Low-Temperature Properties of Alkyl Esters of Tallow and Grease

Thomas A. Foglia[a,*], Lloyd A. Nelson[a], Robert O. Dunn[b], and William N. Marmer[a]

[a]USDA, ARS, ERRC, Wyndmoor, Pennsylvania 19038, and [b]USDA, ARS, NCAUR, Peoria, Illinois 61604

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.
JAOCS 74, 951–955 (1997).

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

---

*To whom correspondence should be addressed.
E-mail: tfoglia@arserrc.gov.

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.

in the diesel blends. Ethyl and 2-butyl esters of greases had better PP than their tallow counterparts and showed comparable or better PP than the leading biodiesel candidates, neat methyl soyate and ethyl soyate. PP of esters from greases with high fatty acid content are lower than the corresponding data from tallow. For example, the ethyl ester of grease (EG-9) shows the same properties as the 2-butyl ester of tallow, even though the feedstocks are different.

In general, blending the tallow alkyl esters in diesel fuel decreases their PP to −12°C and compares favorably with methyl soyate in diesel fuel (Table 1). Alkyl esters from greases give better PP in the neat form than those of tallow and give results comparable to methyl soyate. The branched alcohol esters of greases also have improved cold- temperature properties over the normal neat esters, as was observed for the tallow esters.

In Table 1, the CP of the normal alkyl esters of tallow showed a nearly linear relationship with increasing molecular weight of the alcohol residue. Blending the esters in diesel fuel produced a leveling effect in the CP with CP values ranging between −8 and −5°C. Branching in general improved this cold-temperature property, but not to the extent that was observed for PP. Even though a decrease was observed between methyl and isopropyl tallowate, there was no observable trend among the branched esters. Moreover, blending with diesel fuel reduced the CP difference observed for the neat esters. As with normal esters, there was a leveling effect upon blending, but the branched and higher homolog alkyl esters still resulted in slightly improved CP. A similar trend was also found for CP of the primary alcohol-based fatty alkyl esters. Here again, there was a tendency for crystal formation to occur at a lower temperature as the molecular weight of the alcohol residue increased. This effect, however, was not as dramatic as was observed for the PP.

The mono-alkyl esters derived from the greases again show an advantage over their tallow counterparts in the neat form. This is understandable because these esters are blends of animal fats and vegetable oils. Thus, while ethyl tallowate has a CP of 15°C, the ethyl ester of the 9% FFA grease has a CP of 9°C. This trend was also noted for the 2-butyl esters of tallow and the 9% FFA grease, where a difference of 6°C was observed. Blending the grease alkyl esters in diesel fuel gave PP similar to the PP of methyl soyate blended in diesel fuel. As with the tallow esters, there was little difference in CP between the normal and secondary alkyl esters when blended in diesel fuel.

Other important criteria for prospective biofuels are their low-temperature properties as measured by the CFPP and LTFT (15). The normal alkyl esters from methyl to butyl showed a minimal but significant decrease in CFPP temperature (Table 2). In general, branched alcohol esters do not impart improved CFPP over those of the neat tallow esters with the exception of the 2-butyl ester. Similar trends were observed when the tallow esters were blended in diesel fuel, but blending with a petroleum diesel greatly improved the CFPP of the ester blends. Blending of the alkyl ester derivative of greases gave better or similar CFPP, compared to methyl soyate and a blend of methyl soyate (80%) and methyl tallowate (20%). Overall, the greases show promise as diesel fuel extenders or alternatives to tallow and soy oil as judged by the CFPP, the standard European method for measuring the operability of diesel fuels.

In Table 2, the LTFT results on neat normal alkyl esters of tallow show an interesting trend between odd and even carbon chain alkyl esters. The methyl and isopropyl esters have a high LTFT, whereas the ethyl and butyl esters have a lower LTFT. The branched alkyl tallow esters do not show much difference in the neat form, but results indicated that when the higher alkyl ester derivatives of tallow are blended with methyl soyate (20:80), they attain better LTFT for this test. Ethyl and 2-butyl tallowate are the only ester derivatives in this series that would have potential as a biodiesel fuel, based on LTFT results alone. Both branched and normal grease-derived esters gave satisfactory LTFT results, both in the neat form and as blends in diesel fuel. However, the latter values did not compare favorably with the methyl and ethyl derivatives of soy oil. Some encouraging results could be obtained by blending these esters with methyl soyate.

