Improving the Low-Temperature Properties of Alternative Diesel Fuels: Vegetable Oil-Derived Methyl Esters

R.O. Dunn,* M.W. Shockley, and M.O. Bagby
Oil Chemical Research, USDA, ARS, NCAUR, Peoria, Illinois 61604

ABSTRACT: This work explores near-term approaches for improving the low-temperature properties of triglyceride oil-derived fuels for direct-injection compression–ignition (diesel) engines. Methyl esters from transesterified soybean oil were evaluated as a neat fuel and in blends with petroleum middle distillates. Winterization showed that the cloud point (CP) of methyl soyate may be reduced to −16°C. Twelve cold-flow additives marketed for distillates were tested by standard petroleum methodologies, including CP, pour point (PP), kinematic viscosity, cold filter plugging point (CFPP), and low-temperature flow test (LTFT). Results showed that additive treatment significantly improves the PP of distillate/methyl ester blends; however, additives do not greatly affect CP or viscosity. Both CFPP and LTFT were nearly linear functions of CP, a result that compares well with earlier studies with untreated distillate/methyl ester blends. In particular, additives proved capable of reducing LTFT of neat methyl esters by 5–6°C. This work supports earlier research on the low-temperature properties; that is, approaches for improving the cold flow of methyl ester-based diesel fuels should continue to focus on reducing CP.

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KEY WORDS: Biodiesel, cloud point, cold filter plugging point, diesel fuel, kinematic viscosity, low-temperature flow test, methyl esters, pour point, soybean oil, winterization.

Methyl esters from transesterified vegetable oils or animal fats are attractive as alternative fuels for combustion in direct-injection compression–ignition (diesel) engines (1–3). Fuel characteristics, such as viscosity, gross heat of combustion and cetane rating, compare well between methyl esters and petroleum middle distillates (2,4,5). Due to their innocuous nature and relatively high flash points (154°C for methyl soyate), methyl esters are safer to handle and store than distillates. Under steady-state conditions, methyl esters can significantly reduce exhaust emissions, including smoke, particulates, unburned hydrocarbons and carbon dioxide, and slightly reduce carbon monoxide emissions (6–8). However, one crucial issue that must be resolved before they can be employed in moderate-temperature climates during cooler seasons is their low-temperature properties.

Distillate fuels are plagued by growth and agglomeration of solid wax crystals when ambient temperatures decrease below the cloud point (CP) (9–11). During start-up, solid crystals in the fuel tank may cause operability problems, such as plugged filters and fuel lines. With respect to conditions in North America, diesel fuels develop problems when temperatures drop into the range of −10 to −15°C (9,12).

Earlier research with methyl esters from soybean oil (SME) has shown that their analogous "cut-off" temperature is near 0°C (13). This research also showed that blending methyl esters with distillates significantly improves low-temperature properties. However, this method is only effective when methyl ester contents are held at relatively low blend ratios (vol% methyl esters). For example, 20 vol% methyl soyate in No. 2 diesel fuel, or 30 vol% in No. 1 diesel fuel, ensures that cut-off temperatures will be less than or equal to −10°C.

This work explores two near-term approaches for improving low-temperature flow properties of methyl esters. The first approach, winterization, involves equilibrating a quiescent mixture of methyl esters at a temperature between its CP and pour point (PP). Under these conditions, saturated methyl esters precipitate and form a suspension of small, wax-like crystals in a liquid phase. Filtering the solids leaves behind a liquid with an enhanced concentration of unsaturated methyl esters. Consequently, the liquid product should demonstrate improved cold-flow properties. This work presents a preliminary evaluation of winterization to determine its potential for improving low-temperature properties of neat SME. Products were evaluated by yield and comparison of CP and PP data.

The second approach involves treatment with off-the-shelf cold-flow additives. With respect to distillates, cold-flow improvers significantly alter the size and habit of wax crystal formation, producing smaller and more compact crystals (9–11,14–16). When these crystals become trapped in the fuel filter, they form a permeable cake layer that allows liquid fuel to flow to the injectors. This study examines the suitability of additives marketed for distillates for improving low-temperature properties of alternative fuels that contain methyl esters. Neat methyl esters from soybean oil and their blends with No. 1 and No. 2 diesel fuel were treated with additives and evaluated by standard petroleum industry methodologies, includ-

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*To whom correspondence should be addressed at Oil Chemical Research, USDA, ARS, NCAUR, 1815 N. University St., Peoria, IL 61604.

ing CP, PP, kinematic viscosity (ν), cold filter plugging point (CFPP), and low-temperature flow test (LTFT).

EXPERIMENTAL PROCEDURES

Materials. SME was from Interchem Environmental (Overland Park, KS), obtained through the National Biodiesel Board (Jefferson City, MO). Physical property data and experimental preparation have been described elsewhere (13). Prior to experimentation, gas chromatography analysis showed a fatty acid composition of 10.6 wt% hexadecanoate (C_{16}), 4.3% octadecanoate (C_{18}), 24.4% octadecenoate ($C_{18:1}$), 51.9% octadecadienoate ($C_{18:2}$), 8.2% octadecatrienoate ($C_{18:3}$), and 0.6% unknowns. Pure (99+%) samples of unsaturated methyl esters ($C_{18:1}$, $C_{18:2}$, and $C_{18:3}$) were from Nu-Chek-Prep (Elysian, MN).

Low-sulfur Phillips standard No. 2 diesel fuel (DF2) was from the National Institute for Petroleum and Energy Research (Bartlesville, OK). No. 1 diesel fuel (DF1) was from Midwest Oil (East Peoria, IL). Physical property data for these materials were reported earlier (13).

