Low-Temperature Properties of Triglyceride-Based Diesel Fuels: Transesterified Methyl Esters and Petroleum Middle Distillate/Ester Blends

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ABSTRACT: This work examines low-temperature properties of triglyceride-based alternate fuels for direct-injection compression-ignition engines. Methyl esters from transesterified soybean oil were studied as neat fuels and in blends with petroleum middle distillates (No. 1 or No. 2 diesel fuel). Admixed methyl esters composed of 5–30 vol% tallowate methyl esters in soyate methyl esters were also examined. Pour points, cloud points, and kinematic viscosities were measured; viscosities at cooler temperatures were studied to evaluate effects of sustained exposure. Low-temperature filterability studies were conducted in accordance with two standard methodologies. The North American standard was the low-temperature flow test (LTFT), and its European equivalent was the cold-filter plugging point (CFPP). With respect to cold-flow properties, blending methyl esters with middle distillates is limited to relatively low ester contents before the properties become preclusive. Under most conditions, cold-flow properties were not greatly affected by admixing the methyl esters with up to 30 vol% tallowate (before blending). Least squares analysis showed that both LTFT and CFPP of formulations containing at least 10 vol% methyl esters are linear functions of cloud point. In addition, statistical analysis of the LTFT data showed a strong 1:1 correlation between LTFT and CP. This result may prove crucial in efforts to improve low-temperature flow properties of alternate diesel fuels that contain methyl esters derived from triglycerides.
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KEY WORDS: Blends, cloud point, cold-filter plugging point, kinematic viscosity, low-temperature flow test, methyl esters, methyl soyate, methyl tallowate, pour point.

The notion of developing alternate or emergency diesel fuels from plant oils and/or animal fats (triglycerides) has been around for some time. Triglycerides have many fuel-related physical properties that compare well with middle distillates, properties that include gross heats of combustion and cetane ratings (1,2). Short-term performance and Engine Manufacturer's Association engine tests have shown that triglycerides are sufficient fuels or fuel extenders for direct-injection diesel engines (3–8). However, other tests identified at least one limiting characteristic—viscosity (1,9,10). Typically, triglycerides have viscosities that are an order in magnitude greater than No. 2 diesel fuel. Experimental evidence has indicated that relatively high triglyceride viscosities degrade fuel atomization and aggravate conditions that lead to incomplete combustion (10). Thus, development of triglycerides as alternate fuels for direct-injection diesel engines depends on reducing their viscosities through physicochemical modification.

There are several technologies for reducing the viscosity of triglycerides. At present, most parties interested in marketing triglyceride diesel fuels are focusing their attention on transesterification. This technology converts the triglyceride into another ester-based fuel by reaction with a readily available short-chain alcohol, such as methanol or ethanol (1, 11–13). An excess of alcohol is generally required to convert one mole of triglyceride into three moles of esters of its corresponding fatty acids plus one mole of glycerine by-product. At 60°C and with an alkali catalyst, transesterification can attain ~98% conversion in one hour, under anhydrous conditions (1,14). Methyl and ethyl esters from soybean oil have viscosities that are 85–90% reduced from that of the original triglyceride. Also, conversion into methyl or ethyl esters enhances other fuel characteristics such as cetane rating and volatility. Conversion does not greatly affect the gross heat of combustion (1).

The potential for combustion of methyl or ethyl esters in moderate climates may be further compromised by seasonal reductions in ambient temperature. These esters have cloud points (CP) and pour points (PP) that are 15–25°C higher than those of No. 2 diesel fuel (1). In general, diesel fuels develop operability problems when ambient temperatures cool to a point between corresponding CP and PP (15–19).

Consider the case of petroleum middle distillates. As ambient temperatures cool to a point slightly higher than the CP, *n*-paraffins (C_{18}–C_{30} *n*-alkanes) in the fuel reach their saturation temperature. Under these conditions, the fuel becomes a suspension of wax crystals in a mixture of shorter-chained *n*-alkanes, olefins, and aromatics (15,17,19). Although the crystals are initially submicron in size and invisible to the human eye, as temperatures drop further, they grow in size. When the particle size reaches ~0.5 μm, the crystals become

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visible, and the temperature at this point is defined as the CP (15,19). Left unchecked, the crystals continue to grow into large flat plate-like structures (16–18). As temperatures drop below the CP, the crystals become large enough (0.5–1 mm) to fuse together into large agglomerates (15,18). This results in restricted flow through fuel lines and blocked filters, and eventually in fuel starvation and stalled engines.

With respect to long-chain methyl esters, the problem is further aggravated because their CPs are significantly higher than that of diesel fuel. Consider methyl esters from soybean oil (SME). As temperatures approach freezing (0°C), crystals large enough to cloud the mixture become visible. These crystals are primarily composed of methyl octadecanoate. The growth of the crystals depends on the composition of saturated methyl esters other than octadecanoate (e.g., hexadecanoate) and morphology relative to the nature of the remaining liquid portion of the mixture (15,17). Another complication for the methyl esters may reside in the relatively small difference between CP and PP (for methyl soyate, PP is only ~2°C below CP).

One method of mitigating the effects of wax crystal formation is to blend the methyl esters with diesel fuel. This dilutes the fraction of saturated long-chain methyl esters in the mixture, lowering both CP and PP. One recent report (20) suggests that the most attractive option for marketing SME is to blend them with diesel fuel to improve emissions. Several recent studies (21–25) have shown that, under steady-state conditions, diesel/methyl ester blends significantly reduce smoke opacity, particulates, unburned hydrocarbons, and carbon dioxide, with respect to baseline diesel fuels. Methyl ester-based fuels also showed a slight reduction in carbon monoxide emissions, although nitrous oxide emissions were at best unchanged.