TABLE 2
Low-Temperature Properties of Alkyl Esters of Triglycerides

		LTFT (°C)		CFPP (°C)	
Substrate	Alkyl ester	Neat	Blend[a]	Neat	Blend[a]
Tallow	Methyl (MT)	20	—	9	−8
	Ethyl (ET)	13	1	8	−10
	Propyl (PT)	18	15	7	−10
	Butyl (BT)	13	14	3	−12
	Isopropyl (IPT)	19	12	7	−8
	Isobutyl (IBT)	17	14	8	−13
	2-Butyl (2-BT)	12	15	4	−3
Soy	Methyl (MS)	2	−12	−3	−14
Soy/Tallow[b]	MS/MT	3	−10	0	−13
Grease (9% FFA)	Ethyl	9	−3	0	−12
	2-Butyl	9	−2	−4	−18
#2 Diesel fuel		−14	—	−27	—

[a] Blend of alkyl ester in diesel fuel, 20:80 (vol/vol).

[b] 80:20 (vol/vol) blend of methyl soyate: methyl tallowate. See Table 1 for other abbreviation.

Discrimination as to the effect of alkyl ester structure on low-temperature properties was more evident in CFPP than LTFT when blended in diesel fuel. In general, differences between the CFPP and LTFTvalues for the straight-chain alkyl ester blends, ranged from 14–17°C; this difference was 7–20°C for the branched-chain ester blends. The 2-butyl tallowate blend failed at 15°C (LTFT), and operability problems would be expected when this material is exposed to temperatures below 14°C (57°F). The 20% ethyl tallowate blend gave an anomalous LTFT of 1°C. The lower homologs of normal alcohols were more sensitive to blending in diesel fuel than were their branched-chain counterparts in the LTFT evaluation. Overall, the tallow ester blends had LTFT values that were almost 20°C higher than diesel fuel. The effect of blending on LTFT decreased as the extent of branching increased in the alcohol structure of the tallowate ester molecule.

The effect of increasing molecular weight showed no regular pattern in the LTFT results. The esters of odd-chain alcohols showed high LTFT in neat form, whereas the esters of even-chain alcohols showed no pattern in LTFT as molecular weight increased. Variation of alcohol branching for the esters of four-carbon alcohols did not affect the LTFT in the neat form, and a similar trend was also observed for the esters when blended in diesel. A similar trend is seen for the esters of three-carbon alcohols when evaluated in the neat form. There was a change, however, when they were evaluated as 20% blends in diesel fuel. In these instances, a decrease in LTFT was observed as the ester was changed from primary to secondary. In general, the effect of blending was most effective with the lower homolog normal alkyl esters but was less pronounced in three-carbon (or more) alcohols and as branching increased.

Branching and alcohol chainlength for alkyl esters of greases did not appear to affect LTFT, whether in neat form or when blended in diesel. The grease esters, however, show more promise in their LTFT values than their tallow ester counterparts. This is consistent with the observation of Dunn *et al.* (15) who obtained LTFT values of 3 and −10°C for methyl soyate/methyl tallowate (80/20) neat and blended with diesel fuel, respectively. For most of the alkyl esters studied, the CFPP results were lower than the LTFT results. This difference was 6–12°C for the neat esters and 10–25°C for the 20% blends.

Earlier work on methyl soyate gave a difference of ~3°C for both the 20% blend and the neat ester. The difference in the severity between the two filterability tests was not obvious when using methyl soyate as the biofuel. In contrast, the present work shows that varying the alkyl groups of a biofuel dramatically highlights the differences between the tests. These differences between LTFT and CFPP arise from either an increase in the degree of branching in the head groups (e.g., 2-propyl tallowate gave a difference of ~12°C) or an increase in the molecular weight of the head group (e.g., ethyl tallowate gave a difference of ~5°C). Dunn *et al.* (14) found a 1:1 correlation between CP and LTFT with methyl esters. This relationship also was observed with the higher alkyl ester homologs.