The following five cold-flow additives were obtained from major industrial suppliers: DFI-100 and DFI-200 from Du Pont (Wilmington, DE); Hitec 672 from Ethyl Petroleum Additives (Rolling Meadows, IL); OS 110050 from SVO Enterprises (Eastlake, OH); and Paramins from Exxon Chemical (Abington, Oxfordshire, England). In addition, the following seven additives were tested: 409 Flowmaster from Primrose Oil (Dallas, TX); 8500 Winterflow from Starreon Corp. (Englewood, CO); Diesel Conditioner AntiGel from R.B. Howes & Co. (Coventry, RI); Diesel Fuel Supplement from Power Service Products (Weatherford, TX); Diesel XL from Dieseltech (Tempe, AZ); Fuel Power Diesel Fuel Treatment from FPPF Chemical (Buffalo, NY); and Winter Pow-R Plus from Penray Companies, Inc. (Elk Grove Village, IL). Although many additives contained proprietary compounds, in most cases they were mixtures of ethylene vinyl acetate copolymers and naphthenic distillates.

Methods. Winterization studies were carried out by immersing 1-L bottles filled with methyl esters in a Neslab (Portsmouth, NH) Endocal LT-50 refrigerated bath and equilibrating overnight. Two bottles, each containing approximately 0.65 kg methyl esters, were immersed simultaneously. Initial bath temperature was 4 ± 0.5°C. If solids formed, they were collected by rapid filtration through a sintered glass filter. Filtered liquid was re-equilibrated for the next step by reducing bath temperature 1–2°C. This method was repeated until liquid immersed at a bath temperature equaling −10°C showed no observable clouding for a minimum of three hours.

Blending SME with petroleum middle distillates was performed on a volumetric basis. In this work, the term "blend ratio" refers specifically to "vol% SME" in a given formulation. Blend ratios were 0, 10, 20, 30, 50, and 100 vol% SME. Additives at loadings on the order of parts per million (ppm) were mixed with SME and distillate components separately before blending. To facilitate mixing on a mass basis, specific gravities of additives DF1, DF2, and SME were determined at 25 ± 0.2°C relative to water at 25°C with a standard 50 mL pycnometer.

Apparatus and methodology for measuring PP, CP, CFPP, LTFT, and ν have been detailed elsewhere (13). Viscosities were measured at standard (40°C) as well as at two cooler temperatures (−3°C and +5°C).

RESULTS AND DISCUSSION

Winterization. Traditionally, winterization has been employed to facilitate easier handling and pouring of vegetable oils and their derivatives (17). For example, winterization is necessary in the food industry to improve the quality of salad oils and dressings. One common technique has been to artificially refrigerate large storage tanks for a prescribed period of time, then draw the liquid portion off from partially solidified material that has settled toward the bottom. A more energy-efficient (and time-consuming) alternative is to allow tanks to stand outside during colder weather before drawing off the liquid portion. Conceptually, this technology should be adaptable to methyl esters.

In this work, SME samples were step-by-step winterized until they withstood a minimum of three hours at a bath temperature of −10°C with no observable clouding. In two separate trials, SME was successfully winterized to a point where CP and PP did not exceed −16°C. Typically, five to six iterations over a period of approximately one week were required to obtain product. Finally, product yields for each trial were relatively low, averaging 25% (0.32 kg), while mass balances from the second trial revealed a total loss of starting material of nearly 20%.

Table 1 is a comparison between gas chromatography analyses of untreated and winterized methyl esters from the second trial. As expected, both mixtures were composed primarily of long-chain (C_{16} and C_{18}) methyl esters. Methyl hexadecanoate (C_{16}) experienced the largest decrease, decreasing by a factor of three; methyl octadecatrienoate ($C_{18:3}$) experienced the largest increase, increasing by more than half. With respect to total ester content, winterization enriched the total unsaturated methyl esters by 13.3 wt%, an increase that was approximately equivalent to the decrease in total saturated esters. However, the degree of enrichment was relatively small with respect to removing (or losing) nearly

TABLE 1
Effect of Winterization on Fatty Acid Composition of Long-Chain Methyl Esters (gas chromatography results)

Fatty acid	Untreated (wt%)	Winterized (wt%)
Hexadecanoate ($C_{16:0}$)	12.9	4.3
Octadecanoate ($C_{18:0}$)	5.2	1.3
Octadecenoate ($C_{18:1}$)	23.8	30.3
Octadecadienoate ($C_{18:2}$)	46.6	49.6
Octadecatrienoate ($C_{18:3}$)	7.8	11.9
Other	3.7	2.6

75% of the starting material during winterization. Apparently, the mechanism for precipitation of solids was characterized by significant co-crystallization of unsaturated methyl esters after the formation of crystalline nuclei in the mixture.

In the winterized fraction, the presence of a small concentration of saturated long-chain methyl esters exerts a dominant influence on cold-flow properties. This assertion was tested by measuring the properties of a laboratory mixture of pure unsaturated C_{18} components. A mixture consisting of 26.0 wt% methyl octadecenoate, 68.3% methyl octadecadienoate, and 5.7% methyl octadecatrienoate gave CP = −23°C and PP = −48°C. These results are 7 to 32°C beneath those for winterized SME. Hence, a small concentration (5.6 wt%) of saturated methyl esters carries a formidable impact on the low-temperature properties of the winterized SME.

Although this study was limited to a preliminary examination, results indicate that improving the adaptation may not be difficult. Pretreatment of methyl esters to reduce their "solid" limit (e.g., treatment with PP improvers) or more advanced techniques for removing solids (e.g., ultrafiltration, extraction) may decrease the amount of lost starting material, boost liquid product yields, and optimize production. Winterization may prove to be effective in removing nearly all saturated long-chain methyl esters from SME. However, complete removal of saturated methyl esters may not be recommended because doing so would significantly reduce their ignition quality (18).

