from seven cultivars were collected from fields located near Dawson, GA, during the 2005 cropping season. A single peanut cultivar (Flavorunner-458) was sampled from Seminole, TX, during the same cropping season. The cultivars were AgraTech 201, Georgia-02C, Flavorunner-458, Georgia-01R, C-99R, AP-3, Georgia Green, C11-239, and these are abbreviated as AT-201, GA-02C, FR-458, GA-01R, C99R, AP-3, GaGreen, and C11-239 respectively. Refined soybean and canola oils were purchased locally.

Peanut Oil Extraction

Peanut shells were removed from each sample using a Hattaway (Cordele, GA) Model No. 4 lab sheller-separator. Medium-sized seed (those seed that will ride a 0.72 cm slotted screen but not a 0.84 cm screen) were kept separate for oil analysis. Peanut seed of each variety were processed in a Hander (Osaka, Japan) New 52 screw-type oil expeller. Prior to expelling, peanut seed were pre-heated between 95 and 100 °C to improve efficiency of oil expression [6]. Oil was collected in 9.5 L plastic containers and allowed to settle for 48 h at 30 ± 3 °C. Vacuum filtration was applied to the bilayer of oil to remove any unsettled particulates in preparation for further testing.

Biodiesel Preparation

Biodiesel was produced from 500 mL (0.46 mol) of peanut oil, 100 mL (2.5 mol) of methanol and 4.5 g of potassium hydroxide (.08 mol) as a catalyst. The acid number of the oil was determined by simple colorimetric titration and excess KOH was added at proper concentration to neutralize any free fatty acids. KOH and methanol were mixed in separate containers. Oils were contained in 1 L Erlenmeyer flasks and heated to a reaction temperature of 60 °C, at which time the methanol/KOH solution was added and the mixture subsequently stirred for 90 min at 120 rpm. After the reaction time was complete, the mixture was transferred to a 1-L separatory funnel for 3 h. The glycerol layer was decanted and the biodiesel was heated to 65 °C to remove excess methanol. The product was washed 5 times with 100 mL warm tap water. The final, washed product was polished by heating to 100 °C to remove water until boiling ceased. One cultivar, DP-1, which was previously evaluated for its oil physical properties [4, 5], was unavailable for biodiesel production due to logistical reasons.

Density and Viscosity Measurements

Dynamic viscosity and density were determined using an Anton-Paar (Graz, Austria) SVM3000 Stabinger-type dual viscometer/density meter from 100 to 15 °C [4, 7]. Density is simultaneously measured in the Stabinger-type viscometer to allow for the automatic calculation of kinematic viscosity. Dynamic viscosity and density were measured as a function of temperature which was automatically adjusted beginning at 100 down to 15 °C.

Fatty Acid Methyl Ester (FAME) Profile Analyses

Samples of biodiesel were analyzed according to the method of Bannon et al. [8]. Samples were diluted into hexane and analyzed by gas chromatography (GC) using a Perkin Elmer Autosampler XL GC (Perkin Elmer Instruments, Norwalk, CN) with a flame ionization detector (FID) and an SGE® capillary column containing 70% cyanopropyl polysilphenylene-siloxane as the stationary phase (30 m length 0.25 mm i.d., 0.25 μm film thickness) purchased from Phenomenex (part no. CG0-5512). Helium was used as the carrier gas at 1.85 mL/min. A temperature program was used with an initial temperature of 60 °C held for 2 min. The temperature was increased to 180 °C at 10 °C/min, then to a final temperature of 235 °C at 4 °C/min. The injector was heated to 265 °C and the split flow was 76.9 mL/min. The detector temperature was 265 °C. FAMEs were identified by comparison with FAME standards purchased from Matreya (Matreya, Inc., Pleasant Gap, PA).

