Reducing the Crystallization Temperature of Biodiesel by Winterizing Methyl Soyate

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ABSTRACT: Methyl soyate, made from typical soybean varieties, has a crystallization onset temperature (T_{co}) of 3.7°C and, as a biodiesel fuel, is prone to crystallization of its high-melting saturated methyl esters at cold operating temperatures. Removal of saturated esters by winterization was assessed as a means of reducing the T_{co} of methyl soyate. Winterizing neat methyl esters of typical soybean oil produced a T_{co} of −7.1°C, but this was not an efficient way of removing saturated methyl esters because of the low yield (26%) of the separated liquid fraction. However, a T_{co} of −6.5°C with 86% yield was obtained by winterizing the neat methyl esters of a low-palmitate soybean oil; a T_{co} of −5.8°C with 77% yield was obtained by winterizing methyl esters of normal soybean oil diluted with hexane.
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KEY WORDS: Biodiesel, crystallization, differential scanning calorimetry, low-palmitate soybean oil, methyl soyate, soydiesel, winterization.

The use of biodiesel fuels, based on blends of methyl soyate and diesel fuel (soy diesel), is limited in spite of their significant environmental benefits (1–5). Unfavorable economics and handling problems discourage widespread acceptance. The cost of producing methyl soyate is considerably greater than the cost of producing diesel fuel. Problems with soydiesel often develop from plugged fuel lines and filters, caused by crystallization of high-melting saturated methyl esters at cold operating temperatures. The crystallization properties of biodiesel fuels, traditionally methyl or ethyl esters of vegetable oils or animal fats, can be improved by replacing the straight-chain methyl or ethyl moieties with branched-chain alcohol moieties, such as isopropyl or 2-butyl (6).

Another alternative is to remove saturated methyl esters by inducing crystallization with cooling, and separating the high-melting components by filtration, a process known as winterization. Winterization is commonly used in producing refrigerator-stable salad oils by removing components that are responsible for turbidity in certain vegetable oils (7–9). Typical soybean oil contains 14–16% saturated fatty acids (~11% palmitate and 4% stearate). As a third alternative, new varieties, low in palmitic acid, have been developed that should have lower crystallization temperatures and give higher yields of winterized methyl esters. In this study, winterization was assessed as a process for reducing the crystallization temperature of biodiesel fuels, based on the methyl esters of typical and low-palmitate soybean oils.

EXPERIMENTAL PROCEDURES

Materials. Typical refined, bleached, and deodorized soybean oil (Hunt-Wesson, Inc., Fullerton, CA) was purchased locally, and refined low-palmitate soybean oil (LPSBO) that contained 3.8% palmitate was obtained from Pioneer Hi-bred International, Inc. (Johnston, IA). Reagent-grade methanol, acetone, chloroform, and hexanes were purchased from Fisher Scientific (Pittsburgh, PA). Methyl esters were prepared by transesterifying the oils with methanol (fatty acid/methanol, 1:2 on a molar basis) at room temperature by using 1% sodium methoxide as catalyst. After transesterification, the upper methyl ester layer was separated and washed with water, and the remaining methanol was evaporated from the washed methyl esters under reduced pressure.

Winterization. For winterizing neat methyl esters, about 500 mL of esters in a 600-mL Berzelius beaker was placed in a Haake F3 refrigerated bath (Haake Mess-Technik GmbH u. Co., Karlsruhe, Germany) filled with silicone XLT bath fluid (Cole-Parmer, Niles, IL). The temperature was reduced stepwise in 0.2 or 0.3°C intervals, starting from the crystallization onset temperature (T_{co}) of the unwinterized methyl esters, until crystals formed. When appropriate amounts of crystals accumulated in the methyl ester sample, the liquid fraction was transferred to another beaker through an 80-µm filter by means of water-pump vacuum. The filtered liquid methyl esters were again placed in the refrigerated bath for additional winterization at lower temperatures. The extent of crystallization at each temperature was usually tested for 16 h before the temperature was lowered. Typically, if significant crystallization occurred, the crystals accumulated rapidly, and filtration was carried out within 2 h. Yields of winterized fractions were determined by weight. Winterization was also carried out on methyl soyate mixed with various solvents (108.5 g methyl soyate in 500-mL mixture) in attempts to improve the yields.