Additives. The physical chemistry of nucleation and crystallization in distillates at lower temperatures has been well documented (9,10,14–16,19,20). As temperature decreases toward CP, paraffin molecules (saturated C_{18+}) stack together side-by-side along their hydrocarbon chains to form orthorhombic-structured crystals. By definition, at the CP, a sufficient quantity of wax crystals with diameters exceeding 0.5 μm has formed a visible and cloudy suspension. Left unchecked, exposure to temperatures between CP and PP allows rapid two-dimensional crystalline growth. Growth in the Z-direction is relatively slow, resulting in the formation of large (0.5–1.0 mm) flat-plate structures. These crystals are easily caught in fuel filters designed to retain particles with diameters of 10 μm or larger. Plugging greatly restricts fuel flow through the filters and leads to fuel starvation and stalled engines.

Additives for improving cold-flow properties of distillates also have been extensively studied (9–11,14–16,19–22). Initially, additives were developed to co-crystallize with paraffin molecules to alter their size and growth habit. Their molecular structure consisted of several protruding moieties attached to a paraffin backbone. As the backbone competes for lattice sites on the crystal surface, the protruding moieties inhibit incorporation of more paraffin molecules. Examples include ethylene vinyl acetate (EVA) copolymers, alkenyl succinic amides, high-molecular-weight long-chain polyacrylates, fumarate-vinyl acetate (FVA) copolymers, and copolymers of linear α-olefins with acrylic, vinylic, and maleic compounds. These additives are capable of significantly reducing PP of distillate fuels; however, they largely have no impact on CP because the presence of crystalline nuclei is required before they can activate.

Most additives promote the formation of small (10–100 μm) needle-shaped crystals. These crystals experience significantly reduced growth and agglomeration rates as temperatures decrease below CP. However, the rate of nucleation is promoted and causes the formation of a large quantity of the relatively small and more compact crystals. Although most of these crystals will be caught in fuel filters, the cake layer formed on the filter surface is considerably more permeable to fuel flow. As long as excess fuel can be recycled back to the fuel tank, warming of the fuel eventually melts the cake layer and engine operability will be maintained (9–11,14,15,19,20).

Recent work has led to the development of additives that are tailored to reduce the CP of diesel fuels. These additive molecules are "comb-type" copolymers whose lateral groups are the co-crystallizing segments with chainlengths similar to those of the longer paraffin molecules in the fuel. The teeth of the combs attach themselves to the longer-chained paraffins, increasing their solubility and effectively reducing the temperature of nucleation. Currently, CP depressants can reduce CP by a maximum of only 2–5°C, while many are not compatible with more traditional PP depressants (9,10,14,16,21,22).

PP studies. Table 2 shows a summary of PP data for selected DF1/SME blends (30 vol% SME), DF2/SME blends (20 vol%), and neat SME formulations that were treated with 1000 ppm additives. Only six additives were studied in DF1-blends. With respect to improving PP, additives were more effective at lower blend ratios. In many blends, this reduction was linear with respect to blend ratio. For example, 8500 Winterflow produced the following PP reductions: SME = 6°C and DF2 = 23°C. Interpolating these data for a 20 vol% SME-in-DF2 blend yields a predicted reduction of 19°C; in Table 2, the measured reduction for the 20% blend was 18°C.

Additives were evaluated for overall effectiveness as follows: taking the mean value across six blend ratios (0, 10, 20, 30, 50, and 100 vol% SME) for untreated formulations; taking the mean value across six blend ratios for each given additive; and calculating two-sample Student's *t*-values, assuming unequal variances, with respect to a given additive and the untreated blends. With respect to a significance level of 0.10, most of the additives were not effective in reducing PP of distillate/SME blends. For DF2-blends, only 8500 Winterflow > DFI-200 were effective; for DF1-blends, only Hitec 672 ~ DFI-200 were effective. The results for 8500 Winterflow in DF2-blends were interesting because this additive contained no EVA copolymers. Also interesting was the result for Fuel Power Diesel Fuel Treatment in DF2-blends. Its low overall performance was not surprising because it was rated 100% soluble in water by its supplier. However, the *t*-value from its comparison with untreated blends revealed no significant impact, positive or negative, on mean PP. Finally, the best all-around performance in either DF1- or DF2-blends was given by DFI-200.

Evaluation of neat SME data showed that seven additives reduced PP by 3 to 6°C. Similarly, nonblended distillates showed PP reductions of 1 to 7°C for DF1 and −2 to 23°C for DF2. Thus, mechanisms associated with crystalline growth

TABLE 2
Low-Temperature Properties of Neat Soyate Methyl Ester (SME) and SME-in-Distillate Blends Treated with 1000 ppm Additive

