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Low-Temperature Properties of Alkyl Esters of Tallow and Grease

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ABSTRACT: The low-temperature properties of mono-alkyl esters derived from tallow and recycled greases were determined for neat esters and 20% ester blends in No. 2 low-sulfur diesel fuel. Properties studied included cloud point, pour point, cold filter plugging point, low-temperature flow test, crystallization onset temperature, and kinematic viscosity. Compositional properties of the alkyl esters determined included water, residual free fatty acids, and free glycerol content. In general, the secondary alkyl esters of tallow showed significantly improved cold-temperature properties over the normal tallow alkyl ester derivatives. The low-temperature flow test did not show a 1:1 correlation with cloud point as previously observed with methyl soyate and methyl tallowate. For the homologous series methyl to *n*-butyl tallowate, ethyl tallowate had the best broad-spectrum low-temperature properties, both neat and when blended in diesel fuel. For the greases studied, both the normal and branched alkyl ester derivatives showed improved properties over corresponding tallow esters, especially with neat esters.
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KEY WORDS: Alkyl esters, cloud point (CP), cold filter plugging point (CFPP), crystallization onset temperatures, kinematic viscosity, low-temperature flow test (LTFT), pour point (PP).

Since the environmental effects of fossil fuels continue to be issues of concern to governmental agencies and environmental groups, the push for alternative fuels has increased. The use of fats and oils as alternative fuels has been investigated since the advent of the automobile (1–4). It has been the general opinion that the high viscosities of vegetables oils place restrictions on their use as fuels for diesel engines. To reduce their viscosity and make them more competitive as alternative fuels, fats and oils were converted to their respective mono-alkyl esters (5–8). Studies to date on the alkyl esters as fuels have suggested additional beneficial effects in the form of lower emissions (9–11), biodegradability, and no net contribution to the greenhouse effect because they are derived from renewable resources.

The U.S. produces more surplus tallow than the rest of the industrialized world. Value-added products from tallow can include nutraceuticals, cleaning solvents, and biofuels. Biomaterials that can be derived from fats and oils may include lubricants, lubricant additives, as well as biodiesel. Biodiesel is the general term for mono-alkyl ester derivatives of fats and oils when they are used as neat diesel fuel or diesel fuel extenders. The thrust of work done on biodiesel has been on the methyl and ethyl esters of rapeseed and soybean oils.

One major technical obstacle facing the use of alkyl esters as diesel fuels or extenders is their poor low-temperature properties compared to petroleum-based diesel fuel. The cold-temperature properties of tallow methyl esters have been studied by several groups (12–15). Recently, the low-temperature properties of branched esters of tallow have been reported (16). That study suggested that branching could improve the cold-temperature properties of the alkyl esters of fats and oils. The literature is replete with work done on the fuel properties of alkyl esters of tallow, soybean, and rapeseed oils (17).

This study is intended to incorporate other less-studied normal and branched esters as biofuels and relate their cold temperature properties to the more documented methyl and ethyl esters of fats and oils. This information should provide a better insight into ways and means of improving the cold-temperature properties of alkyl esters of fats and oils. The tests used to evaluate alkyl ester low-temperature properties include cloud point (CP), pour point (PP), cold filter plugging point (CFPP), low-temperature flow test (LTFT), and crystallization onset temperature (T_c). Other properties that are relevant to the performance of these alkyl esters to perform as diesel fuels or extenders, such as kinematic viscosity, residual glycerol, and free fatty acid (FFA), and moisture content, were also evaluated.

EXPERIMENTAL PROCEDURES

Materials. Tallow was obtained from Chemol Corp. (Greensboro, NC), and FFA-containing greases ("restaurant" or "yellow grease") were donated by Kaluzny Bros. (Joliet, IL). FFA content of the greases used in this study were 9 and 32%, respectively. Both greases had the following fatty acid profile: $C_{14:0}$, 1%; $C_{16:0}$, 14%; $C_{16:1}$, 1%, $C_{18:0}$, 9%; $C_{18:1}$, 47%; $C_{18:2}$, 25%; and $C_{18:3}$, 2%. Alkyl esters used in this study were prepared in the authors' laboratories as described (18). The esters were analyzed for their water, residual FFA, and free glycerol content. Diesel fuel No. 2 was purchased from

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Phillips Petroleum (Bartlesville, OK). Unless otherwise stated, all other chemicals were purchased from Aldrich (Milwaukee, WI). Karl Fisher apparatus was purchased from Mettler Toledo (Hightstown, NJ). A differential scanning calorimeter with an intracooler system II (Perkin Elmer, Norwalk, CT) was used to obtain cooling and heating thermograms by following the protocol of Lee *et al.* (16).

