

Crystallization Characteristics of Methyl Tallowate and Its Blends with Ethanol and Diesel Fuel

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ABSTRACT: Methyl tallowate was prepared from edible beef tallow via transesterification, and was blended with ethanol and/or No. 2 diesel fuel in different ratios. Crystallization characteristics of methyl tallowate and its blends were studied at temperatures ranging from 22 to -16°C . Blending ethanol with methyl tallowate reduced crystal formation at all temperatures. As the temperature of the blends was reduced from 22 to 0°C , there was no effect on crystal formation of saturated vs. unsaturated fatty acids. Below 0°C , the saturated fatty acids crystallized at a much faster rate than the unsaturated fatty acids. *JAACS* 73, 759–763 (1996).

KEY WORDS: Crystallization characteristics, diesel fuel, ethanol, methyl tallowate, saturated fatty acids, unsaturated fatty acids.

Beef tallow is a triglyceride of fatty acids. Triglycerides are composed of one mole of glycerol and three moles of fatty acids (1). Although about 180 to 200 individual fatty acids may occur in tallow, only six of them are major acids. Myristic, palmitic, and stearic are the major saturated fatty acids and palmitoleic, oleic, and linoleic are the major unsaturated fatty acids. The saturated fatty acid composition in tallow ranges from 47 to 55%, whereas the unsaturated fatty acids range from 43 to 52%. The presence of a high percentage of saturated fatty acids causes tallow to be solid at room temperature.

Tallow and its esters can be used as components of biodiesel in direct-injection diesel engines, but there are some limitations on their use. It has fuel properties fairly close to those of diesel fuel, but the physical properties are not close to diesel fuel. Viscosity is one of the major problems that can be overcome by the process of transesterification. Another very important issue with respect to using beef tallow as biodiesel fuel is its high melting point. Because beef tallow is solid at room temperature, it cannot be fed directly into the engine as fuel. This problem can be reduced by the process of esterification. By esterifying tallow with methanol to produce methyl tallowate, the melting point is reduced threefold (2),

but after esterification, the methyl tallowate will crystallize if stored at room temperature.

Crystallization from a melt is the formation of solid particles in a homogeneous phase. It occurs in two steps: the first is formation of a seed crystal, a process called nucleation; the second is crystal growth (3). Nucleation is a consequence of rapid local fluctuations on a molecular scale in a homogeneous phase that is in a state of metastable equilibrium (4). Molecules that move rapidly in a homogeneous phase are called kinetic units. Because of their fluctuations, individual kinetic units may enter another field of force, causing two particles to join momentarily. They usually break up immediately. If they stick together, they may be joined by a third kinetic unit. Sometimes, more than three kinetic units may join together. Combinations of this sort are called clusters. As the size of the cluster increases, it is called an embryo. If the embryo continues to grow, it becomes a nucleus. Nuclei grow to become crystals. At any of these stages, particles can stop growing and dissolve when they lose units (4).

During crystal growth, crystallizing molecules must diffuse from the melt to the growing crystal (4). The concentration of the crystallizing molecules in the mixture is uniform. The concentration of the molecules decreases at the crystal mixture interface. Therefore, there is a layer of concentration gradient. The crystallizing components diffuse from the melt to the crystal surface because of the driving force of the concentration gradient. They incorporate into the crystal lattice by an appropriate growth mechanism (4).

This research was undertaken to study the crystallization properties of methyl tallowate and its blends with ethanol and No. 2 diesel fuel at temperatures ranging from room temperature to -16°C . The study was designed to determine whether blending would enhance the adaptability of methyl tallowate as a fuel at low temperatures.

MATERIALS AND METHODS

The edible beef tallow used in this study was obtained gratis from Excel Corp. (Schuyler, NE). Freedman *et al.* (5) recommended that, if the free fatty acid (FFA) content of a triacylglyceride was more than 0.5%, chemical refining was needed to eliminate the FFA effect on the esterification reaction. The

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FFA content of the tallow was found to be 0.27%, so no further chemical refining was performed (6).

Transesterification reaction procedure. The esterification reaction conditions used in this study were based on the methods described by Tanaka *et al.* (7) and Freedman *et al.* (5). A sample of 500 g (0.5814 mol) of tallow was placed in a 1000-mL flat-bottom flask, equipped with a magnetic stirrer, thermometer, and condenser. The tallow was stirred and heated to 60°C. In another beaker, 111.6 g (3.4884 mol) of methanol was mixed with 5.55 g of NaOH (1% by weight, assuming 90% pure NaOH). A 6:1 molar ratio of methanol to tallow was used as suggested by Freedman *et al.* (5) for better esterification. The mixture of methanol and NaOH was heated to 60°C and stirred until the NaOH was dissolved. This mixture was then added to the tallow, stirred vigorously, and further heated to 70°C. After heating and stirring for 30 min, the mixture was allowed to cool to room temperature, and the ester and glycerol layers were separated in a separatory funnel. The top liquid portion was poured into another reaction flask. It was reheated to 60°C. Based on the weight of the esters, a heated mixture of 0.2% NaOH and 20% methanol was added to the flask. After a reaction time of one hour, the esters were separated and washed three times with distilled water to remove the glycerol, unreacted NaOH, and methanol. After washing, the tallow methyl esters were dried under vacuum.