Differential Scanning Calorimetry (DSC)

Crystallization and melting characteristics for the peanut biodiesels were measured with a DSC-7 equipped with an intracooler II refrigeration unit (Perkin Elmer, Norwalk, Conn.). The DSC was calibrated with mercury (onset of melting = −38.8 °C) and indium (onset of melting = 156.6 °C; heat of fusion = 28.45 J/g) and nitrogen was used as a purge gas at 30 mL/min. For each sample, 2.5 (±0.2) mg of biodiesel was loaded into a standard aluminum pan, crimped with the manufacturer's crimping tool, and accurately weighed by difference. Samples were cooled from 20 to −70 °C at 10 °C/min. Samples were run against an empty reference pan and peak temperatures were determined using PYRIS software (v. 5.0) by PerkinElmer (Waltham, Massachusetts). DSC figures were compiled using Universal Analysis software (v. 4.2E) by TA Instruments (New Castle, Delaware).

Statistical Analyses

All measurements were independently replicated a minimum of three times except for viscosity and density data, which was replicated a minimum of two times. Random samples were replicated three or more times for viscosity and density measurements, with coefficients of variation being below 2% for all samples. Statistical Analysis Software (v. 9.1) by SAS Institute Inc. (Cary, NC) was used for data analysis. Means were differentiated using PROC GLM and the Tukey multiple adjustment ($p < 0.05$). PROC REG was used to determine which fatty acid categories best correlated to cold temperature crystallization data from the DSC.

Results and Discussion

FAME profiles for the various peanut biodiesels, as well as soy and canola biodiesels, are presented in Table 1. Three of the peanut biodiesels, AT-201, GA-02C and FR-458, were produced from high oleic cultivars. Oleic acid content within these samples was approximately 80% compared to approximately 49.5–57.9% for normal oleic varieties (Table 1). The category "others" accounts for any trace FAMEs found in the peanut biodiesels and is simply computed by subtracting from 100% the summation of all the other FAME categories. For soy and canola the relative percentage of "others" was 7.3 and 9.0 respectively. Both soy and canola contain roughly 8% of C18:3 [9], which is not typically found in peanut oils at any appreciable amount, thus 18:3 comprises the majority of the "others" category for soy and canola.

To determine whether the fatty acid profiles of the oil feedstocks changed upon conversion to biodiesel, biodiesel FAMEs were compared to the FAPs of the corresponding oil feedstocks, which have been reported previously [4]. Individual plots of biodiesel vs. corresponding oil feedstock for the 9 different fatty acid (methyl ester) categories seen in Table 1 revealed linear correlations ≥0.99 for all categories excluding C24:0 and "others," for which the correlations were 0.90 and 0.70 respectively (plots not shown). Note these two categories contained the lowest percentages of fatty acids (methyl esters), meaning slight changes in fatty acid (methyl ester) content upon biodiesel conversion and/or experimental error would more strongly influence the correlation. As a whole, these comparisons showed that the fatty acid content of the oils was practically unchanged upon biodiesel conversion.

Table 1 Average relative percentage of fatty acid methyl esters found in biodiesels prepared from oils of various peanut cultivars, soy and canola

Cultivar	C 16:0	C 18:0	C 18:1	C 18:2	C 20:0	C 20:1	C 22:0	C 24:0	Others
C11-239	9.3c	2.7d	49.5f	29.0b	1.5b	1.4cd	4.2a	1.8ab	0.5d
Ga-Green	10.2a	2.6d	52.1e	27.4c	1.4cb	1.2def	2.9c	1.5de	0.6d
AP3	9.6b	2.4e	55.0d	24.1e	1.3bcd	1.5c	3.5b	1.7bc	0.8d
C99R	9.7b	3.1c	55.3d	24.3d	1.5bc	1.1f	3.0c	1.4e	0.7d
GA01R	8.2d	4.3a	57.9c	20.0f	2.1a	1.1ef	4.2a	1.6cd	0.5d
FR-458[a]	5.1f	1.8h	80.4a	4.0h	1.0de	2.3a	2.5d	1.7bc	1.2cd
AT-201[a]	6.1e	2.3f	79.9a	3.7i	1.3bcd	1.8b	2.6cd	1.6cd	0.5d
GA-02C[a]	6.0e	2.0g	79.8a	2.6k	1.2cde	2.2a	2.9c	2.0a	1.3c
SOY	10.0a	4.0b	22.3g	55.8a	0.2f	0.0g	0.4e	0.0f	7.3b
CANOLA	3.9g	1.8h	63.6b	19.0g	0.9e	1.4cde	0.3e	0.0f	9.0a