Lee *et al.* (16) have done work on branched esters and developed a differential scanning calorimetry (DSC) method that correlates well with CP and PP. This is especially encouraging because DSC requires small sample amounts and little time for analysis. Being able to use DSC as a predictive tool should allow for a quicker screening method for evaluating prospective biofuels. While that work was done on some tallow derivatives, application of the method to some of the authors' esters will help to fill the gap left for alkyl esters of tallow and greases. The DSC thermograms of this study agreed with the previous observation that cooling and heating give different T_c values. Cooling thermograms give lower values. The results obtained in this study parallel those obtained in that study (16) and corroborate the finding that branching in the esters enhances their cold-temperature properties. Again, the crystallization onset temperature showed a fair correlation ($R = 0.878$) with both CP and PP (Table 1).

The alkyl ester content for the samples studied was between 94 and 99%, with the remainder of the mixture being mono, di, and triglycerides and minor amounts of FFA, as measured by capillary gas–liquid chromatography (Table 3). These compositional data are important parameters because excessive levels of these minor components may cause fuel-

TABLE 3
Alkyl Esters from Tallow and Greases: Glycerides; Free Fatty Acid; Moisture; and Glycerol Content

		% Composition[a]						
Substrate	Ester	AE	TG	DG	MG	% FFA[b]	% Moisture	% Glycerol[c]
Tallow	Methyl	98	1.0	0.4	0.6	0.03	0.05	n.d.[d]
	Ethyl	99	0.3	0.3	0.4	0.02	0.04	n.d.
	Propyl	98	1.2	0.4	0.6	0.02	0.04	n.d.
	Butyl	98	1.0	0.6	0.4	0.02	0.02	n.d.
	Isopropyl	97	1.3	0.4	0.3	0.14	0.05	n.d.
	Isobutyl	99	0.2	0.6	0.2	0.03	0.04	n.d.
	2-Butyl	97	1.2	0.3	0.5	0.22	0.04	n.d.
Grease (9% FFA)	Ethyl	97	1.7	0.6	0.7	0.67	0.06	0.001
Grease (32% FFA)	2-Butyl	94	1.5	0.7	0.8	2.50	0.08	0.002

[a] Wt% composition of ester sample from Nelson *et al.* (Ref. 18). AE = alkyl ester; TG = triglyceride; DG = diglyceride; MG = monoglyceride.

[b] Free fatty acid.

[c] Free glycerol content.

[d] n.d. = not detected.

system problems by precipitation or can lead to injector fouling or higher emissions. The moisture content of the samples ranged between 0.02–0.05 wt%. The residual fatty acid content varied from a low of 0.02% for the normal alkyl esters to 0.22% for the branched alkyl esters of tallow. As expected for the high FFA grease, residual FFA was higher. The free glycerol content in the alkyl esters was measured by the Mittelbach's procedure (20). Free glycerol was always well below the maximal 0.02% level specification recommended for biodiesel (19).

In conclusion, alkyl esters derived from tallow have been shown to have properties that would limit their use as neat diesel fuels. However, selected tallow esters have acceptable low-temperature properties when blended in diesel that allows their use as diesel fuel extenders. Alkyl esters of restaurant greases showed better cold-temperature properties, making these findings more encouraging because greases are cheaper and can be used in conjunction with the more expensive soybean oil derivative to reduce production costs for biofuels.

ACKNOWLEDGMENTS

The authors thank H. Khoury and R. Burke of the National Center for Agricultural Utilization Research for their assistance in the CFPP and LTFT studies.