Methods. Alkyl ester blends in diesel fuel were prepared in volumetric flasks. CP were measured according to ASTM method number D2500 of the American Society for Testing Materials (ASTM) book of standard test methods. Pour points were measured according to ASTM method D97. Kinematic viscosities were measured at 40°C with Cannon-Fenske viscometers obtained from Koehler (Bohemia, NY). Cold filter plugging point and low-temperature flow tests were performed at the National Center for Agricultural Utilization Research (NCAUR) in Peoria, IL, as described by Dunn *et al.* (15).

RESULTS AND DISCUSSION

Even though fluid alkyl esters were obtained from solid tallow, little difference was observed in the viscosities of the esters even as the molecular weight of the alcohol increased (Table 1). The only outlier was ethyl tallowate, but the viscosities are all within 1 cSt of each other. The viscosities observed were ~6–8 cSt, still within the European specification (19) for biodiesel (~6–9 cSt). The same trend was observed upon blending the esters; the viscosities of the blends were close to the viscosity of neat diesel fuel. The viscosity of the 2-butyl ester from the 32% FFA grease was high in the neat form but was within an acceptable range when blended with diesel fuel. This promotes the use of grease-derived biodiesel blended with diesel fuel. The higher viscosity observed for the 2-butyl ester of the 32% FFA grease may reflect the presence of oxidized materials that increase viscosity.

The PP of an oil is defined as the last incremental 3°C decrease in temperature for which a liquid is observed to flow when the sample is tilted. For the homologous series of neat alkyl esters from methyl to butyl tallowate, a steady decrease in PP is observed (Table 1). This is understandable because, with increasing chainlength in the alcohol portion of saturated fatty acid esters, there is a concomitant decrease in their crystallization temperature. The formation of solid particles will also hinder the smooth flow of the alkyl ester molecules. Branching in the alcohol moiety of esters helps to augment this effect. As shown in Table 1, the PP of the isopropyl ester is 9°C lower than that of the *n*-propyl esters; that of the 2-butyl ester is 6°C lower than the *n*-butyl ester. This effect is less pronounced when branched alcohols are compared. There is a leveling effect from isopropyl through isobutyl to 2-butyl esters. In general, blends of the tallow esters in diesel fuel gave PP that ranged between –9 and –15°C, values which are approximately 15°C higher than the PP of diesel fuel. The trend seen in the homologous series of neat esters disappeared

TABLE 1
Physical Properties of Alkyl Esters from Triglycerides

Substrate	Ester	Viscosity[a] (cSt)	Pour point[b] (°C)	Cloud point[b] (°C)	T_c[c] (°C)
Tallow	Methyl (MT)	7.9	15	17	21.2
	Ethyl (ET)	6.2	12	15	
	Propyl (PT)	7.3	9	12	6.6
	Butyl (BT)	6.9	6	9	
	Isopropyl (IPT)	7.1	0	8	
	Isobutyl (IBT)	7.4	3	8	
	2-Butyl (2-BT)	6.8	0	9	9.6
Soy oil	Methyl (MS)	4.3	–2	0	5.2
	Ethyl (ES)	4.4	–4	1	1.4
Grease (9% FFA)	Ethyl (EG-9)	6.0	–3	9	3.5
	2-Butyl (2-BG-9)	6.3	–8	3	1.2
Grease (32% FFA)	2-Butyl (2-BG-32)	11.7	–3	9	
Diesel (D)		2.8	–27	–16	–11.9
MS/D[d]		3.1	–21	–14	
MT/D		3.1	–9	–5	
ET/D		3.2	–12	–3	
PT/D		3.8	–9	–5	
BT/D		3.4	–12	–5	
IPT/D		4.0	–12	–8	
IBT/D		3.9	–12	–5	
2-BT/D		3.4	–15	–5	
EG-9/D		3.7	–15	–9	
2-BG-9/D		3.3	–21	–8	
2-BG-32/D		3.8	–15	–15	

[a]Means (n = 5), standard deviation ± 0.3 cS.
[b]Means (n = 5), standard deviation ± 2°C.
[c]Means (n = 5), standard deviation ± 0.5°C.
[d]Blend of alkyl ester in diesel fuel (20:80, vol/vol); FFA, free fatty acid.