The same letter within a column indicates no significant difference ($p < 0.05$) between means

[a] High oleic acid cultivar

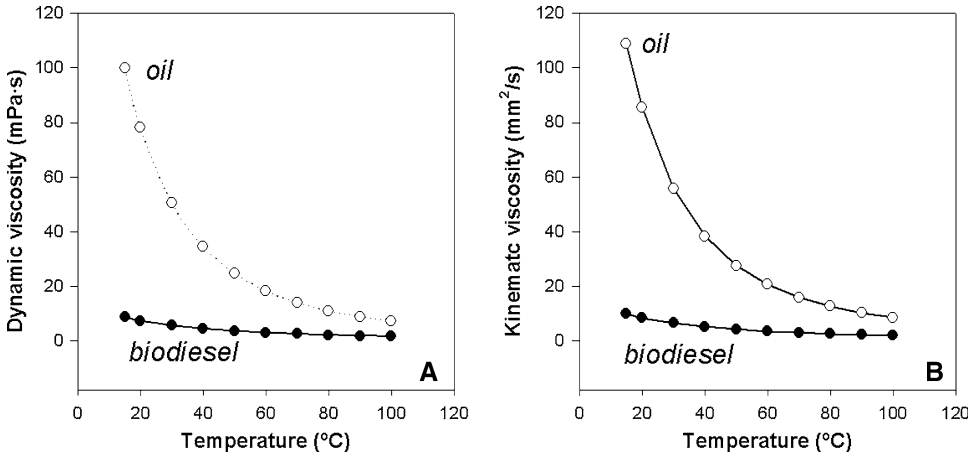

Fig. 1 Typical dynamic (**a**) and kinematic (**b**) viscosity response as a function of temperature for an unrefined peanut oil and the corresponding biodiesel produced from the same oil. Cultivar is AP-3

Seed oils are not directly utilized in unmodified diesel engines because the relatively viscous oils (as compared to standard diesel fuel) do not fully combust, leading to carbon deposition in diesel engines [10, 11]. Accordingly, seed oils are converted to biodiesel primarily to reduce fuel viscosity, thereby increasing combustibility. The viscosity of a biodiesel is approximately an order of magnitude less than the corresponding oil feedstock from which the biodiesel was prepared [12–14]. To illustrate this for peanut based fuel, plots of dynamic viscosity (A) and kinematic viscosity (B) each as a function of temperature for oil and biodiesel from peanut cultivar AP-3, which was selected at random from the peanut cultivars, is depicted in Fig. 1. Note that kinematic viscosity has units of mm^2/s and is simply the dynamic viscosity divide by the density. As seen in Fig. 1, trends for dynamic and kinematic viscosity as a function of temperature were equivalent, although the magnitudes of kinematic viscosity were slightly greater when compared at the same temperature. At 15 °C, dynamic and kinematic viscosities for oil AP-3 were approximately 99.8 mPa s and 108.9 mm^2/s, respectively, whereas the dynamic and kinematic viscosities of the biodiesel were approximately 8.7 mPa s and 9.9 mm^2/s, respectively (Fig. 1). At 100 °C, dynamic and kinematic viscosities for the oil were approximately 7.3 mPa s and 8.5 mm^2/s, respectively, whereas dynamic and kinematic viscosities of the biodiesel were 1.6 mPa s and 1.9 mm^2/s, respectively (Fig. 1). Differences in oil and biodiesel viscosity (either dynamic or kinematic) were greater at lower temperatures, with an approximate 91% reduction upon biodiesel conversion at 15 °C for AP3, as compared to an approximate 78% reduction at 100 °C.