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Analytical methods. T_{co} was measured by using a differential scanning calorimeter (DSC7), equipped with an Intracooler System II (Perkin-Elmer, Norwalk, CT). Samples of approximately 7.5 mg were weighed into aluminum pans. Empty aluminum pans were used as references. Samples were cooled to –70°C at 100°C/min and held until the heat flow stabilized. Then, samples were heated from –70 to 60°C at 5°C/min. T_{co} was determined as the high-temperature end of the highest melting transition peak from the DSC, that is, the lowest temperature at which the sample was completely liquid.

To determine T_{co} for purified methyl esters, crude methyl esters were subjected to thin-layer chromatography (TLC). Thus, 250 mg of crude methyl esters, diluted with 250 µL of hexane, was applied to a 1-mm TLC plate, and the plates were developed in hexane/diethyl ether/acetic acid (90:10:1). After the bands were visualized by spraying with 0.2% dichlorofluorescein in ethanol and were viewed under ultraviolet light, the purified esters were eluted from the plates with diethyl ether, and the solvent was evaporated under vacuum.

For fatty acid composition, the methyl esters were analyzed isothermally at 200°C by using a Hewlett-Packard Model 5890 gas chromatograph (Kennet Square, PA), equipped with a J&W (Folsom, CA) DB-23 fused-silica column (15-m length, 0.25-mm i.d., 0.25-µm film thickness) and a flame-ionization detector (6). Data for all analytical measurements are means of duplicates.

RESULTS AND DISCUSSION

Winterizing neat methyl esters of typical soy oil. Winterizing neat methyl esters of typical soy oil (typical methyl soyate) required frequent filtrations to prevent the methyl esters from congealing (Table 1). It was difficult to separate the liquid esters from the crystals, and poor yields of liquid fractions were achieved. The increased viscosity of the methyl esters at lower temperatures also reduced the mobility of saturated methyl esters and impeded the growth of the crystals, which is important for filtration efficiency (8). The methyl esters congealed if more than about 2% of saturated esters crystallized.

Thermograms of (A) unwinterized, typical methyl soyate and (B) the liquid fraction after winterizing at –10.0°C are compared in Figure 1. The T_{co} is indicated with an arrow. The peak at the higher temperature is the melting transition of saturated methyl esters, and the peak at the lower temperature is that of unsaturated esters. The size of the saturated ester peak, which represents melting enthalpy, decreased, and T_{co} shifted to a lower temperature as more winterization steps were completed. On the other hand, the size of the unsaturated ester peak, increased because of the increased portion of the unsaturates in the filtrate. The unwinterized methyl soyate had a T_{co} at 3.7°C, about 1°C lower than that of methyl esters of typical soy oil purified by TLC, probably because of melting point depression by minor impurities, such as partial glycerides or residual alcohol. The first filtration was carried out at –1.6°C, close to the cloud point of the methyl soyate, –2°C. Subsequent filtrations were carried out after about every 0.8 or 0.9°C decrease. Generally, T_{co} of the liquid fractions decreased linearly with winterization temperature [slope = 1.05, correlation coefficient (r) = 0.98]. Typically, T_{co} of the filtrate was 3–5°C higher than its winterization temperature; however, cooling time also affected the T_{co} reduction. For example, when the liquid fraction winterized at –3.0°C was cooled to –4.0°C, crystallization was so rapid and extensive that filtration was carried out after only 2 h, and T_{co} was reduced only 0.1°C.