On the other hand, a number of applications exist where triglyceride-based diesel fuels are suitable with the mandate that no petroleum distillate fuels are present in the formulation. One example is in marine applications, where spillage, exhaust odor, and emissions pose significant environmental hazards. Another example is in underground mining, where emissions and ventilation are major economic considerations. Thus, investigation of low-temperature operability problems should not overlook the neat esters standpoint.

This work is a preliminary study of low-temperature flow problems associated with methyl esters from triglycerides. This work examines the significance of the limitations of the methyl esters as well as how the limitations are affected in blends with petroleum middle distillates. The most substantial contribution of this work will be in the area of identifying pertinent approaches to predict low-temperature operability on the basis of laboratory experimental analysis.

Two types of methyl esters were examined, SME and admixtures of methyl esters from tallow (TME) and SME. Blends with distillates included both No. 1 (DF1) and No. 2 (DF2) diesel fuel. In accordance with routine petroleum industry practices for evaluating diesel fuels (2,15), CP and PP studies were conducted. Kinematic viscosity measurements at nonstandard temperatures (at −3 and +5°C) were conducted to examine the effects of quiescent, sustained exposure to cooler temperatures. The conditions were selected to exemplify those that might be expected during operation in temperate climates. Viscosities also were measured at 40°C, the American Society for Testing Materials (ASTM) standardized temperature for testing diesel fuels.

Low-temperature filterability studies were conducted according to two standard methods, cold-filter plugging point (CFPP) and low-temperature flow test (LTFT). Both methods were developed to predict minimum overnight operability temperatures more accurately than CP or PP data (15,18,19). Currently, LTFT is the most reliable predictor for low-temperature operability of North American diesel equipment (15,26,27); while CFPP is the accepted methodology in Europe, South America, Africa, and the Asia-Pacific rim (15,19). In this work, CFPP studies were conducted to allow comparison with LTFT data and to enhance the usefulness of the results worldwide.

EXPERIMENTAL PROCEDURES

Materials. SME were from Interchem (Overland Park, KS) and obtained courtesy of the National Biodiesel Board (Jefferson City, MO). The esters were double-distilled by the manufacturer to remove nearly all traces of glycerine. As received, the samples contained a small amount [~200 mL in a total of 10 gal (38 L) of sample] of an immiscible brown liquid. This material was analyzed by gas chromatography and found to contain mostly water (9.9% by Karl Fischer titration) and glycerine. Its pH was 6.8, and moisture/volatiles was 13.2% determined by evaporation. The material was thoroughly removed from the esters *via* separatory funnel prior to any experimentation.

Gas chromatography analysis of SME yielded 10.7 wt% hexadecanoate ($C_{16:0}$), 4.3% octadecanoate ($C_{18:0}$), 24.5% octadecenoate ($C_{18:1}$), 52.2% octadecadienoate ($C_{18:2}$), and 8.3% octadecatrienoate ($C_{18:3}$). Water content was 0.07% (Karl Fischer method) and moisture/volatiles was 0.19% by evaporation. Acid value was 0.28, peroxide value was 126, calculated iodine value was 132.6, and phosphorus content was less than 0.1 ppm. Cetane rating was ~46.2, and gross heat of combustion was ~39.8 MJ/kg (1). Viscosity was 4.3 cSt (mm^2/s) at 40°C, CP was 0°C, PP was −2°C, flash point (T_{FL}) was = 154°C (closed cup), specific gravity (SG) was 0.887 at 15.6°C relative to distilled water at 15.6°C, and ash content was 0.12 wt%.

TME, Kemester 143, were from Witco (Memphis, TN). Gas chromatography analysis showed 0.2 wt% tetradecanoate ($C_{14:0}$), 28.7% hexadecanoate, 2.6% hexadecenoate ($C_{16:1}$), 20.8% octadecanoate, 43.0% octadecenoate, 4.3% octadecadienoate, 0.4% octadecatrienoate and a trace (<0.1%) of unknown material. Water content was 0.73% (Karl Fischer method), and moisture/volatiles was 0.11% by evaporation. Calculated iodine value was 47.7, phosphorous content was

0.34 ppm, T_{FL} was 145°C (closed cup), and SG was 0.876 at 15.6°C relative to water at 15.6°C.

Low-sulfur (<0.05 wt%) Phillips Standard diesel fuel (DF2) was obtained from the National Institute for Petroleum and Energy Research (Bartlesville, OK). Cetane rating was 45.8, and gross heat of combustion was 45.3 MJ/kg (1). Viscosity was 2.8 cSt (mm^2/s) at 40°C, CP was −16°C, PP was −27°C, T_{FL} was 69°C (closed cup), and SG = 0.848 at 15.6°C relative to water at 15.6°C.

DF1 was from Midwest Oil (East Peoria, IL). Viscosity was 1.6 cSt (mm^2/s), CP was −31°C, PP was −45°C, T_{FL} was = 55°C (closed cup), and SG was 0.811 at 15.6°C relative to water at 15.6°C.

Methods. Methyl esters were blended with diesel fuel in standard volumetric flasks. In this work, blend ratios are reported as vol% esters; the term "vol% esters" refers specifically to the total volume percent of methyl esters in a formulation. With respect to admixed methyl esters, the term "volume ratio" refers specifically to the SME/TME volume ratio *prior* to blending with diesel fuel.

CPs were measured according to ASTM method number D2500 (28); PPs were measured according to ASTM D97 (19). Equipment was from Koehler (Bohemia, NY). Samples were filtered to remove moisture, then sealed in glass jars fitted with cork stoppers. The jars were placed in a cooling bath containing an ethanol/dry-ice mixture. Cooling rate of a given sample depended on its heat capacity and its temperature with respect to the temperature of the ethanol/dry-ice bath. The samples were examined at 1°C intervals for CP and at 3°C intervals for PP. The temperature where haziness was observed near the bottom of the liquid was the CP. The lowest temperature where movement of the liquid was observed was the PP. A minimum of three replicate measurements was averaged for each data point.