Fuel blend preparation. Methyl tallowate was blended with ethanol and/or No. 2 diesel fuel. Tables 1 and 2 present the blend formulations.

Storage of samples at different temperatures. Two 400-mL sets of each blend were prepared and poured into glass bottles. One set with thirty bottles was stored at room temperature. Observations on crystal formation were made each day for a period of three months.

The second set with twenty-seven bottles was stored sequentially at 10, 0, -5, -10, and -16°C. The samples were first stored in a 10°C environmental chamber. Daily observa-

tions were made for three weeks to record development of cloudiness and crystal formation. At the end of three weeks, the crystals formed in any sample were separated at the same temperature through filter paper and stored at -5°C for further analysis. If most of the sample crystallized at any one of the storage temperatures, the tests were terminated after separating the crystals. The first sample in Table 1 with 100% methyl tallowate was not used in low-temperature storage because the melting point of methyl tallowate was 13.5°C (2); it would solidify before reaching the temperature of 10°C.

The remaining liquid portions, separated at 10°C, were moved to a 0°C walk-in cooler and once again stored for a period of three weeks. Again, the crystals formed in the samples were separated, and liquid portions were moved to a -5°C walk-in cooler. The same procedure was repeated in -10 and -16°C refrigerated baths. Samples containing 24% methyl tallowate, 6% ethanol, and 70% No. 2 diesel fuel solidified at -10°C; therefore, these were rerun at a storage temperature of -8°C. All experiments were triplicated, and the crystals collected at each temperature were stored at -5°C, and analyzed for their fatty acid compositions by gas chromatography (GC).

Fatty acid composition. A Hewlett-Packard (Avondale, PA) 5890 Series II gas chromatograph was used to determine the fatty acid composition of the crystal and liquid portions collected at each temperature. The capillary column was purchased from Alltech Associates, Inc. (Deerfield, IL). It had a Carbowax phase, was 30-m long, and had a 0.32-mm inside diameter and a 0.25- μ m film thickness. N₂ was used as the carrier gas with a split ratio of 2 to 200. At the end of each run, the HP3396A integrator gave individual peak retention times, peak areas, and area percentages of each peak.

When calculating the peak areas of samples, only the fatty acid esters present in the standard mixture were counted to calculate total peak area of each run. The percentage area of each fatty acid ester was also based on the standard fatty acid

TABLE 1
Crystallization Characteristics of Methyl Tallowate and Its Blends with Ethanol and Diesel Fuel at Different Temperatures^a

Sample MT/E/D % (vol/vol/vol)	Temperature (°C)						
	22	10	0	-5	-8	-10	-16
100:0:0	Crystals	Samples not stored at lower temperatures					
95:5:0	No crystals	Solidified	Experiments terminated				
80:20:0	No crystals	Crystals	Experiments terminated				
65:35:0	No crystals	Crystals	Experiments terminated				
10:0:90	Crystals	Crystals	Crystals	Crystals	—	No crystals	Crystals
8:2:90	No crystals	No crystals	Crystals	Crystals	—	No crystals	Crystals
5.5:4.5:90	No crystals	No crystals	No crystals	No crystals	—	No crystals	Crystals
30:0:70	Crystals	Crystals	Crystals	Crystals		Experiments terminated	
24:6:70	Crystals	Crystals	No crystals	Crystals	Crystals	Experiments terminated	
16.5:13.5:70	No crystals	No crystals	Crystals	No crystals	—	Crystals	Experiments terminated

^aMT = methyl tallowate; E = ethanol; D = No. 2 diesel fuel.