Additive	DF Grade	Blend ratio (vol% SME)	PP (°C)	CP (°C)
None	No. 1	30	–25	–14
8500 Winterflow	No. 1	30	–39	–19
DFI-100	No. 1	30	–49	–14
DFI-200	No. 1	30	–45	–21
Hitec 672	No. 1	30	–44	–13
OS 110050	No. 1	30	–46	–17
Paramins	No. 1	30	–29	–14
None	No. 2	20	–21	–13
409 Flowmaster	No. 2	20	–22	–14
8500 Winterflow	No. 2	20	–39	–13
Diesel Conditioner AntiGel	No. 2	20	–23	–14
DFI-100	No. 2	20	–26	–14
DFI-200	No. 2	20	–32	–14
Diesel Fuel Supplement	No. 2	20	–19	–14
Diesel XL	No. 2	20	–28	–14
Fuel Power Diesel Fuel Treatment	No. 2	20	–18	–15
Hitec 672	No. 2	20	–27	–14
OS 110050	No. 2	20	–18	–15
Paramins	No. 2	20	–27	–14
Winter Pow-R Plus	No. 2	20	–23	–12
None	—	100	–2	0
409 Flowmaster	—	100	–3	–1
8500 Winterflow	—	100	–8	0
Diesel Conditioner AntiGel	—	100	–3	0
DFI-100	—	100	–6	–2
DFI-200	—	100	–8	–1
Diesel Fuel Supplement	—	100	–4	0
Diesel XL	—	100	–5	0
Fuel Power Diesel Fuel Treatment	—	100	–4	0
Hitec 672	—	100	–6	–2
OS 110050	—	100	–7	1
Paramins	—	100	–5	0
Winter Pow-R Plus	—	100	–4	6

and agglomeration in neat SME may be similar to those for distillate fuels. These results are encouraging with respect to employing diesel fuel additives to improve the storage stability or enhancing the winterization of methyl esters.

CP studies. Table 2 also shows a summary of CP data for selected DF1/SME blends (30 vol% SME), DF2/SME blends (20 vol%) and neat SME formulations treated with 1000 ppm additives. Only six additives were studied in DF1 blends. In general, most additives studied in this work did not greatly affect CP of distillate/SME blends. This was not surprising, owing to their efficacy in reducing PP. Notable exceptions include 8500 Winterflow, DFI-200, and OS 110050 in the DF1-blends, where CP reductions were in the range of 3 to 7°C.

Figure 1 shows mean CP values (CP_{Mean}) for DF2 blends taken across $n = 12$ additives and at constant blend ratio. Additive loading was 1000 ppm; data for untreated blends (CP°) were excluded from calculation of mean values. Confidence intervals (0.90 level) were in the range of 0.9 to 2.2°C. These intervals are relatively small in contrast to the American Society for Testing and Materials (ASTM) method D2500 guideline for repeatability, which is 6°C for oils other than petroleum middle distillates (23). None of the additives studied in this work distinguished themselves with respect to confidence intervals for a given blend ratio. The data in Figure 1 also allowed comparison of CP_{Mean} data with corresponding CP° data. The largest CP reduction by additive treatment was only 1.8°C on average for 30 vol% SME-in-DF2. Thus, additive treatment does not greatly affect CP of DF2/SME blends with respect to blend ratio.

Similar analyses were performed for DF1 blends, and the results are shown in Figure 2. CP_{Mean} data for DF1 blends treated with six additives (see Table 2) at 1000 ppm loading gave confidence intervals in the range of 3.3 to 5.5°C. These intervals are within the ASTM D2500 guideline for repeatability. Thus, analogous to DF2 blends, none of the additives distinguished themselves with respect to confidence intervals

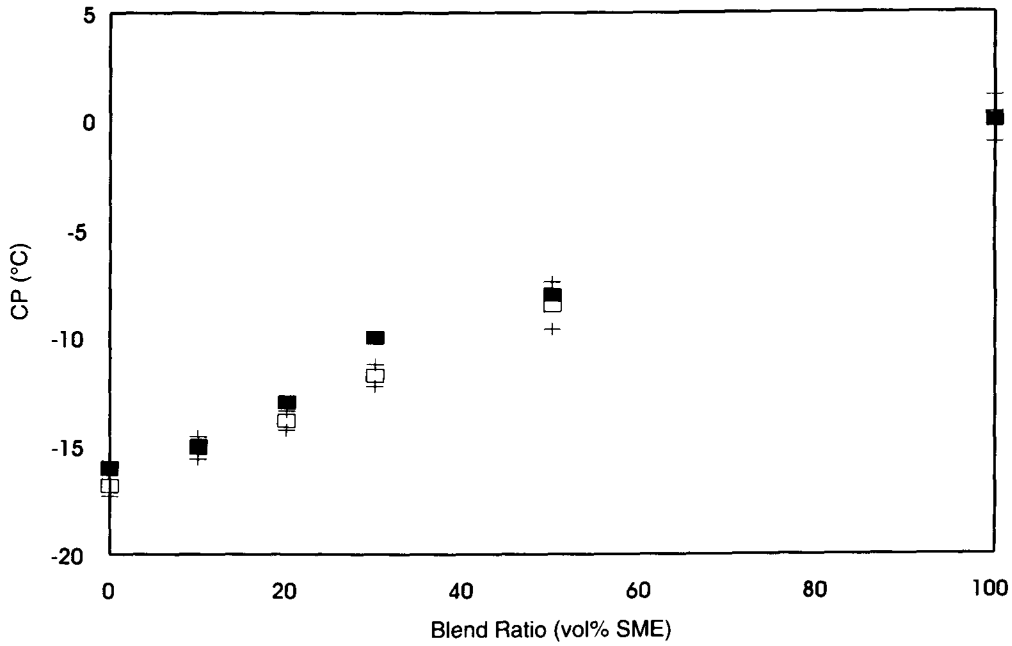

FIG. 1. Cloud point (CP) of soyate methyl ester (SME)-in-No. 2 diesel fuel (DF2) blends. CP_{Mean} = mean values at 1000 ppm additive loading and constant blend ratio (vol% SME); CP° = CP of untreated blends. Confidence intervals (+) are 0.90-level. CP_{Mean}, □; CP°, ■.

for a given blend ratio. In contrast to Figure 1, comparison of CP_{Mean} and CP° data in Figure 2 shows that additive treatment may affect CP of formulations with smaller blend ratios. Blend ratios not exceeding 30 vol% SME showed CP° values well above upper confidence limits for corresponding CP_{Mean} values. For example, treatment of blends with 20 vol% SME gave an average CP reduction of 6°C, while treatment with DFI-200 gave a maximum CP reduction of 8°C.