CFPP has no formal ASTM protocol; however, CFPP methodology is outlined in IP 309 (15,19). The apparatus was from Koehler. The procedure began by pouring the liquid sample into a test jar and covering it with a stopper fitted with a thermometer (ASTM-equivalent) and a pipette/filter joint containing a 45 µm wire-mesh filter screen. The jar was secured by spacers and a support ring within a water-tight brass jacket that extended into a cooling bath filled with an ethanol/dry-ice mixture. The sample cooling rate was similar to those outlined in ASTM D2500 (CP) and ASTM D97 (PP). At 1°C intervals, the liquid sample was filtered under a 200-mm H_2O (0.0194 atm) vacuum. The lowest temperature where 20 mL successfully filters within 1 min (60 s) was the CFPP. Filter screens were washed with petroleum ether and acetone between tests.

LTFT was performed in accordance with ASTM D4539 (30). Although LTFT apparatus and methodology are analogous to CFPP, the method is significantly less user-friendly than CFPP. Also, no vendor offering packaged LTFT-specific equipment could be located. Figure 1 is a schematic of the apparatus as it was built according to specifications outlined in ASTM D4539. The sample container was placed in a Neslab (Portsmouth, NH) Endocal LT-50 refrigerated bath. Between tests, the sample container was covered with a rubber stopper. During a test, the rubber stopper was replaced by the glass lid and filtering tube shown in Figure 1. The filtering tube was connected by radiator tubing to a brass joint that contained a 17-µm stainless-steel wire-mesh filter screen. The 400-mL tall-form receiving beaker was mounted on a ring stand sitting adjacent to the bath. Radiator tubing connected the glass tubes

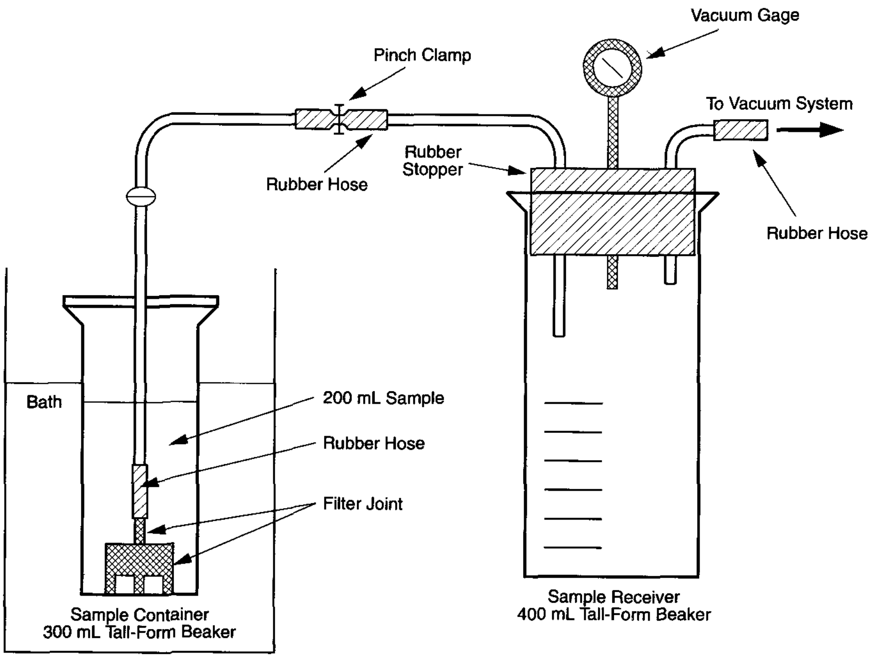

FIG. 1. Schematic of low-temperature flow test (ASTM D4539, Ref. 30) apparatus.

on either side of the pinch clamp, and heavy rubber tubing connected the receiving beaker to the vacuum source.

Prior to measurement, liquid samples were filtered to remove moisture and large dust particles. During a run, the 300-mL tall-form beaker, containing 200 mL of sample, was placed in the cooling bath. Sample cooling rate was regulated at 1°C/h by programming the Endocal LT-50 with a personal computer. At 1°C intervals, the liquid sample was filtered under a vacuum of 20 kPa (0.197 atm). The lowest temperature where 180 mL of sample successfully filters into the 400-mL tall-form beaker within 1 min (60 s) was the LTFT. Filter screens were washed with *n*-heptane and acetone between tests.

Kinematic viscosities (ν) were measured at 40°C according to ASTM D445 (31). Calibrated Cannon-Fenske routine viscometers were from Cannon (State College, PA). The viscometers were equilibrated for at least an hour after immersion in a Cannon model CT-1000 distilled-water viscometer bath. Viscosities were also measured at +5 and −3°C by methods similar to those outlined in ASTM D445. Equilibration time was overnight (~15 h). Viscometers were re-calibrated for the lower temperatures with a mineral oil standard obtained from Cannon. In these studies, viscometers were equilibrated overnight in a Cannon model TE-1000 refrigerated methanol viscometer bath.

RESULTS AND DISCUSSION

PPs and CPs. The petroleum industry routinely uses PPs and CPs to characterize low-temperature properties of diesel fuels. PPs are useful as quality-control specifications or low-temperature handling indicators for large storage tanks and pipelines at refineries and terminals. CPs are useful to the refiner or terminal operator when blending DF1 and DF2 during cooler months (15,18,19).

Figure 2 is a graph of PP results for blends of DF1/SME, DF2/SME, DF1/admixed methyl esters, and DF2/admixed methyl esters. The admixed methyl esters volume ratio was 80 SME/20 TME before blending. Figure 3 is an analogous graph of CP results for the same four blended systems.