Table 2 summarizes dynamic viscosity and density data for the eight cultivars, both for the unrefined oil feedstocks and the corresponding biodiesels produced from these same oils. Differences in biodiesel viscosity among the cultivars were more pronounced at lower temperatures with values at 15 °C ranging from 15.8 to 8.7 mPa s for GA-02C and AP-3, respectively (Table 2). Furthermore, the reduction in viscosity upon conversion of the oils to biodiesels was approximately 90% for all cultivars at 15 °C, whereas at 100 °C this reduction was closer to 80% (Table 2). The density of all peanut biodiesels were lower than the corresponding feedstocks; however these differences were minor, with a typical 3–4% density reduction observed at 15 °C and a 4–5% density reduction observed at 100 °C (Table 2). Difference ($p < 0.05$) among means were most apparent at 15 °C and as such, statistical analysis is only included for this temperature (Table 2).

ASTM Biodiesel Standard D6751-07b states that within the United States 100% biodiesel at 40 °C should have a *kinematic* viscosity between 1.9 and 6.0 mm^2/s. Kinematic viscosity is the dynamic viscosity divided by density, so for the peanut biodiesels at 40 °C, the kinematic viscosities ranged from 5.2 (AP-3, FR-458) to 6.2 (GA-01R, GA-02C and GA-Green). Three of the peanut biodiesels, GA-01R, GA-02C and GA-Green had kinematic viscosities that were 0.2 mm^2/s over specification. Optimization of the oil expelling, oil handling and transesterification processes is expected to bring all future peanut biodiesels within this specification.

Viscosity and density data for the peanut biodiesels were compared to biodiesels produced from soy and canola, as these feedstocks are more typical within the biodiesel industry. Average kinematic viscosity for soy and canola biodiesel at 40 °C was 4.3 and 5.1 mm^2/s respectively. While the value for soy was significantly lower ($p < 0.05$) than all peanut biodiesels, the value for the canola biodiesel was not significantly different than several of the peanut biodiesels. It is important to note that both the soy and canola biodiesels were prepared from refined cooking oils. In contrast, all peanut biodiesels were prepared from unrefined peanut oils. Typical seed oil refining steps remove a number of impurities from the crude oils, namely phospholipids, which were present in the peanut oils upon biodiesel production. Phospholipids are known to inhibit

Table 2 Comparison of unrefined oil and resulting biodiesel physical properties for different cultivars of peanut

	Cultivar	Oil viscosity (mPa s)	Oil density (g/cm^3)	Biodiesel viscosity (mPa s)	Biodiesel density (g/cm^3)	% Viscosity reduction	% Density reduction
100 °C	AP-3	7.3	0.8605	1.6	0.8205	78	5
	AT-201	7.5	0.8580	1.7	0.8192	78	5
	C11-2-39	7.3	0.8607	1.6	0.8218	77	5
	C-99R	7.2	0.8600	1.7	0.8219	77	4
	FR-458	7.5	0.8580	1.6	0.8178	79	5
	GA-01R	7.4	0.8592	1.8	0.8237	76	4
	GA-02C	7.6	0.8580	1.8	0.8216	76	4
	GA-Green	7.2	0.8609	1.8	0.8263	75	4
	AP-3	34.5	0.8999	4.5	0.8636	87	4
40 °C	AT-201	36.8	0.8974	4.8	0.8622	87	4
	C11-2-39	34.1	0.9001	4.6	0.8650	86	4
	C-99R	34.2	0.8996	4.7	0.8651	86	4
	FR-458	36.7	0.8975	4.5	0.8612	88	4
	GA-01R	35.4	0.8988	5.4	0.8671	85	4
	GA-02C	37.2	0.8973	5.3	0.8645	86	4
	GA-Green	33.8	0.9003	5.4	0.8693	84	3
15 °C	AP-3	99.8d	0.9169c	8.7d	0.8818e	91	4
	AT-201	109.4b	0.9143g	9.5d	0.8803f	91	4
	C11-2-39	98.1ef	0.9171b	13.7b	0.8851b	86	4
	C-99R	98.9e	0.9165d	9.3d	0.8832d	91	4
	FR-458	108.9b	0.9145f	9.5d	0.8793g	91	4
	GA-01R	103.4c	0.9158e	13.1b	0.8853b	87	3
	GA-02C	110.7a	0.9143g	15.8a	0.8842c	86	3
	GA-Green	97.3f	0.9173a	11.0c	0.8874a	89	3

The same letter within a column (15 °C) indicates no significant difference ($p < 0.05$) between means

the transesterification reaction central to biodiesel production [15], which would likely increase the types of impurities in the final peanut biodiesel products and potentially contribute to a higher viscosity. However, as oil refining is an expensive process, peanut oils were intentionally left unrefined prior to biodiesel production to replicate biodiesel production as it would likely occur on a small-scale or on-farm operation.