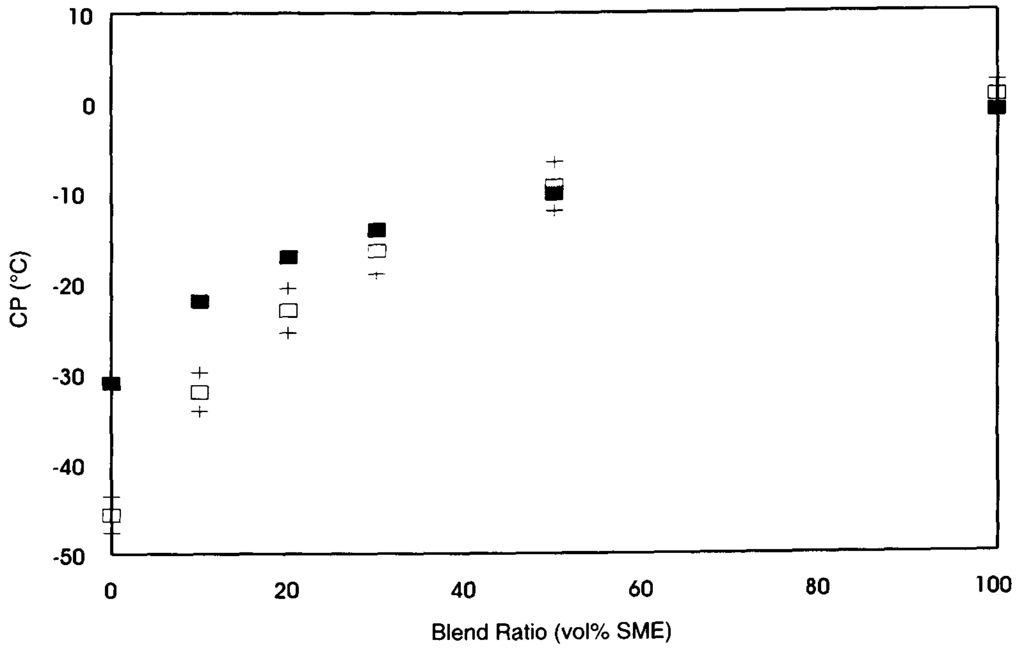

FIG. 2. CP of SME-in-No. 1 diesel fuel (DF1) blends. CP_{Mean} = mean values at 1000 ppm and constant blend ratio; CP° = CP of untreated blends. Confidence intervals (+) are 0.90-level. See Figure 1 for abbreviations and symbols.

Finally, blend ratios exceeding 30 vol% SME showed essentially no effects of additive treatment.

Earlier work with untreated distillate/methyl ester formulations pointed out the advantage of blending methyl esters with DF1 over DF2 to more efficiently reduce CP (13). Furthermore, the magnitude of this advantage was measurable only for blends not exceeding 30 vol% methyl esters. This work shows that additive treatment may enhance this advantage when blend ratios do not exceed 30 vol% SME.

Effects of additive loading. Five additives, 8500 Winterflow, DFI-200, Hitec 672, OS 110050 and Paramins, were selected to study the effects of additive loading in DF2 blends. Treating with loadings of 500, 1000, 1500, and 2000 ppm showed little impact on CP or low-temperature filterability (CFPP and LTFT). In most blends, PP decreased with increasing additive loading. Although this decrease in PP is nearly proportional to additive loading, its magnitude varied between additives.

At 2000 ppm, 8500 Winterflow was the most effective additive and reduced PP of a 20 vol% SME-in-DF2 blend to −59°C, a 35° reduction compared to the untreated blend. In addition, at 2000 ppm loading, 8500 Winterflow gave the maximum reduction in filterability, reducing CFPP by 8°C for a 20 vol% blend. Not surprisingly, increasing blend ratio reduces the magnitude of additive loading effects.

Anomalous behavior in the PP data was noted for OS 110050. For 20 vol% SME-in-DF2 blends, PP increased as additive loading increased from 0 to 1000 ppm, then decreased as loading increased in excess of 1000 ppm. In fact, OS 110050 did not positively influence PP until its loading exceeded 1700 ppm. At 2000 ppm, the net PP decrease was only 3°C. For 30 vol% SME-in-DF2 blends, minimum loading was 1600 ppm, and net PP reduction was 6°C. Neat SME formulations saw an immediate PP reduction at 500 ppm and gave a net PP reduction of 11°C. Thus, increasing blend ratio increased the efficacy of OS 110050.

Similar to data shown in Figure 1, CP_{Mean} values were determined across n = 12 additives at 2000 ppm loading and across n = 5 additives, 8500 Winterflow, DFI-200, Hitec 672, OS 110050 and Paramins, at 500 and 1500 ppm loadings, with respect to blend ratio. With respect to 0.90-level confidence limits and corresponding data for untreated blends (CP°), these results were nearly identical to those in Figure 1. Thus, additive loading does not greatly affect CP_{Mean} for loadings up to 2000 ppm.

