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Effects of blending alcohols with poultry fat methyl esters on cold flow properties☆

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ABSTRACT

The low temperature operability, kinematic viscosity, and acid value of poultry fat methyl esters were improved with addition of ethanol, isopropanol, and butanol with increasing alcohol content. The flash point decreased and moisture content increased upon addition of alcohols to poultry fat methyl esters. The alcohol type did not result in a statistically significant difference in low temperature performance at similar blend ratios in poultry fat methyl esters. In addition, blends of ethanol in poultry fat methyl esters afforded the least viscous mixtures, whereas isopropanol and butanol blends were progressively more viscous, but still within specifications contained in ASTM D6751 and EN 14214. Blends of alcohols in poultry fat methyl esters resulted in failure of the flash point specifications found in ASTM D6751 and EN 14214. Flash points of butanol blends were superior to those of isopropanol and ethanol blends, with the 5 vol.% butanol blend exhibiting a flash point (57 °C) superior to that of No. 2 diesel fuel (52 °C). Blends of alcohols in poultry fat methyl esters resulted in an improvement in acid value with increasing content of alcohol. An increase in moisture content of biodiesel was observed with increasing alcohol content, with the effect being more pronounced in ethanol blends versus isopropanol and butanol blends. Finally, none of the alcohol–methyl ester samples exhibited a phase separation at sub-ambient temperatures.

1. Introduction

Low-level blends of ethanol in diesel fuel (E-diesel) are known to significantly reduce harmful exhaust emissions such as particulate matter (PM), hydrocarbons (HC) and carbon monoxide (CO) as a result of increased fuel oxygenation. For example, E20 (20% ethanol in diesel fuel) resulted in reductions of 55, 36, and 51% in CO, HC, and PM exhaust emissions, respectively [1]. However, drawbacks of E-diesel include reduced energy content [2,3], cetane number [3], flash point [3], lubricity [4] and immiscibility of ethanol in diesel over a wide range of temperatures [3–5]. To correct the immiscibility problem, surfactants at levels of up to 5% are required to stabilize E-diesel mixtures [4,5]. A recent study explored the utility of ethanol–biodiesel–diesel blends (EB-diesel) as a means to mitigate the miscibility issues of E-diesel [4]. The disadvantages of E-diesel were substantially reduced or eliminated in the case of EB-diesel prepared from 5% ethanol and 20% biodiesel (soybean oil methyl esters) in ultra low sulfur diesel fuel (ULSD, <15 ppm S) [4]. A later study [6] revealed that 3% ethanol, 2% biodiesel (sunflower oil methyl esters), and 95% low sulfur diesel (LSD, <500 ppm S) improved the pour point (PP) of the resultant blend. In general, EB-diesel blends resulted in reduced CO and HC exhaust emissions versus neat LSD [6]. Also elucidated were the effects of blending ethanol with biodiesel (E-biodiesel) in a 6:4 ratio on PP, kinematic viscosity, and flash point (FP). Specifically, the PP of biodiesel was reduced from −3 to −9 °C, kinematic viscosity (40 °C) was reduced from 4.22 to 1.65 mm^2/s, and FP was reduced from 187 to 14 °C after blending with ethanol [6]. Analogously, a blend of ethanol and biodiesel prepared from *Madhuca indica* oil exhibited lower FP, kinematic viscosity, PP, CO and NO$_x$ exhaust emissions, and slightly higher HC emissions versus unblended *M. indica* oil methyl esters [7].

The objective of the current study was to improve the low temperature operability of poultry fat methyl esters (PFME) through addition of ethanol, isopropanol, and butanol. Of additional interest was a comparison of alcohol–PFME fuel properties to ASTM D6751 [8] (Table 1) and EN 14214 [9], the American and

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Table 1
ASTM 6751 specifications for B-100 biodiesel and properties of Southeast biodiesel B-100.

Property	Approved ASTM method	Units	ASTM D6751 limits	Test results
Free glycerin	D6584	%mass	0.020 max	0.005
Total glycerin	D6584	%mass	0.240 max	0.169
Flash point	D93	°C	130 min	156
Acid number	D664	mg KOH/g	0.50 max	0.54
Water and sediment	D2709	%vol.	0.050 max	<0.01
Sulfur	D5453	ppm	15	8
Oxidation stability	EN 14112	hours	3 min	>18
Moisture by Karl Fischer	D6304	ppm	n/a	746
Calcium and magnesium	EN 14538	combined ppm	5 max	<1
Phosphorous	D4951	%mass	0.001 max	0.0005
Sodium and potassium	EN 14538	combined ppm	5 max	2
Copper strip corrosion	D130	n/a	no. 3 max	1a
Distillation temp. AET 90%	D1160	°C	360 max	360
Cetane number	D613	n/a	47 min	56
Sulfated Ash	D874	%mass	0.020 max	<0.005
Carbon residue	D4530	%mass	0.050 max	<0.02

European biodiesel standards, respectively. Poultry fat methyl esters were investigated as a result of their relatively high saturated fatty ester content. Saturated fatty esters have higher melting points than their corresponding unsaturated analogues, so low temperature fluidity is of particular concern for PFME. The low temperature operability of the resultant alcohol–PFME blends was ascertained through measurement of cloud point (CP), PP, and cold filter plugging point (CFPP). Also of interest was the influence of alcohol addition on the kinematic viscosity (40 °C), FP, acid value (AV), and moisture content of PFME.