REFERENCES

1. Samson, W.D., C.G. Vidrine, and W.D. Robbins, Chinese Tallow Seed as a Diesel Fuel Extender, *Transact. ASAE 28(5)*:1407 (1995).
2. Pryde, E.H., Vegetable Oils as Fuel Alternatives, *J. Am. Oil Chem. Soc. 61*:1609–1610 (1984).
3. Ryan, T.W. III, L.G. Dodge, and T.J. Callahan, The Effects of Vegetable Oil Properties on Injection and Combustion in Two Diesel Engines, *Ibid. 61*:1611–1619 (1984).
4. Ziejewski, M., K.R. Kaufman, A.W. Schwab, and E.H. Pryde, Diesel Engine Evaluation of a Nonionic Sunflower Oil-Aqueous Ethanol Microemulsion, *Ibid. 61*:1620–1626 (1984).
5. Clark, S.J., L. Wagner, M.D. Schrock, and P.G. Piennaar. Methyl and Ethyl Soybean Esters as Renewable Fuels for Diesel, *Ibid. 61*:1632–1637 (1984).
6. Ali, Y., M.A. Hanna, and S.L. Cuppert, Fuel Properties of Tallow and Soybean Oil Esters, *Ibid. 72*:1557–1564 (1995).
7. Natusch, D.F.S., D.W. Richardson, and R.J. Joyce, Methyl Esters of Tallow as Diesel Extender, *Proceedings, VI International Symposium on Alcohol Fuels Technology Conference*, 2-340-346, 21–25 May 1984, Ottawa, Canada.
8. Richardson, D.W., R.J. Joyce, T.A. Lister, and D.F.S. Natusch, Methyl Esters of Tallow as a Diesel Component, in *Proceedings of the International Conference on Energy from Biomass*, edited by W. Palz, J. Coombs, and D.O. Hall, 1985, pp. 736–743.
9. Ali, Y., M.A. Hanna, and L.I., Leviticus, Emissions and Power Characteristics of Diesel Engines on Methyl Soyate and Diesel Fuel Blends, *Bioresources Tech. 52*:185–195 (1995).
10. Laforgia, D., and V. Ardito, Biodiesel Fueled IDI Engine: Performances, Emissions, and Heat Release Investigation, *Ibid. 51*:53–59 (1995).
11. Sii, H.S., H. Masjuki, and A.M. Zaki, Dynamometer Evaluation and Engine Wear Characteristics of Palm Oil Diesel Emulsions, *J. Am. Oil Chem. Soc. 70*:905–909 (1995).
12. Sims, R.E.H., Tallow Esters as an Alternative Diesel Fuel, *Trans. of ASAE, 28 (3)*:717 (1985).
13. Ali, Y., and M.A. Hanna, Physical Properties of Tallow Ester and Diesel Fuel Blends, *Bioresources Tech. 47*:131–134 (1994).
14. Dunn, R.O., M.W. Shockley, and M.O. Bagby, Improving the Low-Temperature Properties of Alternative Diesel Fuels: Vegetable Oil-Derived Methyl Esters, *J. Am. Oil Chem. Soc.* (in press).
15. Dunn, R.O., and M.O. Bagby, Low-Temperature Properties of Triglyceride-Based Diesel Fuels: Transesterified Methyl Esters and Petroleum Middle Distillate/Ester Blends, *Ibid. 72*:895–904 (1995).
16. Lee, I., L.A. Johnson, and E.G. Hammond, Use of Branched-Chain Esters to Reduce the Crystallization Temperature of Biodiesel, *Ibid. 72*:1115–1160 (1995).
17. Ali, Y., and M.A. Hanna, Alternative Diesel Fuels from Vegetable Oils, *Bioresources Tech. 50*:153–163 (1994).
18. Nelson, L.A., T.A. Foglia, and W.N. Marmer, Lipase-Catalyzed Production of Biodiesel, *J. Am. Oil Chem. Soc. 73*:1191–1195 (1996).
19. Knothe, G., R.O. Dunn, and M.O. Bagby, Technical Aspects of Biodiesel Standards, *INFORM 7*:827–829 (1996).
20. Mittelbach, M., Diesel Fuel Derived from Vegetable Oils, V [1]: Gas Chromatographic Determination of Free Glycerol in Transesterfied Vegetable Oils, *Chromatographia 37*:623–626 (1993).

[Received October 11, 1996; accepted April 30, 1997]