

# The Influence of Trace Components on the Melting Point of Methyl Soyate

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**ABSTRACT:** The objective of this study was to determine the effect of various amounts of unsaponifiables and bound glycerol on the crystallization temperatures of methyl soyate used as biodiesel. The preparation of methyl esters did not affect the amount of unsaponifiable matter in biodiesel. A synthetic unsaponifiable mixture added to distilled methyl soyate and blends of methyl soyate and No. 1 diesel fuel (20:80, vol/vol) did not affect the crystallization onset temperature, cloud point, or pour point at concentrations up to 3% by weight. The amounts of monoglycerides and diglycerides in methyl soyate decreased from 2.60 and 9.87%, respectively, to 0% as the methanol/soybean oil ratio increased from 90 to 200% of the theoretical requirement. Transesterification reactions conducted with less than 130% of the theoretical amount of methanol resulted in methyl soyate with a higher cloud point because of the presence of saturated mono- and diglycerides. Pure mono- and diglycerides added to distilled methyl soyate at 0 to 1.0% did not change the pour point of the esters, but the cloud point of esters increased with increasing amount of saturated mono- or diglyceride. Pure saturated mono- or diglyceride presented in concentrations as low as 0.1% increased the cloud point of methyl soyate. Similar results were obtained with mono- and diglyceride mixtures present in incompletely converted methyl soyate.

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**KEY WORDS:** Biodiesel, diglycerides, melting point, methyl soyate, monoglycerides, unsaponifiable matter.

Methyl soyate is produced for use as a diesel fuel by transesterification of soybean oil with methanol and, depending on production methods, may contain unsaponifiable matter, glycerol, and partial glycerides in various amounts. These impurities may affect the suitability of the methyl soyate as a diesel fuel, and criteria and specifications for methyl soyate are under development by The American Society for Testing and Materials (ASTM) and the American Society of Agricultural Engineers (ASAE) (1).

Typical crude soybean oil contains as much as 1.6% unsaponifiable matter, composed of plant sterols, tocopherols, hydrocarbons, and traces of pigments and minerals (2,3). Un-

saponifiable matter does not seem to be affected during the transesterification reaction, and it is likely to be present in biodiesel at levels similar to the original vegetable oil (4).

Although mono- and diglycerides should be present in methyl soyate in very small amounts when transesterification is properly executed, we have recovered both mono- and diglycerides from plugged diesel fuel filters (5). The presence of mono- and diglycerides in biodiesel may contribute to injector deposits, increased viscosity, and lube oil thickening (6,7) and cause fuel crystallization at low temperatures (8).

The objectives of this study were to determine the effect of various amounts of unsaponifiables and bound glycerol on the crystallization properties of methyl soyate and to provide a basis for setting realistic specifications for these trace components.

## EXPERIMENTAL PROCEDURES

Methyl soyate was obtained from Interchem Environmental (Kansas City, MO) and Calgene, Inc. (Davis, CA). Number 1 diesel fuel was obtained locally. Methyl heptadecanoate, monoglycerides, and diglycerides were purchased from Sigma (St. Louis, MO); other chemicals were from Aldrich Chemical Co., Inc. (Milwaukee, WI).

Commercial soybean oil (Hunt-Wesson, Inc., Fullerton, CA) was purchased locally. Crude soybean oil and the methyl esters produced from it were from West Central Cooperative (Ralston, IA). The soybean oil was converted into methyl esters with methanol and sodium methoxide using amounts of methanol that were 90, 100, 110, 130, 150, or 200% of the stoichiometric requirement. The methyl esters were washed with distilled water and dried using a rotary evaporator at 90°C for 20 min.

To isolate the mono- and diglycerides from the methyl esters, methyl esters were applied to 1-mm silica gel thin-layer plates and developed with hexane/ethyl ether/acetic acid (50:50:1, vol/vol/vol). The plates were sprayed with 0.1% dichlorofluorescein in methanol, and the bands were visualized under ultraviolet light. The mono- and diglycerides were eluted from the silica gel with methanol, converted to methyl esters by using sodium methoxide as a catalyst, and quantified by gas chromatography using methyl heptadecanoate as

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an internal standard. The gas chromatograph was a Hewlett-Packard Model 5890 (Avondale, PA) equipped with a J&W Scientific (Deerfield, IL) DB-23 fused-silica column (15 m, 0.25 mm i.d., 0.25  $\mu$ m film thickness) (9).

A simulated unsaponifiable mixture was formulated with 70%  $\beta$ -sitosterol, 14%  $\alpha$ -tocopherol, 8% squalane, and 8% squalene. Unsaponifiable matter in the methyl soyates and soybean oil was measured by the AOCS Official Methods Ca 6a-40 (10).