The effects of additive loading on CP were examined *via* analysis of variance (ANOVA). Grand mean CP values were calculated with respect to blend ratio (additive loading ≥500 ppm). Results showed equivalent variances between grand mean CP values and their constituent CP_{Mean} values with respect to blend ratio. Neat SME formulations gave the lowest degree of acceptance and showed that the hypothesis was acceptable at significance levels as high as 0.442. Confidence intervals (0.90-level) about the grand mean CP values were in the range of 0.8 to 2.0°C, values that were within ASTM D2500 guidelines for repeatability. Given these results and those from comparisons between CP_{Mean} and CP° values discussed above (Fig. 1), it was not surprising that maximum separation between grand mean CP and CP° values was only 2°C.

Kinematic viscosity (ν) studies. Table 3 shows a summary of ν data for 20 vol% SME-in-DF2 blends at 40°C and −3°C. Data for nontreated blends are raw values. Data for additive-treated blends are mean values that are calculated across blends treated with 8500 Winterflow, DFI-100 (1000 and 2000 ppm only), DFI-200, Hitech 672, OS 110050, and Paramins at constant loadings of 500, 1000, 1500, and 2000 ppm. Finally, variances and 0.90-level confidence intervals were inferred for each mean ν value.

Variances were two to three orders in magnitude smaller than their corresponding mean ν values. As a result, confidence intervals were relatively narrow, an indication of good to excellent agreement between mean values and their constituent sample data. Although not presented in tabular form, similar results were obtained at 40°C for 0, 10, 30, 50, and 100 vol% blends, at −3°C for 0, 10, 30, and 50% blends, and at 5°C for neat SME (PP >−3°C for neat SME).

TABLE 3
Kinematic Viscosities (ν) of 20 vol% SME-in-No. 2 Diesel Fuel Blends Treated with Additives[a]

Loading (ppm)	T (°C)	ν[b] (mm²/s)	Variance	Confidence interval[c] Lower	Upper
0	40	2.994	—	—	—
500	40	3.136	0.0009	3.107	3.165
1000	40	3.053	0.0081	2.979	3.127
1500	40	3.160	0.0021	3.117	3.203
2000	40	3.097	0.0053	3.037	3.156
0	−3	11.56	—	—	—
500	−3	10.60	0.0751	10.34	10.86
1000	−3	10.07	0.0959	9.812	10.32
1500	−3	10.66	0.4203	10.04	11.28
2000	−3	10.23	0.1635	9.899	10.56

[a] Additives were 8500 Winterflow, DFI-100 (1000 and 2000 ppm only), DFI-200, Hitec 672, OS 110050, and Paramins. See Table 2 for abbreviations.

[b] Raw data for 0 ppm; mean values taken at constant additive loading (≥500 ppm).

[c] At 0.90-level (± 0.05).

In general, qualitative comparison of mean ν data showed that increasing additive loading does not greatly affect ν with respect to constant blend ratio. Similar to ANOVA of mean CP data, mean ν values were tested by comparing them with grand mean ν values taken for each blend ratio at 40°C, for 10 to 50 vol% blend ratios at −3°C, and for neat SME at 5°C, independent of additive loading (>500 ppm). At 40°C, results indicated that ν was not dependent on additive loading between 500 and 2000 ppm. This was also true for neat SME formulations at 5°C. For 10 to 50 vol% blends at −3°C, scatter between adjacent mean ν values precluded accepting the hypothesis of equivalent means. For example, the data in Table 3 show fluctuations in the range of ±0.43 to 0.59 mm^2/s, and ANOVA showed that the significance level for accepting the hypothesis was ~0.095. Typically, significance levels decreased with increasing blend ratio.

With respect to low-temperature properties, the effects of additives on viscosity are important. Additives promote the formation of small, compact crystals; however, they do not retard the rate of precipitation of wax crystals from solution. As temperature approaches a value below CP, additive-treated fuels contain a substantially large quantity of crystals suspended in solution. As the number of crystals per unit volume increases, ν increases. Thus, the effectiveness of cold-flow improver additives may be inferred from measuring their effect on ν.

Comparison of treated and untreated blends at 40°C showed that additives significantly increased ν of 0 to 50 vol% SME-in-DF2 blends. For these blends, ν values for untreated blends were consistently below confidence intervals for corresponding additive-treated blends. In addition, neat SME solutions experienced a slight increase in ν (at 40°C) when treated with additives. In general, these results are consistent with the notion that additives studied in this work should have a positive impact on low-temperature properties of distillate/SME blends.

In contrast to results at 40°C, those for ν data taken at temperatures closer to CP of neat SME showed very different effects of additive treatment. At −3°C, ν values for untreated blends were consistently above confidence intervals for corresponding additive-treated blends. At +5°C, neat SME solutions experienced a slight decrease in ν when treated with additives. Thus, for all blend ratios tested, additives reduced ν. These results indicate that the effect of additives studied in this work on hindering nucleation and early stages of growth in distillate/SME blends and at temperatures close to the CP of neat SME are minimal.

Filterability studies. Low-temperature filterability of untreated distillate/methyl ester blends has been investigated, and the results were reported by Dunn and Bagby (13). These filterability studies extend the reference study by examining the effects of additives on distillate/SME blends. Below, the term "reference study" refers exclusively to the earlier work.