For blends containing as little as 10 vol% esters, both PP and CP were significantly affected. The presence of saturated long-chain methyl esters, which constituted a minimum of 15 wt% of the total methyl esters, has a substantial effect on nucleation and agglomeration kinetics of middle distillate/methyl ester blends. From the practical standpoint of cold-flow properties, these results demonstrate the limitations of blending methyl esters with middle distillates. For example, it is reasonable to place an upper limit on PP of −20°C. At that limit, only 20 vol% esters may be blended with DF2, while only 35 vol% esters may be blended with DF1.

Consider the results for blends with at least 50 vol% esters. Note that PP results between DF1- and DF2-blends show little deviation. Although some separation is noted in the CP results, the deviations are relatively small (2–4°C). Under the conditions of these studies, precipitation does not greatly depend on the grade of distillates in the blend. In other words, for blends with at least 50 vol% methyl esters, the nature of the remaining liquid portion of the mixture relative to precipitation is nearly independent of the grade of distillates.

Table 1 is a summary of PP and CP results for a series of DF2/admixed methyl ester blends with varying TME con-

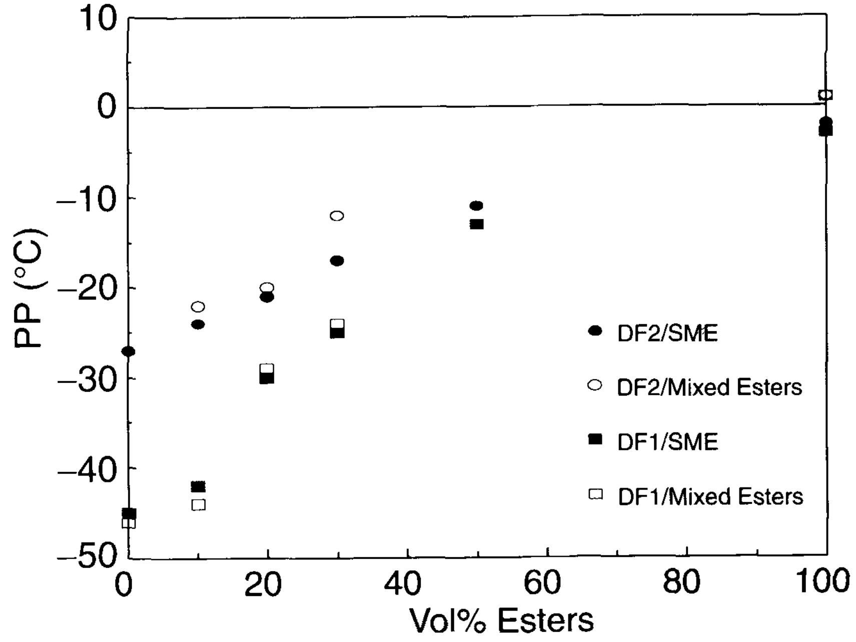

FIG. 2. Pour point (PP) results for diesel fuel/methyl ester blends. DF2 = No. 2 diesel fuel; DF1 = No. 1 diesel fuel; SME = soyate methyl esters; TME = tallowate methyl esters. Mixed esters volume ratio is 80 SME/20 TME (before blending).

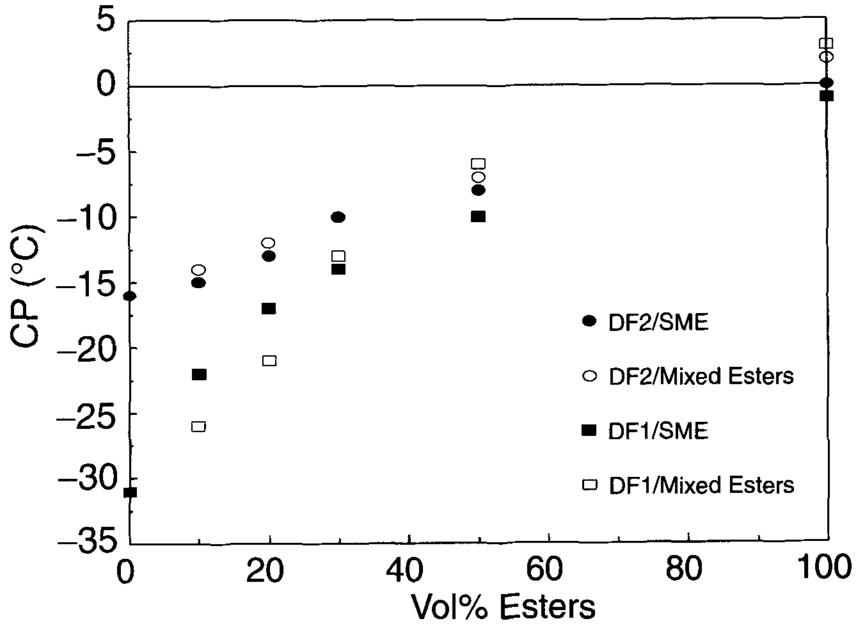

FIG. 3. Cloud point (CP) results for diesel fuel/methyl ester blends. Mixed esters volume ratio is 80 SME/20 TME (before blending). See Figure 2 for abbreviations.

tents. Before admixing the methyl esters, TME had a saturated methyl esters composition of ~49 wt%; therefore, it was reasonable to expect that admixing SME with TME increases PP and CP relative to SME-blends. With respect to vol% esters, PP and CP increase by a maximum of 3–4°C over the range of admixture volume ratios studied in this work. However, effects relative to TME content tend to increase in magnitude with increasing total ester vol%. Hence, increasing TME content beyond those studied in this work would be expected to result in significant effects on both PP and CP, regardless of total ester vol%. Nevertheless, these studies show that methyl ester admixtures with volume ratios up to 70 SME/30 TME may be blended with middle distillates before PP or CP is significantly compromised.

