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Impact of fatty ester composition on low temperature properties of biodiesel–petroleum diesel blends ☆

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HIGHLIGHTS

- Seven biodiesels with different fatty acid profiles were blended with diesel fuel.
- Influence of biodiesel type on cold flow properties of blends was determined.
- Fatty acid profile did not affect cold flow properties at low (1–5%) blend levels.
- Cold flow properties at B1 to B2 were equivalent regardless of fatty acid profile.
- Mathematical relationships were noted between cold flow properties and blend ratio.

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ABSTRACT

Several biodiesel fuels along with neat fatty acid methyl esters (FAMEs) commonly encountered in biodiesel were blended with ultra-low sulfur diesel (ULSD) fuel at blend levels permitted by ASTM D975 (B1–B5) and cold flow properties such as cloud point (CP), cold filter plugging point (CFPP) and pour point (PP) were measured. The objective was to determine whether or not the fatty acid composition of biodiesel affects cold flow properties of blends at levels such as B1 to B5. Statistical methods such as least squares regression and one-way analysis of variance coupled with Tukey's Studentized Range test were applied to the resulting cold flow property data. Statistical analysis revealed that fatty acid profile did not affect cold flow properties at low blend levels unless the biodiesel sample contained a high percentage (>48%) of long-chain saturated FAMEs. Other important conclusions were that variances in cold flow property data at low blend levels (B1 to B2) were minimal and generally statistically equivalent regardless of fatty acid composition. Lastly, application of least-squares statistical regression to CP, CFPP and PP data revealed distinct mathematical relationships between cold flow properties and blend ratio. Specifically, CP was best fit to an exponential decay model whereas PP exhibited linearity and CFPP provided the highest R^2 values when fitted to polynomial equations. In summary, this study demonstrated that in most cases feedstock selection for biodiesel fuel had minimal impact on cold flow properties at the blend levels permitted by ASTM D975, the US standard specification for diesel fuel oils.

1. Introduction

Biodiesel must meet the requirements of fuel standards such as ASTM D6751 or EN 14214 before it may be blended with petrodiesel. Currently, blends up to B5 (5 vol% biodiesel in petrodiesel) and B7 are permitted in ASTM D975 and EN 590, the US and European diesel fuel standards [1,2]. Fuel properties depend on the fatty acid (FA) composition of the lipid from which biodiesel is derived, and as a result biodiesel prepared from different feedstocks will have different FA profiles and consequently different fuel properties [1–8]. The five most commonly encountered FAs in plant oils are palmitic (C16:0; hexadecanoic), stearic (C18:0; octadecanoic), oleic (C18:1; 9*Z*-octadecenoic), linoleic (C18:2; 9*Z*,12*Z*-octadecadienoic),

Abbreviations: AOCS, American Oil Chemists' Society; ASTM, American Society for Testing and Materials; AV, acid value; CEN, European Committee for Standardization; CFPP, cold filter plugging point; CME, canola oil methyl esters; CP, cloud point; FA, fatty acid; FAME, fatty acid methyl ester; FP, flash point; FPME, field pennycress oil methyl esters; KV, kinematic viscosity; mp, melting point; PME, palm oil methyl esters; PP, pour point; SG, specific gravity; SBME, soybean oil methyl esters; SFME, sunflower oil methyl esters; ULSD, ultra-low sulfur (<15 ppm) diesel; WCME, waste cooking oil methyl esters; YGME, yellow grease methyl esters.

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and linolenic (C18:3; 9*Z*,12*Z*,15*Z*-octadecatrienoic) acids. Other FAs, such as erucic (C22:1; 13*Z*-docosenoic) acid, are found in oils from the Brassicaceae family, of which rapeseed and field pennycress [9] are examples. Biodiesel fuels containing less common FAs include capric (C10:0; decanoic) acid-containing cuphea [10], lauric (C12:0; dodecanoic) acid-containing coconut [11], palm kernel [11], and babassu [12], petroselenic (C18:1; 6*Z*-octadecenoic) acid-containing coriander [13], and 5Z-eicosenoic (C20:1) acid-containing meadowfoam [14].

Cold flow is characterized as the ability of a fuel to resist solidification at sub-ambient temperatures. The length of the hydrocarbon tail, nature of the ester group, as well as the location, orientation and number of double bonds impact melting points (mps) of FA methyl esters (FAMEs) [1,3–7]. Consequently, mp increases with increasing hydrocarbon tail length, as indicated by the mps of FAMEs from palmitic (28 °C), stearic (38 °C), arachidic (C20:0; eicosanoic; 46 °C), and behenic (C22:0; docosanoic; 53 °C) acids (Table 1). Additionally, the decreasing mps of FAMEs from stearic (38 °C), oleic (−20 °C) linoleic (−43 °C) and linolenic (−52 °C) acids illustrate the influence of unsaturation on mp (Table 1) [7].

The consensus distilled from several structure–property relationship studies is that monounsaturated FAMEs are ideal components of biodiesel from a fuel property perspective [3,4,6]. Such constituents provide a satisfactory balance between cold flow and oxidative stability as well as between kinematic viscosity (kV) and cetane number. As such, production of biodiesel enriched in monounsaturated FAMEs such as oleic acid has been reported and encouraged [8,15–17]. The objective of the current study was to determine whether or not FA composition impacts cold flow properties of low-level (B5 or below) blends in ultra-low sulfur (<15 ppm S) diesel (ULSD) fuel. In other words, does it matter what the FA composition of biodiesel is at low blend levels? To answer this question, several biodiesel fuels spanning a wide range of FA compositions were blended with ULSD (B1–B5) and cold flow properties such as cloud point (CP), cold filter plugging point (CFPP) and pour point (PP) were determined.