TABLE 2
Average Fatty Acid Composition of Crystals Collected at Different Temperatures

Sample MT/E/D	Storage temperature (°C)	Fatty acid composition (%)						Total saturated fatty acids (%)	Total unsaturated fatty acids (%)
		C _{14:0}	C _{16:0}	C _{16:1}	C _{18:0}	C _{18:1}	C _{18:2}		
100:0:0	22	3.73	26.73	3.70	17.64	46.25	1.95	48.10	51.90
	10 ^a	—	—	—	—	—	—	—	—
95:5:0	22 ^b	—	—	—	—	—	—	—	—
	10 ^a	—	—	—	—	—	—	—	—
80:20:0	22 ^b	—	—	—	—	—	—	—	—
	10	2.86	24.95	3.06	24.59	42.47	2.07	52.40	47.60
	0 ^a	—	—	—	—	—	—	—	—
65:35:0	22 ^b	—	—	—	—	—	—	—	
10:0:90	22	5.45	24.54	3.80	18.22	45.88	2.11	48.21	51.79
	10	7.36	25.45	3.74	17.04	44.20	2.21	49.85	50.15
	0	8.04	25.41	3.74	17.00	43.73	2.08	50.45	49.55
	-5	12.44	25.63	3.76	15.96	40.55	1.66	54.03	45.97
	-10 ^a	—	—	—	—	—	—	—	—
	-16	17.67	24.62	2.10	31.19	24.22	1.20	73.48	26.52
8:2:90	22 ^b	—	—	—	—	—	—	—	—
	10 ^b	—	—	—	—	—	—	—	—
	0	6.59	26.21	3.93	16.99	44.09	2.19	49.79	50.21
	-5	12.96	25.62	3.75	15.83	41.15	1.59	54.41	45.59
	-10	—	—	—	—	—	—	—	—
	-16	24.86	20.46	1.86	32.16	20.66	—	77.48	22.52
5.5:4.5:90	22 ^b	—	—	—	—	—	—	—	—
	10 ^b	—	—	—	—	—	—	—	—
	0 ^b	—	—	—	—	—	—	—	—
	-5 ^b	—	—	—	—	—	—	—	—
	-10 ^b	—	—	—	—	—	—	—	—
	-16	29.75	18.61	2.44	24.42	24.78	—	72.78	27.22
30:0:70	22	4.01	25.40	3.58	18.24	46.51	2.26	47.65	52.35
	10	5.26	25.17	3.38	18.10	45.87	2.22	48.53	51.47
	0	5.70	25.60	3.60	17.56	45.33	2.21	48.86	51.14
	-5	4.88	28.34	2.72	25.69	36.54	1.83	58.91	41.09
	-10 ^a	—	—	—	—	—	—	—	—
	-16 ^a	—	—	—	—	—	—	—	—
24:6:70	22	4.41	25.66	3.46	18.21	45.92	2.34	48.28	51.72
	10	6.04	25.90	3.61	16.73	45.36	2.36	48.67	51.33
	0 ^b	—	—	—	—	—	—	—	—
	-5	5.22	21.48	1.93	43.35	26.71	1.31	70.05	29.95
	-8	5.30	25.99	1.30	50.59	16.57	0.25	81.88	18.12
	-10 ^a	—	—	—	—	—	—	—	—
16.5:13.5:70	22 ^b	—	—	—	—	—	—	—	—
	10 ^b	—	—	—	—	—	—	—	—
	0	7.33	25.50	3.46	17.15	44.50	2.06	49.98	50.02
	-5 ^b	—	—	—	—	—	—	—	—
	-10	7.08	23.32	2.43	34.65	30.95	1.57	65.05	34.95
	-16 ^a	—	—	—	—	—	—	—	—

^aExperiments were terminated because samples solidified at this temperature; see Table 1 for abbreviations.

^bNo crystals formed at this temperature.

esters because those were the major fatty acids present in beef tallow. Peaks other than the fatty acid esters recorded by the integrator were considered to be impurities in the samples.

RESULTS AND DISCUSSION

Results and general observations related to the crystal formation in methyl tallowate and its blends with ethanol and No. 2 diesel fuel are presented in Table 1.

Storage at room temperature. The temperature in the laboratory where the samples were stored ranged between 20 and 23°C during the test period. There was some crystal forma-

tion in neat methyl tallowate over the storage period of three months. When methyl tallowate was blended with 5 and 35% ethanol, no crystals formed during the storage period. When methyl tallowate was blended with No. 2 diesel fuel in ratios of 10:90 and 30:70% (vol/vol), clouds appeared in the blends after about a week, and then a thin layer of crystals formed on the bottom of the glass bottles after a few weeks. No further increases in crystal formation were observed during the remaining storage period.

When ethanol was blended with methyl tallowate and No. 2 diesel fuel, there was no crystal formation throughout the storage period in all samples, except the 24:6:70% (vol/vol/vol)

blend of methyl tallowate/ethanol/diesel fuel. Cloudiness appeared in that sample during the first few weeks. A thin layer of solids developed at the bottom of the glass bottle thereafter.

From this test it was concluded that formation of crystals depended on the amount of methyl tallowate in the blend. As the amount of methyl tallowate increased, the amount of crystals formed also increased. When ethanol was added to methyl tallowate or its blend with diesel fuel, there was no crystal formation at room temperature.