TABLE 1
Pour Points (PPs) and Cloud Points (CPs) of No. 2 Diesel Fuel Blended with Soyate Methyl Ester (SME)/Tallowate Methyl Ester (TME) Admixtures

Ester composition (vol ratio)[a]	Blend (vol% esters)	PP (°C)	CP (°C)
No ester	0	–27	–16
SME	10	–24	–15
SME	20	–21	–14
SME	30	–17	–10
SME	50	–11	–8
SME	100	–2	0
95 SME/5 TME	10	–20	–14
95 SME/5 TME	20	–19	–13
95 SME/5 TME	30	–14	–10
95 SME/5 TME	50	–12	–9
95 SME/5 TME	100	–4	2
90 SME/10 TME	10	–22	–14
90 SME/10 TME	20	–17	–12
90 SME/10 TME	30	–15	–11
90 SME/10 TME	50	–11	–8
90 SME/10 TME	100	–1	1
80 SME/20 TME	10	–22	–14
80 SME/20 TME	20	–20	–12
80 SME/20 TME	30	–12	–10
80 SME/20 TME	50	–11	–7
80 SME/20 TME	100	1	2
70 SME/30 TME	10	–21	–13
70 SME/30 TME	20	–15	–11
70 SME/30 TME	30	–13	–9
70 SME/30 TME	50	–8	–5
70 SME/30 TME	100	1	4

[a] Ratios are for SME/TME mixtures before blending with No. 2 diesel fuel.

Linearity of PP and CP with respect to vol% esters. For DF2-based blends, the PP data (Fig. 2) exhibit a nearly linear dependence on vol% esters. Least squares analysis of SME data yielded the following:

$$\text{PP} = 0.2519 \times [\text{vol\% esters}] - 25.8 \qquad [1]$$

where the coefficient of determination (R^2) = 0.9757, and the standard error of the Y-estimate (S) = 1.6 (variance, S^2 = 2.5879). R^2 represents the proportion of the dependent score variance accounted for by the predictor variable (vol% esters). Adjusting R^2 to remove the sample size distortion yielded R^2_{adj} = 0.9656. Based on 95% limits, the confidence intervals were (0.1967, 0.3071) for the slope and (–28.5, –23.2) for the intercept. Analysis of the admixed methyl esters (volume ratio 80 SME/20 TME) data gave the following:

$$\text{PP} = 0.2679 \times [\text{vol\% esters}] - 24.5 \qquad [2]$$

where R^2_{adj} = 0.9283 and S = 2.7 (S^2 = 7.1503). Based on 95% limits, the confidence intervals were (0.1762, 0.3596) for the slope and (–29.0, –20.1) for the intercept.

For DF2 blends, the CP data (Fig. 3) also exhibit a nearly linear dependence with respect to vol% esters. Least squares analysis gave the following estimates:

$$\mathrm{CP} = 0.1618 \times [\text{vol\% esters}] - 16.0 \qquad [3]$$

for DF2/SME blends and

$$\mathrm{CP} = 0.1779 \times [\text{vol\% esters}] - 15.7 \qquad [4]$$

for DF2/admixed methyl ester (80 SME/20 TME) blends. Analysis yielded $R^2_{adj} = 0.9871$ and $S = 0.67$ ($S^2 = 0.4478$) for Equation 3, and $R^2_{adj} = 0.9982$ and $S = 0.27$ ($S^2 = 0.07252$) for Equation 4. Based on 95% limits, the confidence intervals for Equation 3 were (0.1388, 0.1848) for the slope and (−17.1, −14.9) for the intercept. Confidence intervals for Equation 4 were (0.1687, 0.1871) for the slope and (−16.2, −15.3) for the intercept.

Equations 1–4 allow a convenient means of statistically testing the effect of admixing SME with TME before blending with distillates. If the hypothesis that corresponding equations are coincidental is statistically acceptable, then the conclusion that admixing methyl esters does not affect low-temperature properties of a formulation is valid for volume ratios up to 80 SME/20 TME.

The first part of the test was a comparison of slopes to determine whether lines are parallel. Applied to the PP data (Eqs. 1 and 2) this test yielded a two-tailed probability of 0.696; thus, the hypothesis of parallel lines was acceptable at relatively high significance levels. A common slope of 0.2599 was calculated from a weighted average of the individual slopes. The second part of the test was a comparison of intercepts to determine whether the lines are coincidental. Comparison of PP data yielded a probability of 0.187. Therefore, the hypothesis of identical lines estimated by Equations 1 and 2 was acceptable.

Testing of the slopes in the CP data (Eqs. 3 and 4) showed the hypothesis of parallel lines was acceptable with a two-tailed probability of 0.113. The common slope was 0.1698. Comparison of intercepts yielded a probability of 0.020; thus, the hypothesis of identical intercepts cannot be rejected (unless significance level exceeds 0.020). Furthermore, the ratio of variances for Equations 3 and 4 was 6.39, a value that yields a level of significance of ~0.06. Overall, the hypothesis of identical lines estimated by Equations 3 and 4 was acceptable with some limitations.

Viscosities. The ν results are posted in Table 2. Studies were carried out at cooler temperatures to examine general effects of sustained exposure to those temperatures by equilibrating quiescent samples overnight. Nearly all blended samples demonstrated excellent stability by remaining isotropic after sustained exposure at −3°C. An exception was the neat methyl esters, which solidified when equilibrated at −3°C; these samples were examined at 5°C and showed excellent stability at that temperature.

As expected, viscosity increases with increasing methyl ester content. This result is consistent with organic mixtures because long-chain methyl esters are more viscous than middle distillates (1).

