Fuel property enhancement of biodiesel fuels from common and alternative feedstocks via complementary blending☆

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ABSTRACT

Fatty acid methyl esters (biodiesel) prepared from field pennycress and meadowfoam seed oils were blended with methyl esters from camelina, cottonseed, palm, and soybean oils in an effort to ameliorate technical deficiencies inherent to these biodiesel fuels. For instance, camelina, cottonseed, and soybean oil-derived biodiesels exhibited poor oxidative stabilities but satisfactory kinematic viscosities. Field pennycress and meadowfoam seed oil methyl esters yielded excellent cold flow properties but high kinematic viscosities. Thus, field pennycress and meadowfoam-derived biodiesel fuels were blended with the other biodiesels to simultaneously ameliorate cold flow, oxidative stability, and viscosity deficiencies inherent to the individual fuels. Highly linear correlations were noted between blend ratio and cold flow as well as viscosity after least squares statistical regression whereas a non-linear relationship was observed for oxidative stability. Equations generated from statistical regression were highly accurate at predicting KV, reasonably accurate for prediction of cold flow properties, and less accurate at predicting oxidative stability. In summary, complementary blending enhanced fuel properties such as cold flow, kinematic viscosity, and oxidative stability of biodiesel.

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1. Introduction

Defined as monoalkyl esters of long-chain fatty acids (FAs) prepared from lipids, technical advantages of biodiesel over petrodiesel include derivation from domestic and renewable feedstocks, superior lubricity, higher cetane number, lower toxicity, higher biodegradability, higher flash point, negligible sulfur and aromatics content, and lower overall exhaust emissions [1,2]. Disadvantages of biodiesel relative to petrodiesel primarily include higher feedstock cost and limited availability, inferior oxidative stability, and inferior cold flow properties [1,2]. Biodiesel must meet the requirements of fuel standards such as ASTM D6751 in the U.S. or EN 14214 in the EU (Table 1) before its commercial use is approved either in the neat form or as a blend component in petrodiesel.

Feedstock availability for biodiesel production varies considerably according to geography and climate. Thus, sunflower and especially canola oils are principally used in Europe and Canada, palm and coconut oils predominate in tropical countries, and soybean oil and animal fats are primarily used in the U.S [1,2]. However, the combined supply of these lipids is sufficient to replace only a small percentage of petrodiesel. For instance, only 6% of domestic diesel fuel demand would be satisfied if the entire U.S. soybean harvest was dedicated to biodiesel production [3]. Furthermore, refined commodity oils may account for 80% or more of biodiesel production expenses [4]. Employment of alternative low-cost lipids is one approach to lower feedstock cost [1]. Consequently, reports of biodiesel prepared from alternative feedstocks include camelina (*Camelina sativa* L.), field pennycress (*Thlaspi arvense* L.), jatropha (*Jatropha curcas* L.), karanja (*Pongamia pinnata* L.), single celled organisms (microbes, algae), seashore mallow (*Kosteletzkya pentacarpos*), and distillers' grains, among others [1,2,5–11].

Table 1
Properties of camelina (CSME), cottonseed (CTME), field pennycress (FPME), meadowfoam (MFME), palm (PME), and soybean (SME) oil methyl esters with a comparison to biodiesel standards ASTM D6751 and EN 14214.[a]

	ASTM D6751	EN 14214	CSME	CTME	FPME	MFME	PME	SME
AV, mg KOH/g	0.50 max	0.50 max	0.04 (0.01)	0.02 (0.01)	0.09 (0.01)	0.06 (0.04)	0.01 (0.01)	0.04 (0.01)
Free glycerol, mass %	0.020 max	0.020 max	0.005	0.004	0.001	0.001	0.001	0.001
Total glycerol, mass %	0.240 max	0.250 max	0.152	0.112	0.056	0.035	0.073	0.144
Flash point, °C	93 min	101 min	179 (2)	180 (1)	186 (4)	205 (2)	173 (2)	180 (0)
CP, °C	Report	—[b]	4.1 (0.1)	5.6 (0.1)	−6.5 (0.6)	−6.6 (0.1)	15.3 (0.1)	0.4 (0.1)
CFPP, °C	—[b]	Variable[c]	0.0 (0)	6.3 (0.6)	−18.7 (0.6)	−10.0 (0)	12.3 (0.6)	−3.0 (0)
PP, °C	—[b]	—[b]	0.0 (0)	5.0 (0)	−24.3 (0.6)	−10.0 (0)	14.0 (0)	−1.0 (0)
IP, 110 °C, h	3 min	6 min	2.7 (0)	3.7 (0)	2.4 (0)	67.3 (1.5)	13.9 (0.2)	3.8 (0.1)
IV, g I$_2$/100 g	—[b]	120 max	142	108	105	87	53	131
KV, 40 °C, mm^2/s	1.9—6.0	3.5—5.0	4.37 (0.01)	4.19 (0)	5.49 (0)	6.22 (0)	4.53 (0.01)	4.10 (0.01)
Moisture, ppm	—	500 max	355 (1)	358 (3)	296 (1)	209 (2)	295 (0)	302 (1)

[a] Values in parentheses are standard deviations from the reported means (n = 3; n = 1 for glycerol content).
[b] Not specified.
[c] Varies by location and time of year.