Dynamic viscosity, kinematic viscosity and density of the unrefined peanut oils were each well explained by comparison to FAPs of the different oils [4]. As seen in Fig. 2a, increasing concentrations of oleic acid were associated with a linear ($R^2 = 0.93$) increase in dynamic viscosity at 40 °C, whereas decreasing concentrations of linoleic acid were associated with a linear ($R^2 = 0.97$) increase in viscosity (Fig. 2a). Linoleic acid content concomitantly decreased with increasing oleic acid content for oils of the different peanut cultivars as discussed previously [4] and as seen in Table 1. Accordingly, changes in oil viscosity are attributed to both structural differences and differences in the potential for interactions among oil molecules as the fatty acid profiles change [4]. However, plots of oleic acid (methyl ester) and linoleic acid (methyl ester) content vs. dynamic viscosity at 40 °C for the peanut biodiesels, which as previously discussed had the same relative fatty acid (methyl ester) compositions as the corresponding oils, revealed no meaningful linear ($R^2 \leq 0.0004$) correlations (Fig. 2b). Previous work has shown that the kinematic viscosity of pure FAMEs decreased with an increasing degree of unsaturation [16]. However in this earlier study, kinematic viscosity was measured for single FAMEs [16], whereas in the current work the peanut biodiesels were mixtures of multiple FAMEs, which may explain the lack of any trend. It is also noted that the greatest difference among samples in biodiesel viscosity at 40 °C was only approximately 1 mPa s (Fig. 2b); meaning that correlations might be present but below the sensitivity of the measurement. However, comparison of biodiesel dynamic viscosity data to FAPs at 15 °C again revealed no meaningful correlations, despite differences in dynamic viscosity being approximately 7.0 mPa s between samples with highest and lowest viscosities (data not shown). Taken as a whole, data in Fig. 2 suggests that the higher level triglyceride structure present

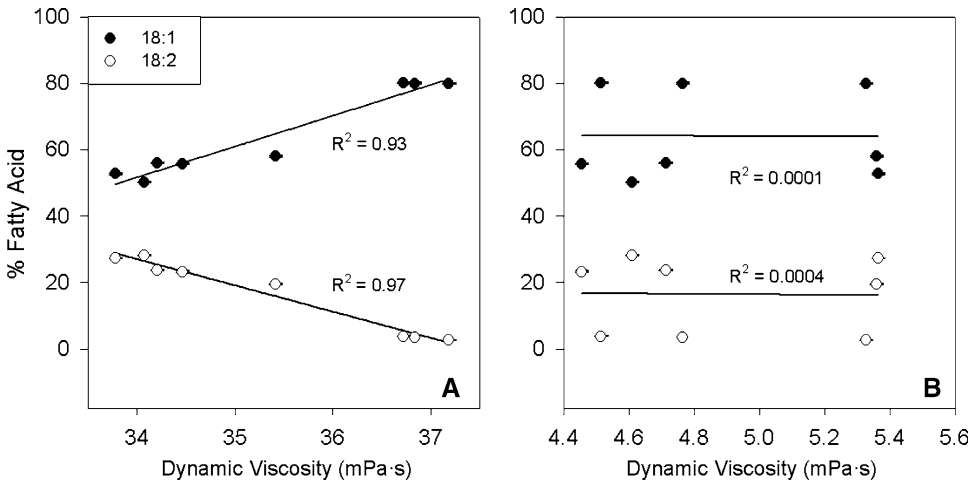

Fig. 2 Relative percentage of fatty acids found in the unrefined oils (**a**) and fatty acid methyl esters in the corresponding biodiesel (**b**) as a function of dynamic viscosity

in the oils, which is lost upon biodiesel conversion, contributes to good linear correlations observed for oil viscosity and FAP but not biodiesel viscosity and FAP.