Crystallization properties were characterized by the cloud point (CP) (ASTM Standard Method D2500) (11), pour point (PP) (ASTM Standard Method D97) (12), and the crystallization onset temperature (Tco) determined by differential scanning calorimeter (DSC) (Perkin-Elmer, Norwalk, CT) (13). For the DSC, approximately 7.5-mg samples were weighed into aluminum pans, cooled to  $-70^{\circ}\text{C}$  at  $100^{\circ}\text{C}/\text{min}$ , held until the heat flow stabilized, and heated from  $-70$  to  $60^{\circ}\text{C}$  at  $5^{\circ}\text{C}/\text{min}$ . The Tco was the temperature at which the DSC scan of the highest melting transition became tangent to the baseline.

## RESULTS AND DISCUSSION

The percentages of unsaponifiable matter in various commercial and experimental methyl soyates and the soybean oils from which they were derived were determined. The Interchem methyl soyate, which was distilled, contained 0.03% unsaponifiable matter. When 1% of the formulated unsaponifiables was added to the Interchem methyl soyate, 0.91% was recovered. The amounts of unsaponifiable matter in the two samples of soybean oil (one commercial refined, bleached, and deodorized soybean oil from Hunt-Wesson Inc. and the other crude soybean oil from West Central Cooperative), in the methyl esters produced from those oils, and in the methyl esters purchased from Calgene were all between 0.4 and 0.5%. These values were on the low end of the expected range since crude soybean oil has been reported to contain an average of 1.6% unsaponifiable matter (2,3). The amount of unsaponifiable matter was not significantly changed during the transesterification and washing of the methyl soyates.

The effect of unsaponifiable matter on the Tco, CP, and PP of biodiesel fuels is presented in Table 1. Unsaponifiable matter up to 2% caused no adverse effect on Tco in neat esters and even slightly decreased the Tco, possibly because of the melting depression effect of such "impurities." At the 3% level of unsaponifiables in neat esters, the Tco was significantly increased ( $P < 0.05$ ), but in a 20:80 (vol/vol) mixture of esters and No. 1 diesel fuel, there was no significant effect on Tco of 3% unsaponifiables. The CP and PP data agreed with those from DSC. Only the sample with 3% unsaponifiables in neat esters had higher CP and PP.

Figure 1 shows the mono- and diglyceride percentages of esters made with various ratios of methanol to soybean oil. Generally, both mono- and diglycerides decreased with increasing proportions of methanol. At 200% of the theoretical methanol requirement, no mono- and diglycerides were detectable. The calculated bound glycerol for the reaction mixtures was greater than the National Biodiesel Board specification value of 0.24%, except for that with 200% of the theoretical methanol. For methyl soyate this value corresponds to 0.92% monoglyceride if all bound glycerol is present as monoglyceride, or 1.59% diglyceride if all of the bound glycerol is present as diglyceride.

The effect of these mono- and diglycerides on the CP and PP of esters is presented in Figure 2. The PP of the esters was not affected at any of the levels of mono- and diglycerides tested. For esters made at 130 and 150% theoretical methanol requirements, the CP was  $-1^{\circ}\text{C}$ , although their total bound glycerol was greater than the National Biodiesel Board specification. Methyl soyates made with less than 130% of the theoretical methanol requirement had an elevated CP.

The effects of added synthetic mono- and diglyceride on the CP and PP of methyl esters are presented in Table 2. The presence of mono- and diglyceride, up to 1%, did not change the PP of any of the ester samples. The CP of the samples increased with increasing amounts of saturated mono- or diglyceride, and even the sample with 0.1% saturated mono- or diglyceride had a CP significantly higher than that of the control. Monoolein (up to 1%) had no effect on the CP and PP of esters. This is consistent with our observation that, of

**TABLE 1**  
The Effect of Unsaponifiable Matter on the Crystallization Properties of Neat Methyl Esters and a 20:80 (vol/vol) Esters–No. 1 Diesel Fuel Blend<sup>a</sup>

Samples	Unsaponifiables (%)	Tco ( $^{\circ}\text{C}$ ) <sup>b</sup>	Cloud point ( $^{\circ}\text{C}$ )	Pour point ( $^{\circ}\text{C}$ )
Neat esters	0 (control)	4.7a	-5	-3
	1	3.8b	-5	-3
	2	3.8b	-5	-3
	3	19.1c	8	+3
Blends: 20% esters	0 (control)	-14.7d	-28	<-36
	1	-14.9d	-28	<-36
	2	-14.2d	-28	<-36
	3	-14.6d	-28	<-36

<sup>a</sup>Means of two replications.

<sup>b</sup>Values in the same column with the same letter are not significantly different ( $P < 0.05$ ). Tco, crystallization onset temperature.