The reference study showed that CFPP was nearly a linear function of CP. Figure 3 is a graph of CFPP vs. CP data that correspond to 102 separate formulations. Although not explicitly noted, formulations were characterized as follows: 20

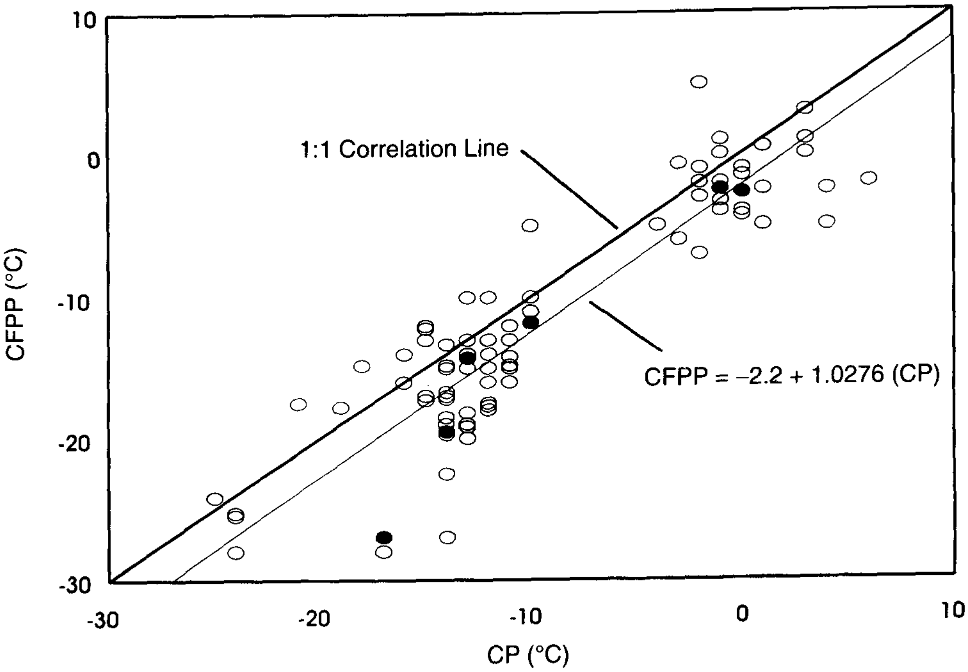

FIG. 3. Cold filter plugging point (CFPP) vs. CP of distillate/SME blends. See Figure 1 for abbreviations. ●, Without additives; ○, with additives.

or 30 vol% SME-in-DF1 blends; 20 or 30 vol% SME-in-DF2 blends; neat SME; additives = 8500 Winterflow, DFI-100, DFI-200, Hitec 672, OS 110050, or Paramins; and loading = 500, 1000, 1500, or 2000 ppm. Data for untreated blends were plotted for comparison. Least-squares regression yielded the following mathematical expression:

$$\text{CFPP} = -2.2 + 1.0276\,(\text{CP}). \qquad [1]$$

The regression coefficient (R^2) was 0.8220; the standard error of the y-estimate (σ) was 3.5, corresponding to a variance from residuals (σ^2) of 12.2966. Confidence intervals (0.90-level) for the slope (β) and intercept (η_0) were $\beta \in (0.9587, 1.1065)$ and $\eta_0 \in (-3.2, -1.3)$.

The coefficients in Equation 1 were tested against null hypotheses *via* ANOVA. Results showed a relatively large probability (0.743) for $\beta = 1$; however, results showed little probability (<0.001) for $\eta_0 = 0$, indicating that the real line does not intersect the origin. Hence, Equation 1 may be parallel but not coincidental to a 1:1 correlation line.

These results are analogous to those from the reference study. Confidence intervals from that study were $\beta \in (0.8872, 1.1510)$ and $\eta_0 \in (-4.3, -1.5)$. The coefficients from Equation 1 lie correspondingly within these intervals. That is, coefficients determined from analysis of combined data from untreated and treated formulations fell within confidence intervals predicted from earlier analysis of untreated formulations. Overall, there is good agreement between results from two studies that separately examined untreated and additive-treated distillate/methyl ester blends. Results discussed earlier showed that additives studied in this work do not greatly affect the CP of distillate/SME blends, under most conditions. Logically, the data in Figure 3 show that additive treatment offers no significant advantages for improving CFPP (or CP) of distillate/SME blends.

Figure 4 is a graph of LTFT vs. CP data that represent 90 formulations similar to those shown in Figure 3. The reference study showed that the relationship between LTFT and CP was close to an empirical 1:1 correlation. Corresponding data pairs of mean CP and LTFT values were compared in a series of two-sample *t*-tests by assuming unequal variances. Results showed a relatively high probability (0.579) that mean CP and LTFT values were equivalent, indicating that CP and LTFT may be directly correlated for distillate/SME blends studied in this work. These results were in agreement with those in the reference study.

Least-squares regression of the data in Figure 4 yielded the following expression:

$$\text{LTFT} = -2.4 + 0.8140\,(\text{CP}) \qquad [2]$$

where $R^2 = 0.8984$ and $\sigma = 2.0$ ($\sigma^2 = 4.0252$). Confidence intervals (0.90-level) for the slope and intercept were $\beta \in (0.7659, 0.8621)$ and $\eta_0 \in (-3.0, -1.8)$.