It was also previously observed that the dynamic viscosity of the oil feedstocks increased linearly ($R^2 \geq 0.95$) with decreasing oil density at any temperature tested [4]; however, this trend was also not observed for the current biodiesels (data not shown). This again suggests that the higher level triglyceride structure present in the oils, but not in the biodiesels, contributed to the previously observed dynamic viscosity/density trend.

The lack of any meaningful observed relationship between peanut biodiesels FAMEs and viscosity suggests breeding a peanut with a specific FAP for low biodiesel viscosity is apparently not practical. It is also important to note that most biodiesel is currently blended with petroleum diesel. Most common is B20 or a 20% biodiesel to 80% petroleum diesel. Blending of this sort has been shown to satisfactorily offset the relatively high biodiesel viscosity, while also improving the functionality of the petroleum diesel, namely lubricity [17, 18]. As such, the differences observed for viscosity among the different peanut cultivars would likely be normalized to the point of practical unimportance upon blending with petroleum diesel, especially at the B20 ratio.

The propensity of a biodiesel to crystallize at sub-ambient temperatures is ultimately more important than the liquid viscosity of the fuel. During low temperature crystallization, molecules formerly in the liquid state begin to pack together, forming orderly crystals [12, 19]. These crystals can plug fuel systems causing operation problems and/or engine failure at low temperatures, which limits the use of pure and high blend biodiesel fuels at low temperatures [20]. DSC is a well established method for determining latent heat changes in a material upon either cooling (exothermic crystallization peaks) or heating (endothermic melting peaks). This method has been

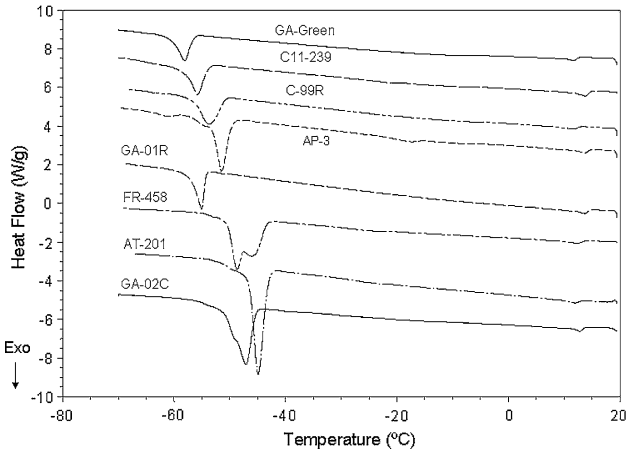

Fig. 3 Typical DSC thermograms for peanut biodiesels upon cooling

applied to monitor biodiesel crystallization and is generally considered more repeatable and more accurate than classical methods such as pour point or cloud point measurements commonly used in industrial settings [19, 20]. Furthermore, DSC transitions, namely the initial onset of crystallization have been well correlated to biodiesel cloud point data [20, 21].

Typical DSC thermograms upon cooling peanut biodiesel samples at 10 °C/min are seen in Fig. 3. Two exothermic peaks were detectable in all peanut biodiesel samples, and the first event, referred to as crystallization peak 1 (CP1), had an approximate onset temperature around 12.6–14.7 °C. The second event was a larger peak with a typical onset around −43.1 to −55.6 °C and is referred to as crystallization peak 2 (CP2). Multiple peaks were not unexpected, as complex mixtures, such as methyl esters prepared from a seed oil, typically do not crystallize at a particular temperature due to the varied chemical makeup within the liquid. Instead, there are multiple transitions that can occur as the substance transforms from a liquid to a solid [5, 20]. Cooling thermograms were also