TABLE 2

Kinematic Viscosities (ν) of Diesel Fuels Blended with SME and SME/TME Admixtures

Diesel fuel grade	Ester composition (vol ratio)[a]	Blend (vol% esters)	ν @ −3°C (cSt)	ν @ 40°C (cSt)
1	No ester	0	4.20	1.59
1	SME	10	4.74	1.68
1	SME	20	5.54	1.80
1	SME	30	5.45	2.04
1	SME	50	7.56	2.53
—	SME	100	11.36[b]	4.34
1	80 SME/20 TME	10	4.29	1.79
1	80 SME/20 TME	20	4.85	1.95
1	80 SME/20 TME	30	5.65	2.15
1	80 SME/20 TME	50	7.39	2.70
—	80 SME/20 TME	100	10.86[b]	4.36
2	No ester	0	10.40	2.81
2	SME	10	11.15	2.83
2	SME	20	11.56	2.99
2	SME	30	12.01	3.18
2	SME	50	13.10	3.41
—	SME	100	11.36[b]	4.34
2	95 SME/5 TME	10	10.80	2.86
2	95 SME/5 TME	20	12.19	3.04
2	95 SME/5 TME	30	12.90	3.09
2	95 SME/5 TME	50	13.71	3.44
—	95 SME/5 TME	100	10.57[b]	4.32
2	90 SME/10 TME	10	11.27	2.86
2	90 SME/10 TME	20	11.63	3.01
2	90 SME/10 TME	30	12.61	3.15
2	90 SME/10 TME	50	13.64	3.42
—	90 SME/10 TME	100	10.54[b]	4.39
2	80 SME/20 TME	10	11.47	2.88
2	80 SME/20 TME	20	12.33	3.04
2	80 SME/20 TME	30	12.75	3.16
2	80 SME/20 TME	50	13.69	3.50
—	80 SME/20 TME	100	10.81[b]	4.36
2	70 SME/30 TME	10	11.10	3.21
2	70 SME/30 TME	20	11.97	3.04
2	70 SME/30 TME	30	12.68	3.16
2	70 SME/30 TME	50	13.85	3.50
—	70 SME/30 TME	100	—[c]	4.46

[a] Ratios are for SME/TME mixtures before blending with diesel fuel. See Table 1 for abbreviations.

[b] Viscosity measured at 5°C.

[c] Plugged viscometer when left overnight at 5°C.

In general, viscosity increases with increasing TME content in blends, with respect to the total vol% esters. That is, decreasing the degree of unsaturation in long-chain methyl ester admixtures increases the viscosity of the blend. This result is consistent with those reported in two other studies. The first (32) examined the effects of the nominal degree of unsaturation of long-chain (C_{18}) fatty alcohols on the relative viscosity of fatty alcohol/methanol mixtures. Another study, reported by Goering *et al.* (2), correlated viscosity with increasing the average number of double bonds in the structure of triglycerides. Given the range of admixture volume ratios studied in this work, viscosity increases were relatively small, typically 0.75 cSt (mm^2/s) or smaller.

Filterability studies. Neither PP or CP data are useful when an accurate prediction of the operability limits of diesel fuels and equipment during cooler weather is desired. This is because CP consistently over-predicts operability temperatures, whereas PP tends to be overly optimistic (15,18,19,33). In the mid-1960s, field tests were conducted in Western Europe to develop a laboratory-scale test that can more accurately predict operabilities (15,19). The result was the development of the cold-filter plugging test, or CFPP (IP 309). This test adequately predicts operability limits when CFPP is no more than 10°C below CP (18,19).

Although CFPP is acceptable nearly worldwide, its methodology is not harsh enough to adequately predict operability limits relative to fuel quality and equipment prevalent in the North American transport industry (15,19). In the early 1980s, a more rigorous analog to CFPP, called the LTFT, was developed (15,19,33). Currently, LTFT is the most reliable predictor of low-temperature limits for fuels and systems running in North America.

Selected low-temperature filterability results are listed in Table 3. Both CFPP and LTFT data showed varying degrees of change with respect to blending distillates with methyl esters. Obviously, DF1/methyl ester blends showed better filterability temperatures than DF2/methyl ester blends. Analogous to PP and CP studies, increasing vol% esters had a substantial impact on low-temperature filterability. For DF1-based blends, increasing from zero to 20 vol% esters increased LTFT by 8–9°C and increasing from 20 to 30 vol% esters increased LTFT by 3–4°C. For DF2-based blends, the same trend was noted except that the magnitude of the increases was smaller (increasing from zero to 30 vol% esters increased LTFT by 2–4°C).

In general, comparing CFPP and LTFT for middle distillate/methyl ester blends is analogous to comparing them for neat distillates. That is, CFPP consistently predicts a lower operability temperature than the corresponding LTFT. However, the difference between predictors, $\Delta T = (\text{LTFT} - \text{CFPP})$, decreases in magnitude as vol% esters increases in the blends. Under conditions of these studies, blending middle distillates with methyl esters reduces the impact on filterability caused by differences in severity between LTFT and CFPP test methods.

TABLE 3
Cold-Filter Plugging Points (CFPP) and Low-Temperature Flow Test (LTFT) Results for Diesel Fuels Blended with SME and SME/TME Admixtures

Diesel fuel grade	Ester composition, (vol ratio)[a]	Blend (vol% esters)	CFPP (°C)	LTFT (°C)
1	No ester	0	–42	-27
1	SME	20	–27	–19
1	SME	30	–20	-16
—	SME	100	-2	0
1	80 SME/20 TME	20	–21	-18
1	80 SME/20 TME	30	–18	–14
—	80 SME/20 TME	100	-2	3
2	No ester	0	–18	–14
2	SME	20	–14	-12
2	SME	30	–12	-12
—	SME	100	–3	2
2	80 SME/20 TME	20	–13	-10
2	80 SME/20 TME	30	–11	-9
—	80 SME/20 TME	100	0	3

[a] Ratios are for SME/TME mixtures before blending with diesel fuel. See Table 1 for other abbreviations.