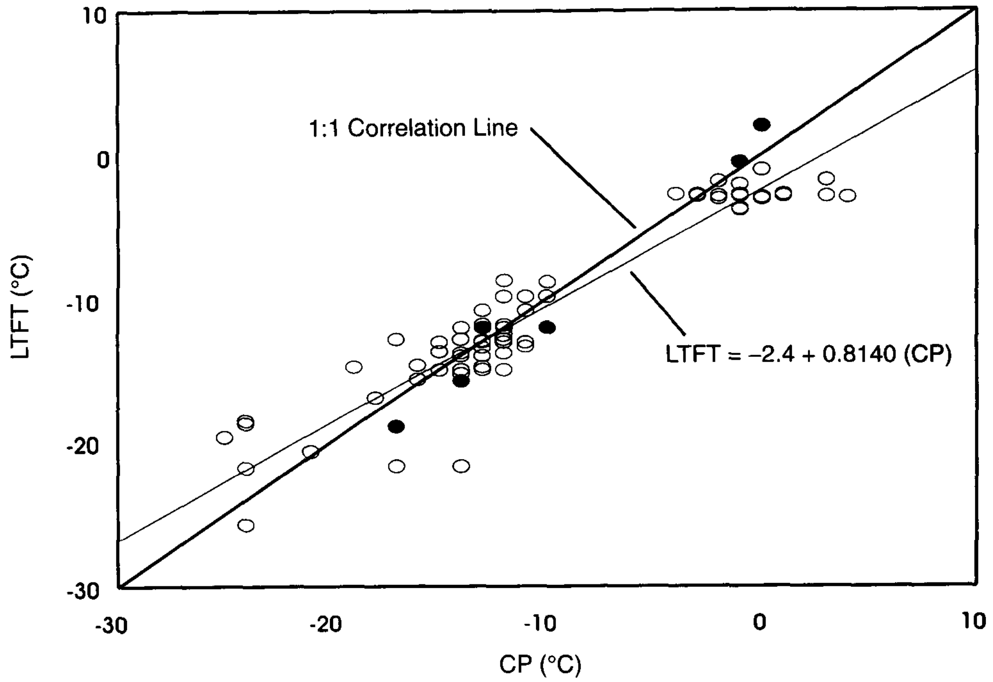

FIG. 4. Low-temperature flow test (LTFT) vs. CP of distillate/SME blends. See Figure 1 for abbreviations and symbols.

Similar to CFPP vs. CP, the coefficients from Equation 2 were tested against null hypotheses *via* ANOVA. Results showed little probability (<0.001) for either hypothesis; thus, $\beta \neq 1$ and $\eta_0 \neq 0$. The reference study reported relatively high probabilities of 0.780 for $\beta = 1$ and 0.605 for $\eta_0 = 0$ for untreated blends. Furthermore, the coefficients from Equation 2 do not lie within confidence intervals predicted by the reference study, which were $\beta \in (0.8959, 1.1434)$ and $\eta_0 \in (-1.0, 1.9)$. This work shows that treating distillate/methyl ester blends with cold-flow additives disrupts the empirical 1:1 correlation between LTFT and CP demonstrated for untreated blends.

A comparison of lines, predicted by Equation 2 and a 1:1 correlation, is also shown in Figure 4. The distance in LTFT between the lines is –3.3 at CP = 5°C and 2.3 at CP = –25°C. These values are close to the ASTM D4539 guideline for repeatability between LTFT measurements, which is 2°C (24). Furthermore, 70 of 90 points plotted in Figure 4 fall within ±2°C of the 1:1 correlation line, making 78% of the CP data adequate predictions for LTFT. Furthermore, the average LTFT distance between the lines is only –0.6°C. Although statistical analysis of Equation 2 rejected the notion that LTFT of additive-treated distillate/SME blends may be estimated from a 1:1 correlation with CP, this work indicates that CP may be effective in predicting LTFT ±2°C.

The statistical failure of Equation 2 may be analyzed by examining the distribution of data points about the 1:1 correlation line. The points appear to be in two clusters, one in a low-CP region defined by the range –25 to –10°C and the other in a high-CP region defined by the range –5 to 5°C. In the low-CP region, distribution appears to be symmetrical with 51 of 60 points that fall within 2°C of the 1:1 correlation line. Thus, additive treatment of distillate/SME blends offers little advantage in reducing LTFT when CP ≤–10°C. These results were analogous to those reported in the reference study.

In the high-CP region, a large portion of the data points representing treated formulations blends are below the 1:1 correlation line predicted by the reference study. For 11 of 28 treated formulations, LTFT is overpredicted by more than 2°C. In addition, 24 points that represent additive-SME mixtures fall below the 1:1 correlation line compared with two points that represent neat SME falling above the line. Thus, in contrast to results for distillate/SME blends, additive treatment of neat SME yields positive improvement of LTFT. Taken as a whole, the distribution of additive-SME data points in the high-CP region is the most likely cause for the failure of the 1:1 correlation line to predict LTFT from CP with respect to the CP range studied in this work.

The reference study also recommended that approaches for improving low-temperature filterability of distillate/methyl ester blends be designed to reduce CP. Earlier discussion in this work points out that additives did not greatly affect CP (or ν) of distillate/SME blends under most conditions. Remarkably, these studies show that some additives not expected to improve low-temperature properties can significantly reduce LTFT with respect to formulations with CP in the range of –5 to 5°C. It is feasible that co-crystallization of additive molecules increases the drag coefficient that is exerted by the bulk liquid solution on solid crystals. This might allow a reduction in the rate of solids deposition on the LTFT filter cloth. In addition, mass transfer of additive-methyl ester crystals onto the filter surface may cause formation of a solid cake with different permeation properties than associated with additive-wax buildup from distillate fuels. Effects such as these would be more readily noticeable in LTFT data, which are collected under more stringent conditions than CFPP data.

Nevertheless, 8500 Winterflow and DFI-200 were the two most effective additives for improving LTFT of neat SME formulations. Both decreased LTFT by 6°C at 2000 ppm loading. At the same loading, DFI-100, Hitec 672, and OS 110050 reduced LTFT by 5°C. Each of these five additives decreased LTFT by 5°C at 1000 ppm loading. This work offers some encouragement for improving low-temperature flow of alternative diesel fuels that cannot be formulated with petroleum derivatives. On the other hand, this work generally reinforces the notion that approaches for improving LTFT or CFPP of distillate/methyl ester blends should focus on reducing CP.

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