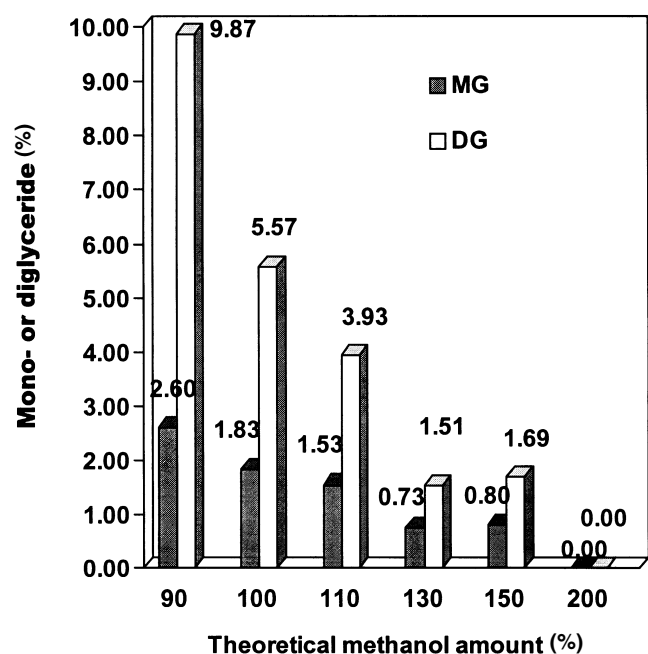


FIG. 1. Monoglyceride (MG) and diglyceride (DG) contents of methyl soyates made with various proportions of methanol.

the monoglycerides isolated from clogged engine filters, about 95% were saturated (5). Unsaturated monoglycerides seem not to contribute greatly to the Tco and CP of the fuels. The effect of mixtures of mono- and diglycerides on the CP and PP reported in Figure 2 are modest compared with those of the pure saturated mono- and diglyceride. This was because only about 16% of the monoglycerides, and an even smaller percentage of the diglycerides in the interesterified esters, were fully saturated.

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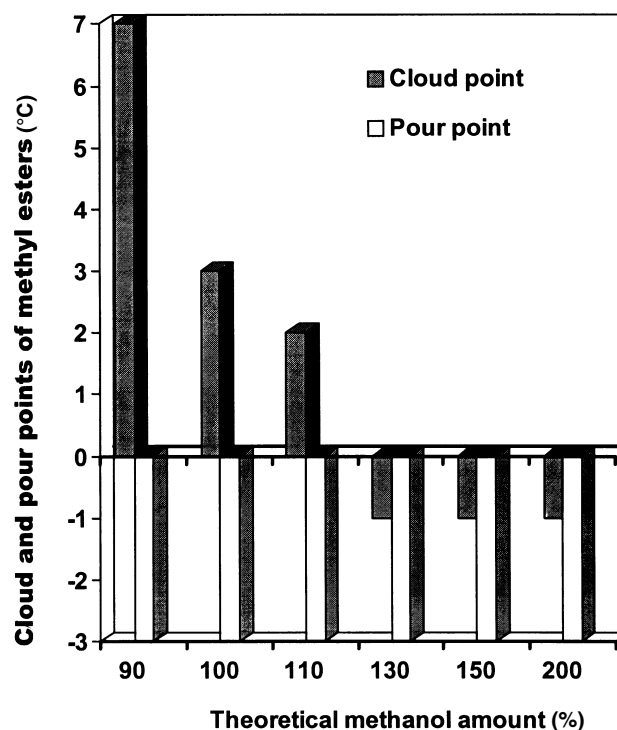


FIG. 2. The effect of residual MG and DG on the cloud and pour points of methyl soyates made with various proportions of methanol. See Figure 1 for abbreviations

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TABLE 2  
Crystallization Properties of Neat Methyl Esters Containing Various Amounts of Pure Mono- or Diglyceride<sup>a</sup>

MG or DG (%) in esters	1-Monopalmitin		1-Monostearin		Monoolein		Dipalmitin	
	CP (°C)	PP (°C)	CP (°C)	PP (°C)	CP (°C)	PP (°C)	CP (°C)	PP (°C)
1.0	22	-3	26	-3	-6	-3	21	-3
0.5	10	-3	22	-3	-6	-3	11	-3
0.4	8	-3	11	-3	-6	-3	5	-3
0.3	1	-3	9	-3	-6	-3	1	-3
0.2	1	-3	7	-3	-6	-3	-3	-3
0.1	-3	-3	-1	-3	-6	-3	-4	-3
0 (control)	-6	-3	-6	-3	-6	-3	-6	-3

<sup>a</sup>Means of two replications. Abbreviations: MG, monoglycerides; DG, diglycerides; CP, cloud point; PP, pour point.

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