Results in Table 3 allow comparison between blends of DF2 with an 80 SME/20 TME methyl ester admixture and blends of DF2 with SME. At constant methyl ester content in blends, admixing TME with SME results in relatively small increases (1–3°C) in either LTFT or CFPP. Comparison of DF1-based blends shows the same trend with increases generally in the range 0–3°C. The lone exception was for 20 vol% ester blends, where CFPP increased by 6°C. Nevertheless, methyl ester admixtures with volume ratios up to 80 SME/20 TME do not significantly affect low-temperature filterability, under most conditions of these study.

Filterability vs. CP. Comparison of low-temperature filterability and CP results allowed the following intuitive observation: LTFTs for formulations containing methyl esters are close to their corresponding CPs. This contrasts distinctly against the case for neat middle distillates where LTFT (and CFPP) is solidly between CP and PP. Figure 4 is a graph of LTFT and CFPP vs. CP for the formulations studied in this work. Aside from the methodology employed to measure filterabilities, Figure 4 is blind toward distinctions such as vol% esters, SME/TME volume ratio, or the grade of distillate.

With one exception, the LTFT results are neatly scattered (±2°C) about the 1:1 correlation line; the lone exception is Point A ($\text{CP} = -31°\text{C}$; $\text{LTFT} = -27°\text{C}$), a point representing neat DF1. Hence, formulations containing at least 10 vol% esters show an empirical 1:1 correlation between CP and LTFT. CFPP data also exhibit a good linear relationship with respect to CP; however, these results are not scattered about the 1:1 correlation line. Figure 4 is consistent with discussions in the preceding section, noting that CFPPs for formulations containing methyl esters were consistently below their corresponding LTFTs.

The empirical relationship between low-temperature filterability and CP was tested in a series of statistical analyses. Only results for samples containing at least 10 vol% esters were treated.

Least squares regression of the LTFT data, performed with CP as the "independent" variable, yielded the following equation:

$$\text{LTFT} = 1.0197 \times \text{CP} + 0.4 \qquad [5]$$

where $R^2_{\text{adj}} = 0.9527$ and $S = 1.8$ ($S^2 = 3.1984$). Based on 95% limits, the confidence intervals were (0.8675, 1.1718) for the slope and (–3.1, 2.2) for the intercept. Testing for agreement between the data and the 1:1 correlation line was done *via* analysis of variance with respect to a comparison of the estimated slope and intercept with hypothesized actual slope (β) and intercept (η_0). The null hypotheses $\beta = 1$ and $\eta_0 = 0$ were both acceptable and yielded two-tailed probabilities of 0.780

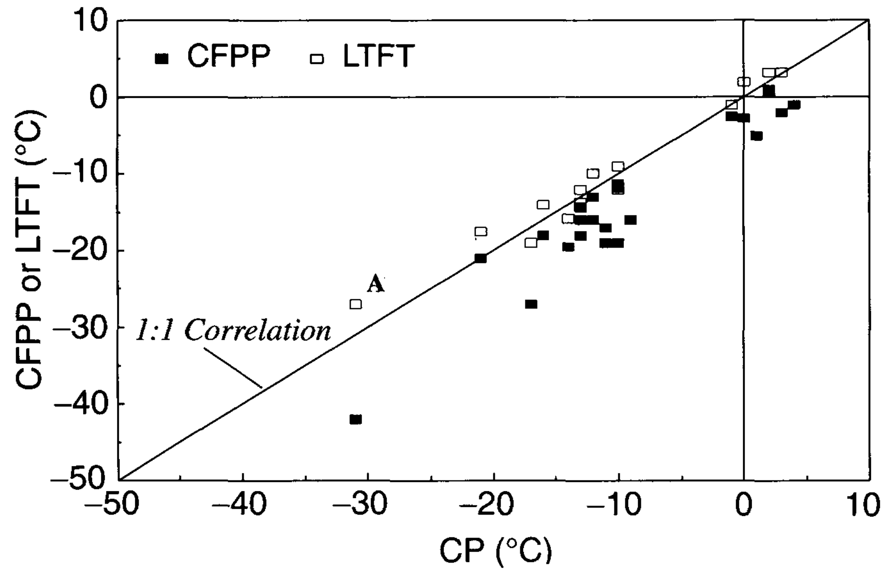

FIG. 4. Low-temperature filterability vs. corresponding CP for several diesel fuel/methyl ester blends. CFPP = cold-filter plugging point; LTFT = low-temperature flow test. See Figure 3 for other abbreviation.

for β and 0.605 for η_0. Based on 95% limits, the joint confidence region for the relationship estimated by Equation 5 was determined for all valid pairs (η_0, β). For the hypothesized parameters, the joint region includes the following intervals: if $\beta = 1$, then $-1.2 \leq \eta_0 \leq 1.7$; and if $\eta_0 = 0$, then $0.8306 \leq \beta \leq 1.1660$. Thus, the hypothesized parameters are mutually acceptable with respect to the 95% joint confidence region.

Least squares regression of the CFPP data, also performed with CP as the independent variable, yielded the following equation:

$$\text{CFPP} = 1.0191 \times \text{CP} - 2.9 \qquad [6]$$

where $R^2_{adj} = 0.8988$ and $S = 2.5$ ($S^2 = 6.2972$). Based on 95% limits, the confidence intervals were (0.8595, 1.1788) for the slope and (−4.6, −1.2) for the intercept. Analysis of variance showed that the null hypotheses $\beta = 1$ was acceptable, yielding a two-tailed probability of 0.808. The null hypothesis $\eta_0 = 0$ yielded a probability less than 0.002; thus, this hypothesis was unacceptable. The joint confidence region, based on 95% limits with respect to the relationship estimated by Equation 6, includes the following interval: if $\beta = 1$, then $-3.8 \leq \eta_0 \leq -2.3$. The joint confidence region did not intersect the line $\eta_0 = 0$.