Fuel properties of biodiesel blends with petrodiesel have been reported extensively. For instance, properties of blends prepared from camelina [18], canola [19], cottonseed [19,20], distillers' grains [21], microalgae [22], palm [23], poultry fat [20], soybean [15,19,23,24], and sunflower [19] were reported, among numerous others. Others investigated the influence of blend ratio (B0–B100) on fuel properties such as oxidative stability [25], kV [26,27], density [27], specific gravity (SG) [28,29], and cold flow [25] and have determined that kV, density and SG all increase as the percentage of biodiesel is increased whereas oxidative stability and cold flow improve significantly as the biodiesel component is decreased. However, none have determined whether or not FA composition played a role in fuel properties of blends, especially at blend ratios permitted by ASTM D975. The current investigation addresses this issue.

2. Materials and methods

2.1. Materials

Fungible ULSD was donated by a petrochemical company. Waste cooking oil methyl esters (WCME) and yellow grease methyl esters (YGME) were donated by commercial producers. Refined, bleached and deodorized canola (low-erucic acid rapeseed), palm, soybean and sunflower (high oleic) oils were purchased from KIC Chemicals, Inc. (New Platz, NY). Field pennycress seeds were collected from a wild population in Peoria County, IL and oil was expelled as described previously [9]. FAMEs (99.9%) were purchased from Nu-Chek Prep, Inc. (Elysian, MN). All other chemicals were obtained from Sigma–Aldrich Corp (St. Louis, MO). All materials were used as received.

2.2. Preparation of fatty acid methyl esters

Methanolysis was accomplished with 0.5 mass% sodium methoxide (with respect to oil) and a 6:1 mol ratio of methanol to oil at 60 °C for 1.0 h. Removal of glycerol by gravity separation and methanol by rotary evaporation (10 mbar; 30 °C) was performed after the mixture cooled to room temperature. FAMEs were washed with water until a neutral pH was achieved and dried with $MgSO_4$ to yield canola oil methyl esters (CME; 98 mass%), field pennycress oil methyl esters (FPME; 96 mass%), palm oil methyl esters (PME; 98 mass%), soybean oil methyl esters (SBME; 99 mass%), and sunflower oil methyl esters (SFME; 97 mass%).

2.3. Fatty acid composition

FAMEs prepared as described previously [8] were analyzed using a Varian (Walnut Creek, CA) 8400 GC equipped with an FID detector and SP2380 (Supelco, Bellefonte, PA) column

Table 1
FAME composition (area%) of CME, FPME, PME, SBME, SFME, WCME, and YGME along with melting points (mps) of individual FAMEs.[a]

FAME	mp (°C)[b]	CME	FPME	PME	SBME	SFME	WCME	YGME
C12:0	4.3	–	–	–	–	–	–	–
C14:0	18.1	–	–	1.2	–	–	–	0.5
C16:0	28.5	4.5 (0.1)	3.1 (0.1)	42.8 (0.3)	10.5	6.3 (0.1)	10.9 (0.1)	6.6 (0.1)
C16:1 9c	−34.1	0.3 (0.1)	0.2	0.2	–	–	0.6 (0.1)	0.5 (0.1)
C18:0	37.7	2.2 (0.2)	0.5	4.4 (0.1)	4.7	4.3	4.0	4.3 (0.1)
C18:1 9c	−20.2	62.7 (0.3)	12.6 (0.1)	40.1 (0.4)	22.7 (0.1)	80.4 (0.1)	38.1 (0.1)	66.1 (0.2)
C18:2 9c, 12c	−43.1	20.6	22.4 (0.1)	10.2	53.4 (0.1)	7.7	40.5 (0.1)	17.2 (0.1)
C18:3 9c, 12c, 15c	N/R	9.7	11.8 (0.1)	0.2	8.2 (0.1)	0.3	4.7	2.0
C20:0	46.4	–	2.4	0.4	–	1.0 (0.1)	0.4	0.4
C20:1 11c	−7.8	–	9.8	–	–	–	–	0.5
C22:0	53.2	–	0.5	–	–	–	–	0.5
C22:1 13c	−3.1	–	35.0 (0.2)	–	–	–	–	–
Unknown (sum)	–	0	1.7	0.5	0.5	0	0.8	1.4
Σ sat[c]	–	6.7	6.5	48.8	15.2	11.6	15.3	12.3
Σ monounsat[c]	–	63.0	57.6	40.3	22.7	80.4	38.7	67.1
Σ polyunsat[c]		30.3	34.2	10.4	61.6	8.0	45.2	19.2
Unknown (sum)	–	0	1.7	0.5	0.5	0	0.8	1.4

[a] For example, C18:1 9c signifies an 18 carbon FA with one *cis* (c) double bond at carbon 9 (methyl oleate); – = not detected; Values in parentheses are standard deviations ($n = 3$); where not indicated, standard deviation was zero; N/R = not reported.
[b] From [18].
[c] Sat = C12:0 + C14:0 + C16:0 + C18:0 + C20:0 + C22:0; Σ monounsat = C16:1 + C18:1 + C20:1 + C22:1; Σ polyunsat = C18:2 + C18:3.

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