Storage at lower temperatures. Neat methyl tallowate was not stored at the prescribed lower temperatures because it solidified around 15°C. Ali *et al.* (2) reported a melting point of 13.5°C for methyl esters from inedible tallow, and Zheng and Hanna (8) reported a melting point of 15.9°C for methyl esters from edible tallow. Therefore, blends of methyl tallowate, ethanol, and/or No. 2 diesel fuel were used for storage studies at temperatures of 10°C and lower.

Various combinations of methyl tallowate, ethanol, and diesel fuel were used to observe crystal formation as a function of temperature. The qualitative results are presented in Table 1. When a sample solidified at a prescribed temperature, the experiment was terminated. It was observed that ethanol decreased the formation of crystals in the methyl tallowate. As the amount of ethanol increased, the amount of crystals and speed of crystallization decreased.

Samples of crystals collected at each temperature were saved for fatty acid composition analyses.

Fatty acid composition. The average fatty acid composition of the crystals collected at each temperature are presented in Table 2. Crystals were collected at the end of each storage period.

GC analyses showed that the fatty acid composition of all crystals collected at room temperature from neat methyl tallowate and from the 10:0:90, 30:0:70, and 24:6:70% (vol/vol/vol) blends of methyl tallowate/ethanol/diesel fuel were more or less the same. Total saturated fatty acids in all samples collected at room temperature varied between 47 and 48%, and unsaturated fatty acids varied between 52 and 53%. It was further observed that the amounts of individual fatty acids were, more or less, the same as that of neat methyl tallowate (Table 2).

When the samples were stored at lower temperatures, the amounts of crystals collected increased according to the major constituents of the blends, as discussed earlier. GC analyses performed on those crystals showed that the fatty acid compositions of crystals collected at temperatures down to 0°C were not significantly different from that of liquid methyl tallowate. When the temperature was reduced below 0°C, the saturated fatty acids crystallized much faster than the unsaturated fatty acids. Figure 1 shows a representative trend of separation of fatty acids at different temperatures of the 10:0:90% (vol/vol/vol) blend of methyl tallowate/ethanol/diesel fuel. Only this sample showed the complete range of crystallization characteristics over the prescribed temperature range. Other fuel blends also followed the same trend, but some of the blends did not form crystals at higher temperatures because of

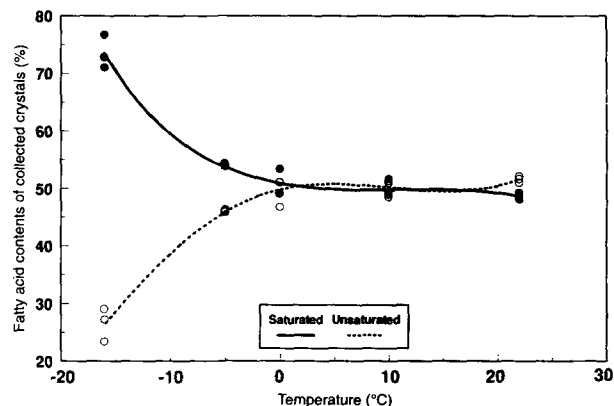


FIG. 1. Effect of temperature reduction on fatty acid composition of crystals.

the presence of ethanol, and some samples solidified at lower temperatures because of the presence of high amounts of methyl tallowate. Regression analyses performed to determine the trends of crystal formation with respect to temperature showed a significant cubic exponential trend for saturated fatty acids ($F = 12.69$, $Pr > F = 0.0044$, and $R^2 = 0.971$), and for unsaturated fatty acids ($F = 16.52$, $Pr > F = 0.0019$, and $R^2 = 0.967$).

Considering the individual fatty acid contents of the crystals collected at each temperature, it was found that, regardless of the blends used, if there was some crystal formation at a particular temperature, the individual fatty acid content was, more or less, the same. For instance, crystals formed at 22°C in the 100:0:0, 10:0:90, 30:0:70, and 24:6:70% (vol/vol/vol) blends of methyl tallowate/ethanol/diesel fuel, myristic acid ranged from 3.75 to 5.5%, palmitic acid from 24.5 to 26.5%, palmitoleic acid from 3.5 to 3.8%, stearic acid from 17.5 to 18.25%, oleic acid from 45.9 to 46.5%, and linoleic acid from 1.95 to 2.35%. Similar trends were observed at all other storage temperatures.

From the GC analyses, it was concluded that, as the temperature reduced the rate of crystallization of both, saturated and unsaturated fatty acids were the same down to a temperature of 0°C. Below 0°C, the rate of crystallization of saturated fatty acids increased with a corresponding reduction in unsaturated fatty acids in the crystals collected.

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