The relationships estimated by Equations 5 and 6 were further tested to determine whether they were identical. First, they were tested for identical slopes (parallel lines). This hypothesis was acceptable with a two-tailed probability of 0.995; therefore, a common slope of 1.0193 was determined from a weighted average of individual slopes. Second, they were tested for identical intercepts. This hypothesis yielded a probability less than 0.001; thus, this hypothesis is unacceptable. Overall, the relationships estimated by Equations 5 and 6 are parallel, but they are not coincidental.

Testing the data by a series of two-sample *t*-tests allowed analysis with no assumption of an independent variable. Correlated groups *t*-tests were performed on data pairs of the form (CP, filtration limit), where the null hypothesis held that the actual difference between the filtration limit and its corresponding CP was zero. For LTFT data, the average difference between elements in data pairs was $(\text{LTFT} - \text{CP})_{avg} = -0.25$. The 95% confidence interval was (−1.34, 0.84), an interval that obviously includes zero. Correlated *t*-tests showed that the hypothesis was acceptable with a probability of 0.623. For the CFPP data, the average difference was $(\text{LTFT} - \text{CP})_{avg} = +3.0$, with a 95% confidence interval of (1.9, 4.1). Not surprisingly, *t*-tests showed that the hypothesis was unacceptable with a probability less than 0.0001.

Two-sample *t*-testing of the means of the filterability measurements against those of their corresponding CPs was also performed. Assuming equivalent variances, testing LTFT and CP gave a 0.940 probability of being comparable to each other, assuming unequal variances only slightly improved the probability to 0.943. Testing CFPP and CP gave probabilities of 0.206 from equivalent variances and 0.215 from unequal variances.

Summarizing the analysis, low-temperature filterabilities are proportional to CP. Estimated slopes of LTFT and CFPP vs. CP results are close to unity, and analyses indicated that the actual slopes may be parallel and equal to unity. In addition, the relationship between LTFT and CP is empirically a 1:1 correlation. On the other hand, CFPP is 3.3 ± 2.1 below their measured LTFT (or CP).

Under the conditions of these studies, the results show that LTFT may be measured by either of two statistically interchangeable methods, the standard LTFT methodology or CP. This is an important result with regard to developing approaches for improving low-temperature flow of diesel fuel formulations that contain methyl esters. If LTFT is a proper indicator of low-temperature operability limits, then development of approaches for improving low-temperature filterability should focus on lowering the CP of the formulation. In other words, if the CP can be reduced, then low-temperature operability will be ameliorated. This conclusion may be crucial, given that traditional methods for improving low-temperature operability of petroleum middle distillates have primarily focused on depressing PP rather than CP (18,19).

Recommendations. This work demonstrates the potential for operability problems at cooler ambient temperatures when long-chain methyl ester fuels are combusted in direct-injection compression-ignition engines. Results from PP, CP, and low-temperature filterability studies demonstrated significant limitations of blending esters with petroleum middle distillates to improve cold flow operability. When blended under cooler ambient conditions in moderate-temperature climates, formulations are essentially limited to relatively small methyl ester contents and should not exceed ~20 vol% in DF2 or ~35 vol% in DF1.

Under most conditions, SME/TME admixtures with up to 30 vol% TME (before blending) did not greatly affect CP, PP, low-temperature operability, or viscosity results, with respect to results for formulations with SME only. This may be economically important because tallow is historically less costly than soybean oil.

Results from CFPP and LTFT studies with middle distillate/methyl ester blends were consistent with those from studies with neat distillates. Although CFPP data tend to be more optimistic than LTFT data, the relative gap between these properties decreases as vol% esters increases in the blends. Blending with as little as 10 vol% methyl esters significantly decreases the effects of increased severity that LTFT methodology was designed to have over CFPP methodology.

Both LTFT and CFPP results showed excellent linear relationships with respect to CP. Furthermore, LTFT was empirically in 1:1 correlation with CP. These results were verified *via* statistical analysis and applied to formulations containing as little as 10 vol% methyl esters.

The 1:1 correlation between LTFT and CP has at least one potentially crucial ramification. If LTFT is a suitable predictor for low-temperature operability limits in North America, then efforts to identify and develop approaches to improve such limits should focus on lowering the CP of the formulation.

One approach might be to examine commercial additives developed by the petroleum industry. Most of these additives improve low-temperature operability of unblended diesel by depressing the PP. Such products may be effective on distillate/ester blends where ester contents are kept relatively small. In general, additives that depress PP have no significant effect on CP. Results from this work indicate that these additives may not be effective at improving neat methyl esters or distillate/ester blends with relatively large ester contents.

A more long-term approach might be to synthesize and develop other compounds, such as additives, that can attack the problem by addressing phenomena related to the esters. This approach may require more fundamental studies, such as electron microscopy, differential scanning calorimetry, or light scattering. These studies might examine the morphology of long-chain esters in model solvents, such as aromatics, medium-chain alkanes, unsaturated methyl esters, and other components that may be present in formulations.

Winterization is a process that depresses the CP of esters by equilibrating them at temperatures below their CP (and above their PP) over an extended period of time, then filtering away the solids. The magnitude of the effect on CP is limited by the corresponding PP; however, additives may be developed to depress PP and allow an enhanced winterization effect. Transesterification of triglycerides with larger alkanols such as ethanol or butanol or sterically bulkier alkanols such as isopropanol may have a substantial impact on low-temperature operabilities. For example, butyl esters have a CP = –3°C and a PP = –7°C (1). However, these esters are more expensive to produce than methyl esters, so their usefulness may be limited to smaller compositions or as additives. Finally, approaches exploiting colloidal properties of surfactants may allow development of formulations with substantially enhanced colligative properties with respect to nucleation and crystallization of esters.

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