T_{co} of typical isopropyl (IP) soyate was –6°C (6), and this T_{co} was expected to be satisfactory in 30% blends when used in extremely cold weather, such as in Minnesota in Jan-

TABLE 1
Yields and Crystallization Onset Temperatures (T_{co}) of Fractions from Winterized Neat Methyl Esters of Typical Soy Oil

Winterization step	Fraction	Temperature (°C) of winterization	Holding time (h)	Yield (%) of liquid fraction	T_{co} (°C)
	Unfractionated		0	100	3.7
1	Liquid	–1.6	16	90	2.0
2	Liquid	–3.0	2	90	1.1
3	Liquid	–4.0	2	90	1.0
4	Liquid	–4.5	10	90	Not measured
5	Liquid	–4.9	8	90	Not measured
6	Liquid	–5.5	8	84	–2.4
7	Liquid	–6.7	3	93	–2.4
8	Liquid	–7.3	6	88	–2.7
9	Liquid	–8.2	8	84	–4.2
10	Liquid	–9.0	5	88	–5.0
11	Liquid	–10.0	16	85	–7.1
6	Crystals	–5.5	8	16	5.3
11	Crystals	–10.0	16	15	–0.2
LSD[a]					0.5

[a] Least significant difference at $P < 0.05$.

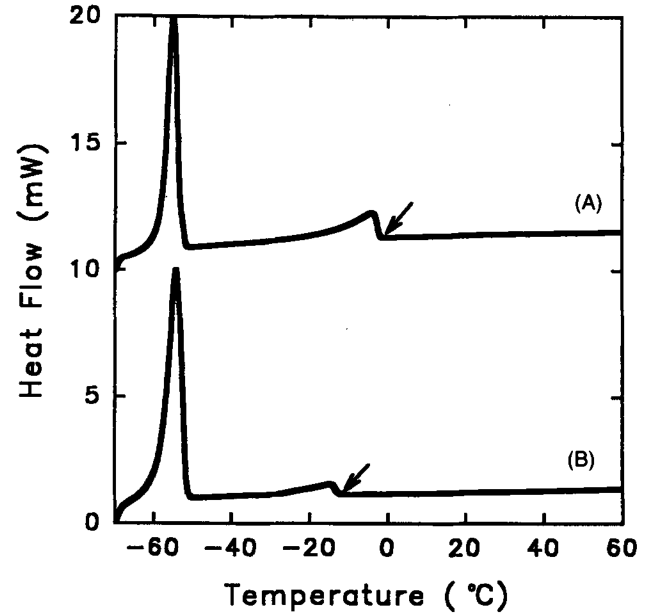

FIG. 1. Thermograms of methyl esters of typical soy oil. (A) Unwinterized control methyl soyate, and (B) liquid fraction winterized at −10.0°C in neat methyl esters.

uary. To obtain a comparable T_{co} (−7.1°C) by winterization, 11 steps were needed. The liquid yield at each winterization step was about 88% (Table 1), resulting in an accumulated total yield of 26% liquid methyl esters. The accumulated mechanical loss after the 11 steps was about 4%, with an average loss of 0.4% at each step. Therefore, winterizing typical neat methyl soyate was not an efficient way to remove high-melting saturated methyl esters because of the numerous filtrations required and the low yield.

The crystal fraction obtained in winterization might be used in warm periods or locations. The crystal fraction at −5.5°C, expected to represent approximately the pooled crystal fractions from all winterization steps (Table 1), had a T_{co} at 5.3°C, only 1.6°C above that of unwinterized methyl soyate. The T_{co} of the crystal fractions winterized at −5.5 and −10.0°C were 7.7 and 7.3°C higher than those of their liquid counterparts, respectively.

The percentages of saturated esters in the liquid fractions decreased by about 0.8%, on average, per winterization step (Table 2). The T_{co} and percentages of saturated esters in both the liquid and crystal fractions were highly correlated (r = 0.99), and the slope of the correlation indicated that the removal of 0.89% saturates decreased T_{co} by 1°C. Winterization removed the higher-melting methyl stearate faster than methyl palmitate, thus a higher palmitate/stearate ratio was observed in the liquid fraction winterized at lower temperature. The unsaturates increased proportionally as the saturates were removed. Material balances of the data in Tables 1 and 2 indicate that about 20% of the crystal fraction was saturated methyl esters, and the rest was entrained unsaturated esters.