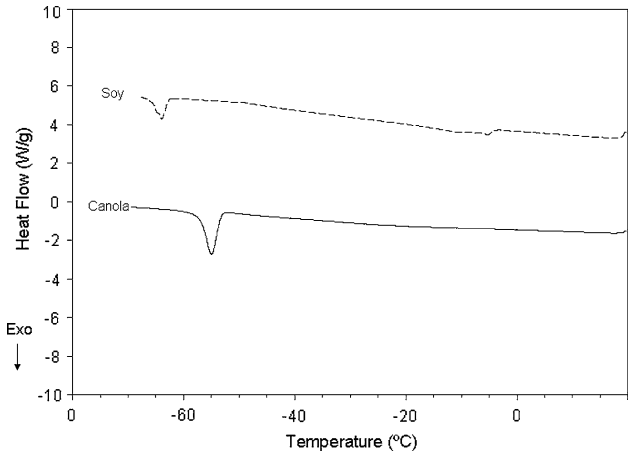

Fig. 4 Typical DSC thermograms for soy and canola biodiesels upon cooling

collected for soy and canola biodiesels for comparison (Fig. 4). Like peanut biodiesels, soy biodiesel had two distinct peaks upon cooling which are also designated CP1 and CP2. The onset of CP1 for soy biodiesel was significantly lower ($p < 0.05$) at approximately -3.8 °C. In contrast, only one cooling peak was noted for canola biodiesel and due to its proximity to CP2 in the peanut and soy samples, the sole canola peak was designated CP2. Note that the DSC scan of canola biodiesel in Fig. 4 could also be interpreted as having two peaks, with the highest melting peak being broadly spread so as to appear part of the baseline.

CP1 is considered the point at which micro-crystals begin to form in the sample and the onset of this peak should correlate to cloud point data [19, 20]. Understanding the factors that affect CP1 is critical from a biodiesel perspective, as the presence of such micro-crystals in an operating engine will cause engine damage [20]. Onset temperature for CP1 was compiled and statistically compared to the 8 FAME categories contained in Table 1 (the category "others" was excluded from this analysis as authentic standards were not experimentally run for this category). In addition to the 8 FAME categories, the summation of C20:0, C22:0 and C24:0, or the sum of all long chain saturated FAMEs, designated as "long chain saturates," was also included in this analysis. Models were constructed with different numbers of independent variables using R^2 as the selection criteria. Only peanut data was included for this analysis as the relatively large difference in crystallization onset for soy and canola artificially skewed R^2 values. From this analysis, the variable best correlated ($R^2 = 0.63$) to crystallization onset was long chain saturates. This suggests that increasing concentrations of these long chain saturates promoted a more rapid onset of crystallization. Longer chain fatty acids that are fully saturated have been shown previously to promote crystallization, both in oils, where the fatty acids are predominately in the triglyceride form [5] and in biodiesels, where the fatty acids are most typically methyl esters [19, 22]. Unsaturation within the hydrocarbon chain of a fatty acid or FAME represents a point at which the relatively linear chain is "kinked" as a result of the double bond geometry [23]. Accordingly, increasing levels of unsaturation within a fatty acid or FAME mixture typically lowers the crystallization temperature as these "kinks" hinder the ordering of the fatty acid hydrocarbon chains into crystals [5]. Soy and canola fuels contained very little of either C20:0, C22:0 or C24:0 as compared to all peanut biodiesel samples (Table 1). This may in part explain the decreased crystallization onset of both canola and soy biodiesels.

To understand factors affecting low temperature crystallization better, biodiesel samples were tempered at 10 °C for approximately 1 week or "winterized," and the soluble fractions at this temperature were subsequently collected and analyzed for any changes in FAME composition (Table 3). Average relative percentage change in biodiesel FAME compositions upon winterization are summarized in Table 3 where a positive sign indicates an enrichment upon winterization and a negative sign indicated a depletion. Of the 8 FAME categories verified against an authentic standard (everything except "others"), C:24, C:22 and C:20 were all depleted in all winterized peanut biodiesel samples. Average depletion across all peanut samples followed the order C:24 > C:22 > C:20. This further suggests that the longer chain saturates more readily crystallized and were subsequently less soluble at 10 °C. Large depletions upon winterization were seen in the category "others" for all peanut samples (Table 3). This at least partially attributable to this category representing such a small portion of the FAMEs present in these samples, i.e., less than $\sim 1.3\%$ (Table 1), meaning small changes in this category upon winterization resulted in large relative percent changes. However, this also suggests that species accounted for in the "others" category could be playing an important role in biodiesel crystallization. Likewise, C20:0 in soy biodiesel and C22:0 in canola biodiesel were actually shown to be enriched by winterization (Table 3). As there is no logical chemical/physical explanation for this finding, this observation is attributed to the very low concentrations of these species prior to winterization, i.e., less than 0.3%, meaning any changes detected upon winterization are likely due to the experimental error associated with these measurements. Finally, it is also noted that the concentration of "others" actually increased for soy and canola biodiesels upon winterization (Table 3). As C18:3 largely accounted for the "others"