2. Experimental

2.1. Materials

Poultry fat methyl esters (PFME) were obtained from Southeast Biodiesel, Inc. (North Charleston, SC, USA) and contained a proprietary antioxidant package. The certificate of analysis of PFME is reported in Table 1. Ethanol (200 proof; $<$0.02 mass% water) was purchased from Decon Labs, Inc. (King of Prussia, PA, USA), isopropanol (2-propanol, 99.9%; $<$0.02 mass% water) from Fisher Scientific (Fair Lawn, NJ, USA), and 1-butanol (99.8%; $<$ 0.02 mass% water) from Sigma–Aldrich Chemical Company (Milwaukee, WI, USA). All alcohols were used immediately as received and were stored over molecular sieves after first use.

2.2. Fatty acid profile of poultry fat methyl esters

Fatty acid methyl esters (FAME) of PFME were separated using a Varian (Walnut Creek, CA) 8400 GC equipped with an FID detector and a SP2380 (Supelco, Bellefonte, PA) column (30 m × 0.25 mm i.d., 0.20 μm film thickness). Carrier gas was He at 1 mL/min. The oven temperature was initially held at 150 °C for 15 min, then increased to 210 °C at 2 °C/min, followed by an increase to 220 °C at 50 °C/min, which was then held for 10 min. The injector and detector temperatures were set to 240 °C and 270 °C, respectively. FAME peaks were identified by comparison to the retention times of known reference standards. Poultry fat contained myristic (0.8 wt.%), palmitic (25.5 wt.%), palmitoleic (7.0 wt.%), stearic (5.6 wt.%), oleic (39.5 wt.%), linoleic (17.8 wt.%), linolenic (0.8 wt.%), and 11*Z*-eicosenoic (0.4 wt.%) acids, with trace amounts ($\leq$0.1 wt.%) of lauric, arachidic, erucic, behenic, lignoceric, 11*Z*,14*Z*-eicosadienoic, and 8*Z*,11*Z*,14*Z*-eicosatrienoic acids, along with a sum (2.4 wt.%) of unidentified fatty acids. FAME determination was run in triplicate and average values are reported.

2.3. Cloud point, pour point, and cold filter plugging point determination

Cloud point (CP) and pour point (PP) were measured in accordance to ASTM D5773 [10] and D5949 [11], respectively, using a model PSA-70S Phase Technology Analyzer (Richmond, B.C., Canada). The CP and PP values were rounded to the nearest whole degree (°C). For a greater degree of accuracy, PP measurements were made with a resolution of 1 °C instead of the specified 3 °C increment. Cold filter plugging point (CFPP) was determined following ASTM D6371 [12] utilizing an ISL Automatic CFPP Analyzer model FPP 5Gs (Houston, Texas, USA). Each experiment was run in triplicate (Table 2).

2.4. Kinematic viscosity determination

Kinematic viscosity (υ, mm^2/s) was measured with a Cannon–Fenske viscometer (Cannon Instrument Co., State College, Pennsylvania, USA) at 40 °C according to ASTM D445 [13]. All experiments were run in triplicate (Table 2).

2.5. Flash point determination

Flash point (FP, °C) was measured with a Pensky–Martens model HFP 339 closed-cup flash point apparatus according to ASTM D93 [14]. The procedure was modified by using dry ice to cool the apparatus before performing the test, as described in the Pensky–Martens manual. All experiments were run in duplicate and mean values are reported (Table 2).

2.6. Acid value and moisture content determination

Acid value (AV, mg KOH/g sample) titrations were performed as described in the official AOCS Acid Value Method Cd 3d-63 [15]. The titration endpoint was determined by the instrument and visually verified using a phenolphthalein indicator. Moisture content was determined using a Karl Fisher titration in accordance with ASTM D6304 [16]. Experiments were run in duplicate and mean values are reported (Table 2).

2.7. Preparation of alcohol:PFME blends

Ethanol, isopropanol, and butanol were added to PFME at 5.0, 10.0, and 20.0 volume percents (vol.%), respectively, resulting in nine alcohol:PFME blends.

2.8. Miscibility of alcohols in PFME at sub-ambient temperatures

All nine alcohol:PFME blend samples were explored at 8, 4, 0, and −15 °C for phase separation at sub-ambient temperatures. A standard laboratory refrigerator was used for storage at 8, 4, and 0 °C, whereas a laboratory freezer was used for the −15 °C increment. Each temperature increment (±1 °C) was held for 24 h.

2.9. Data analysis

Analysis of variance (ANOVA) was performed using the GLM procedure in Statistical Analysis System (SAS) for Windows, version