Winterizing neat methyl esters of low-palmitate soy oil. The first filtration for neat methyl esters of low-palmitate soy oil (LPMS, low-palmitate methyl soyate) was carried out at −5.9°C (Table 3), near the cloud point of −7°C (6). Winterizing neat LPMS gave much better yields than typical methyl soyate because less material had to be removed to achieve a certain T_{co}. The yield of each winterization step for LPMS was about 93%, compared with 88% for that of typical methyl soyate. Three winterization steps were needed to achieve the T_{co} of typical isopropyl soyate (T_{co} was −6.5°C), and the overall yield after the three steps was 86%. This yield was similar to that of salad–cooking oil, achieved in commercial

TABLE 2
Fatty Acid Compositions of Fractions of Winterized Neat Methyl Esters of Typical Soy Oil

Winterization step	Fraction	Temperature (°C) of winterization	Fatty acid (%) 16:0	18:0	18:1	18:2	18:3	Saturates
	Unfractionated		10.5	4.1	23.0	54.0	7.6	14.6
1	Liquid	−1.6	9.9	3.5	23.7	55.2	7.6	13.4
2	Liquid	−3.0	9.1	3.2	24.0	55.9	7.8	12.3
3	Liquid	−4.0	8.7	2.9	24.2	56.3	7.8	11.6
4	Liquid	−5.5	6.8	2.1	24.9	58.1	8.1	8.9
5	Liquid	−6.7	6.6	2.1	25.0	58.3	8.1	8.7
6	Liquid	−7.3	6.2	1.9	25.1	58.6	8.2	8.1
7	Liquid	−8.2	5.7	1.7	25.4	59.1	8.2	7.4
8	Liquid	−9.0	4.9	1.4	25.1	59.2	8.4	6.3
9	Liquid	−10.0	4.3	1.2	25.2	59.0	8.3	5.5
2	Crystals	−3.0	15.6	6.3	21.0	49.3	6.9	21.9
3	Crystals	−4.0	13.2	5.3	21.9	51.4	7.4	18.5
4	Crystals	−5.5	12.4	4.4	22.4	52.6	7.4	16.8
5	Crystals	−6.7	8.4	2.9	23.9	56.1	7.8	11.3
6	Crystals	−7.3	9.0	3.2	23.7	55.6	7.8	12.2
7	Crystals	−8.2	7.8	2.7	24.0	56.5	8.1	10.5
8	Crystals	−9.0	8.6	2.9	23.9	55.9	7.9	11.5
9	Crystals	−10.0	7.7	2.6	24.2	56.8	7.9	10.3
LSD[a]			0.2	0.1				0.1

[a] Least significant difference at $P < 0.05$.

TABLE 3
Yields and Crystallization Onset Temperatures (T_{co}) of Fractions from Winterized Neat Methyl Esters of Low-Palmitate Soy Oil

Winterization step	Fraction	Temperature (°C) of winterization	Holding time (h)	Yield (%) of liquid fraction	T_{co} (°C)
	Unfractionated		0	100	−1.0
1	Liquid	−5.9	16	95	−3.7
2	Liquid	−7.4	8	96	−5.1
3	Liquid	−8.5	16	94	−6.5
4	Liquid	−10.2	3	92	−7.1
5	Liquid	−11.7	6	94	−7.9
6	Liquid	−12.3	11	91	−9.3
7	Liquid	−13.2	16	90	−11.2
1	Crystals	−5.9	16	5	14.0
2	Crystals	−7.4	8	4	11.8
3	Crystals	−8.5	16	6	8.3
4	Crystals	−10.2	3	8	5.1
5	Crystals	−11.7	6	6	−1.6
6	Crystals	−12.3	11	9	0.8
7	Crystals	−13.2	16	10	0.8
LSD[a]					0.6

[a]Least significant difference at $P < 0.05$.

winterization of partially hydrogenated soybean oil, 75–85% (7). T_{co} of the liquid fraction of LPMS correlated with the winterization temperature ($r = 0.97$), with T_{co} 2–4°C higher than the winterization temperature.