Table 3 Average relative percentage change in biodiesel fatty acid methyl ester compositions upon winterization at 10 °C for 1 week

Cultivar	C 16:0	C 18:0	C 18:1	C 18:2	C 20:0	C 20:1	C 22:0	C 24:0	Others
C11-239	0.1	−3.5	4.1	0.4	−8.2	0.0	−20.6	−34.1	−83.6
Ga-Green	1.3	−3.9	3.7	−2.4	−8.1	−1.1	−12.9	−25.3	−44.6
AP3	1.2	−4.9	4.5	0.1	−9.0	−2.0	−24.4	−43.4	−91.1
C99R	0.3	−4.8	3.1	−0.5	−7.2	−1.5	−14.5	−28.0	−82.9
GA01R	6.5	2.6	9.5	−20.3	−3.2	5.5	−22.3	−37.9	−100.0
FR-458[a]	−1.8	−5.6	3.0	−7.7	−7.8	−2.4	−15.7	−34.9	−55.4
AT-201[a]	2.3	1.7	0.3	24.4	−5.2	−6.0	−14.1	−31.8	−36.4
GA-02C[a]	−1.6	−5.8	3.3	−5.1	−8.1	−3.7	−19.6	−38.9	−56.8
Average	1.0	−3.0	3.9	−1.4	−7.1	−1.4	−18.0	−34.3	−68.9
SOY	4.3	−4.4	0.7	−2.3	64.0	n/a	−17.8	n/a	7.5
CANOLA	1.6	−4.2	−0.7	2.1	−36.1	−15.8	10.6	n/a	5.1

A negative sign indicates a loss in FAME percentage upon winterization whereas a positive sign indicates a gain

[a] High oleic acid cultivar

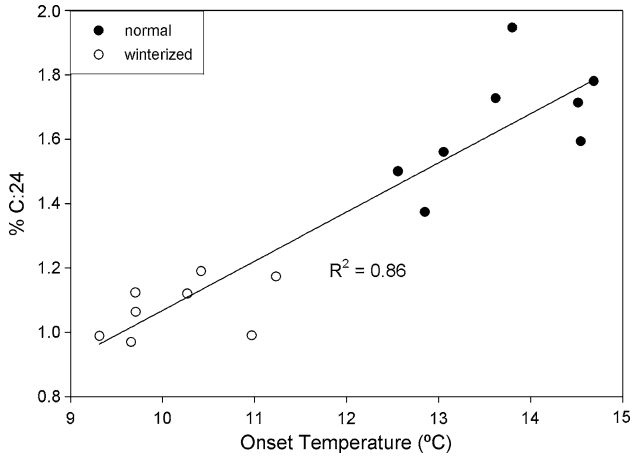

Fig. 5 Onset of crystallization (CP1) vs. concentration of C:24 in peanut biodiesels before (black data points) and after (white data points) winterization

category in the soy and canola biodiesels, it suggests this FAME was enriched upon winterization.

Onset temperature for CP1 for both normal and winterized biodiesel samples were compiled and statistically compared to all 9 FAME categories contained in Table 1 using PROC REG. Models were constructed based on the number of independent variables using R^2 as the selection criteria. From this analysis, the single variable most correlated to CP1 onset was C:24 with an R^2 of 0.88. A graphical representation of this finding is provided in Fig. 5 where it can be seen that all winterized samples crystallized at lower temperatures than the non-winterized samples. This suggests winterization may have practical applications for the improvement of low temperature peanut biodiesel production. As a whole, crystallization data suggests that if a peanut were being bred for biodiesel purposes, it would be desirable to reduce the content of long chain saturated fatty acids to improve low temperature utilization. However, this would be only one of many breeding considerations, including total oil yield, disease resistance, etc.

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