Although low-cost feedstocks improve economics of biodiesel production, in many cases fuel properties of FA methyl esters (FAMEs) resulting from these feedstocks do not compare favorably to biodiesel prepared from commodity feedstocks such as canola or soybean. One example is jatropha-based biodiesel, which due to its high content of saturated FAMEs exhibits undesirably high cloud (CP) and pour (PP) points relative to biodiesels from soybean and canola oils [7]. Another example is biodiesel prepared from camelina seed oil, which yields poor oxidative stability as a result of its high content of polyunsaturated FAMEs [5]. Fuel properties depend on the FA composition of the parent oil or fat from which biodiesel is prepared, with monounsaturated FAMEs identified in previous studies as providing optimum fuel performance [1,12—15]. Therefore, blending to partially offset high feedstock costs represents a method by which biodiesel economics may be improved while simultaneously enhancing fuel performance [1,16—26]. As a result, investigation of blends is not only important from an economic standpoint but is also necessary to understand the impact of blending on fuel properties of biodiesel.

The objectives of this study were to blend FAMEs prepared from traditional biodiesel feedstocks with those of recently reported alternatives and to measure resultant fuel properties such as cold flow, oxidative stability, kinematic viscosity (KV), and iodine value (IV). A further objective was to develop predictive equations based on statistical regression to estimate fuel properties at known blend percentages. Biodiesel from traditional feedstocks included palm oil methyl esters (PME) and soybean oil methyl esters (SME), as these suffer from inferior cold flow and oxidative stability, respectively, relative to FAMEs prepared from canola oil [16]. Biodiesel fuels from alternative oilseed feedstocks included *C. sativa* seed oil methyl esters (CSME) [5], cottonseed (*Gossypium hirsutum*) oil methyl esters (CTME) [27], field pennycress seed oil methyl esters (FPME) [6], and meadowfoam (*Limnanthes alba*) seed oil methyl esters (MFME) [28].

Previous studies on fuel properties of biodiesel blends primarily concentrated on cold flow behavior and/or oxidative stability [19—25,29—33]. Other studies explored the influence of blending on combustion, energy content and cetane number [34—37]. Furthermore, previous studies focused on jatropha or castor seed oil methyl ester blends with commodity FAMEs such as SME, PME or canola oil-based biodiesel [17,19—23,25]. Lastly, a review on the topic of predicting properties of biodiesel blends using mathematical models was focused on cold flow, cetane number, energy content, density, flash point, viscosity, and vapor pressure [38]. The current study differentiates itself from prior art by expanding both the fuel properties investigated of the blends as well as providing insights on hitherto unreported biodiesel blends prepared from

alternative feedstocks. Such information is anticipated to be beneficial to biodiesel producers, distributors and end users who are seeking low-cost alternatives to expensive refined commodity oils as feedstocks for production of biodiesel.

2. Materials and methods

2.1. Materials

Camelina seeds were purchased from Marx Foods (Atlantic Highlands, NJ) and oil was extracted with hexanes as described previously [5]. Cold-pressed cottonseed oil was purchased from a local retailer. Field pennycress seeds were collected from test plots in Peoria County, IL and the oil was mechanically expelled as described previously [6]. Cold-pressed meadowfoam seed oil was purchased from Natural Plant Products, Inc. (Salem, OR). Refined, bleached and deodorized palm oil was purchased from KIC Chemicals, Inc. (New Platz, NY). Selected properties of these oils are displayed in Table 2. Soybean oil methyl esters (SME) were donated by a BQ-9000 certified commercial biodiesel producer. FAME standards (>99%) were purchased from Nu-Chek Prep, Inc. (Elysian, MN). All other reagents were purchased from Sigma—Aldrich Corp (St. Louis, MO). All materials were used as received.

2.2. Fatty acid composition

Derivatization of the seed oils to FAMEs was performed as described previously [39] and analyzed using an HP 890 Series II GC (Palo Alto, CA) equipped with an FID, an HP series 7673 auto sampler/injector and a Supelco (Sigma—Aldrich, Corp) SP2380 capillary column (30 m × 0.25 mm i.d., 0.20 μm film thickness). Carrier gas was He at 1.0 mL/min. The temperature program was 170 °C—190 °C at 4 °C/min, 30 °C/min to 265 °C, hold for 2.5 min. The injector and detector temperatures were 250 °C. FAME peaks were identified (triplicates, means reported) by comparison to reference standards.

2.3. Methanolysis

Camelina, cottonseed, field pennycress, meadowfoam, and palm oils were subjected to homogeneous base-catalyzed methanolysis as described previously [40]. In each case, 1.0 kg of oil was converted into FAMEs using methanol (0.30 L; 6 molar equivalents) and sodium methoxide (5.0 g; 0.50 wt %) at 60 °C for 1 h to afford CSME (0.99 kg; 95% yield), CTME (1.01 kg; 96%), FPME (0.97 kg; 93%), MFME (1.02 kg; 97%), and PME (1.01 kg; 96%).