Based on yield only, we estimate that winterizing LPMS will increase the price of liquid methyl soyate by about 16%, and the costs of the winterization process itself will further increase costs. But these costs may be mitigated by using the crystal fraction in diesel fuel in summer or in warm climates. T_{co} of the highest-melting crystal fraction was about 14°C, which is about 3°C lower than that of the methyl esters of lard or tallow.

Fatty acid compositions of both liquid and crystal fractions from each winterization step of LPMS are shown in Table 4. T_{co} and the percentage of saturated esters, as in typical methyl soyate, were highly correlated ($r = 0.99$). However, the slope was only 0.29, compared with 0.90 for typical methyl soyate, which means that the removal of 0.29% saturates in LPMS caused ~1°C drop in T_{co}. During the first four winterization steps, mainly methyl stearate crystallized out when using LPMS; then, the proportion of methyl palmitate in the crystals began to exceed that of methyl stearate. The data (Table 4) also show that the saturate level of LPMS must be reduced to 5.5% to achieve the T_{co} of IP soyate; however, the palmitate/stearate ratio also affects T_{co}. Material balances of the data in Tables 3 and 4 showed that the average percentage of saturated esters in the crystal fraction was about 13% for LPMS, compared with 20% for typical methyl soyate.

TABLE 4
Fatty Acid Compositions of Fractions of Winterized Neat Methyl Esters of Low-Palmitate Soy Oil

Winterization		Temperature (°C)	Fatty acid (%)					
step	Fraction	of winterization	16:0	18:0	18:1	18:2	18:3	Saturates
	Unfractionated		4.0	2.8	18.8	62.9	10.4	6.8
1	Filtrate	−5.9	4.0	2.3	18.8	63.2	10.4	6.3
2	Filtrate	−7.4	3.9	2.0	19.0	63.7	10.4	5.9
3	Filtrate	−8.5	3.9	1.6	19.1	63.9	10.2	5.5
4	Filtrate	−10.2	3.8	1.5	19.2	64.1	10.4	5.3
5	Filtrate	−11.7	3.8	1.3	19.2	64.4	10.4	5.1
6	Filtrate	−12.3	3.4	1.2	19.3	64.6	10.5	4.6
7	Filtrate	−13.2	2.9	0.9	19.4	65.2	10.5	3.8
1	Crystals	−5.9	5.4	11.2	16.9	56.2	9.1	16.6
2	Crystals	−7.4	5.3	9.4	17.3	57.5	9.4	14.7
3	Crystals	−8.5	5.0	4.9	18.2	60.9	9.9	9.9
4	Crystals	−10.2	5.1	6.7	18.0	59.7	9.5	11.8
5	Crystals	−11.7	5.2	2.7	18.6	62.3	10.1	7.9
6	Crystals	−12.3	7.3	3.4	18.0	60.4	9.7	10.7
7	Crystals	−13.2	8.0	3.1	18.0	60.2	9.7	11.1
LSD[a]			0.2	0.1				0.2

[a]Least significant difference at $P < 0.05$.

TABLE 5
Yields and Crystallization Onset Temperatures (T_{co}) of Fractions from Methyl Esters of Typical Soy Oil Winterized in Hexane

Winterization (°C) step	Fraction	Temperature (°C) of winterization	Holding time (h)	Yield (%) of liquid fraction	T_{co} (°C)
	Unfractionated		0	100	3.7
1	Liquid	−21.5	5	90	0.7
2	Liquid	−25.0	16	88	−3.7
3	Liquid	−28.4	16	95	−5.8
1	Crystals	−21.5	5	10	18.2
2	Crystals	−25.0	16	12	16.8
3	Crystals	−28.4	16	5	13.3
LSD[a]					0.5

[a]Least significant difference at $P < 0.05$.

Winterizing methyl esters of typical soy oil in various solvents. Because of the poor yields of the winterized neat methyl esters of typical soy oil, diluting the esters with various solvents was tested. Methanol, acetone, chloroform, and hexane were used as diluting solvents. Methanol had the advantage that the winterization could be practiced directly on the esterification reaction mixture. But when the methanol/methyl ester solution was cooled to −1.6°C, two separate liquid layers were observed; the ratio of upper to lower layers was 3.7:1 by weight. The upper layer consisted mainly of methanol (15.2 wt% methyl esters), and the lower layer with scattered crystals was mainly methyl esters (83.0 wt% methyl esters). The poor solubility of methyl esters in methanol at low temperature was not desirable for winterization.

No liquid phase separation took place on cooling a methyl ester/acetone mixture (21.7% wt/vol), and filtrations were carried out at −11.3 and −12.3°C, for which the yields were 95 and 83%, respectively. However, because there was little decrease in T_{co} of the filtrates and little change in the fatty acid compositions of the winterized fractions, work with acetone was abandoned.

Table 5 shows the yields and T_{co} of the liquid and crystal fractions that resulted from winterizing a typical methyl soyate/hexane mixture (21.7% wt/vol). There was no liquid phase separation as the methyl ester/hexane mixture was cooled, and the first filtration was carried out after winterizing the sample at −21.5°C. Only three steps of crystallizing were required to give a T_{co} that was comparable to that of typical isopropyl soyate (T_{co} was −5.8°C), and the overall yield was 77%. Fatty acid compositions of both liquid and crystal fractions, winterized in hexane, are shown in Table 6. A plot of T_{co} and percentage saturates of the liquid fractions fit well into the correlation obtained from winterization of neat methyl esters. Material balances from the data in Tables 5 and 6 showed that the percentage of saturated methyl esters in the crystal fractions was 43%, compared with 20% with neat methyl esters, demonstrating the improved separation of crystals from liquid methyl esters that is achieved by diluting with hexane.

A typical methyl soyate/chloroform mixture (21.7% wt/vol) gave neither liquid phase separation nor crystal formation when cooled below −25°C, thus winterization in chloroform was abandoned. Seemingly, crystal formation was affected greatly by the solvent used, and the solubility of methyl esters in a solvent was largely determined by the polarities of the methyl esters and the solvent.

In conclusion, winterizing neat methyl esters of typical soybean oil was not an efficient way to reduce the T_{co} because of poor separation of the liquid from the crystalline fraction. However, winterized esters, having T_{co} comparable to those

TABLE 6
Fatty Acid Compositions of Fractions from Methyl Esters of Normal Soy Oil Winterized in Hexane

Winterization		Temperature (°C)	Fatty acid (%)					
step	Fraction	of winterization	16:0	18:0	18:1	18:2	18:3	Saturates
	Unfractionated		10.5	4.1	23.0	54.0	7.6	14.6
1	Liquid	−21.5	8.5	2.7	24.5	56.3	8.0	11.2
2	Liquid	−25.0	5.8	1.6	25.5	58.8	8.4	7.4
3	Liquid	−28.4	4.8	1.2	25.9	59.6	8.4	6.0
1	Crystals	−21.5	31.8	14.8	15.7	33.2	4.5	46.6
2	Crystals	−25.0	30.3	11.9	16.5	36.2	5.1	42.2
3	Crystals	−28.4	25.0	8.1	18.8	42.2	6.0	33.1
LSD[a]			0.2	0.1				0.2

[a]Least significant difference at $P < 0.05$.

of isopropyl esters, were obtained by winterizing neat LPMS and typical methyl soyate diluted with hexane; the total yields were 86 and 77%, respectively.

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