Fuel 99 (2012) 254–261

Contents lists available at SciVerse ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Efficacy of specific gravity as a tool for prediction of biodiesel–petroleum diesel blend ratio ☆

Bryan R. Moser *

Bio-Oils Research Unit, National Center for Agricultural Utilization Research, Agricultural Research Service, United States Department of Agriculture, 1815 N. University St., Peoria, IL 61604, USA

HIGHLIGHTS

- ▶ Specific gravity was investigated to predict biodiesel/petrodiesel blend ratio.
- ▶ Several biodiesel and petrodiesel fuel blends were investigated.
- ▶ Linear relationships were found between specific gravity and blend ratio.
- ▶ Predictive equations were derived from specific gravity data.
- ▶ Accurate prediction of blend ratio was possible in some cases.

ARTICLE INFO

Article history:
Received 31 January 2012
Received in revised form 25 April 2012
Accepted 26 April 2012
Available online 10 May 2012

Keywords:
Biodiesel
Blend
Diesel
Fatty acid methyl esters
Ultra-low sulfur diesel

ABSTRACT

Prediction of volumetric biodiesel/petrodiesel blend ratio (V_{BD}) from specific gravity (SG) data was the subject of the current investigation. Fatty acid methyl esters obtained from soybean, palm and rapeseed oils along with chicken fat (SME-1, SME-2, PME, RME and CFME) were blended (0–20 vol%) with three ultra-low sulfur (<15 ppm S) diesel (ULSD) fuels and SG at 15.6 °C was measured. Least-squares statistical regression on SG data from each of the biodiesel/ULSD blend sets revealed highly linear relationships ($R^2 > 0.991$) between SG and V_{BD}. Blends with the highest R^2 values from each of the ULSD fuels were used as model systems to develop predictive equations useful for calculation of V_{BD} from SG. The results indicated that accurate prediction of V_{BD} from SG was most effective when applied to blends prepared from the same fuel-types as the model systems used to develop the predictive equations.

Published by Elsevier Ltd.

1. Introduction

Defined as monoalkyl esters of long-chain fatty acids (FAs) prepared from lipids, advantages of biodiesel over petroleum diesel fuel (petrodiesel) include derivation from domestic and renewable feedstocks, superior lubricity and biodegradability, non-toxic and non-flammable, negligible sulfur and aromatics content, lower overall exhaust emissions, and positive energy balance [1,2]. Disadvantages include inferior cold flow properties, limited feedstock availability, inferior storage stability, higher emissions of NOx, and high feedstock cost [2]. Biodiesel must meet the requirements of fuel standards (Table 1) such as ASTM D6751 or EN 14214 before its commercial use as a blend component in petrodiesel is approved [1,3]. Although biodiesel can be used directly in modern unmodified diesel engines, it is normally encountered in blends with petrodiesel. Blends up to B5 (5 vol%) and B7 are permitted in ASTM D975 and EN 590 (Table 1) [4,5]. Additionally, B6–B20 blends are regulated by ASTM D7467 (Table 1) [6].

Sulfur oxides exhaust emissions increase with increasing content of sulfur in fuel [7,8]. Sulfur oxides are corrosive and lead to increased engine wear, contribute to acid rain and produce solid sulfates that add to particulate matter emissions [7,8]. Furthermore, emissions control devices are negatively impacted by fuels

---

Abbreviations: APE, average percent error; AV, acid value; CFME, chicken fat methyl esters; CP, cloud point; FA, fatty acid; FAME, fatty acid methyl ester; HDS, hydrodesulfurization; KV, kinematic viscosity; LSD, low-sulfur (<500 ppm) diesel fuel; PME, palm oil methyl esters; RME, rapeseed oil methyl esters; SD, standard deviation; SG, specific gravity; SME, soybean oil methyl esters; ULSD, ultra-low sulfur (<15 ppm) diesel fuel; V_{BD}, volumetric ratio of biodiesel to petrodiesel; e.g., $V_{BD} = 1.0 = B1 = 1$ vol%; $V_{BD,A}$, actual (measured) volumetric ratio of biodiesel to petrodiesel; $V_{BD,P}$, predicted (calculated) volumetric ratio of biodiesel to petrodiesel.

☆ Disclaimer: Mention of trade names or commercial products in this publication is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the US Department of Agriculture. USDA is an equal opportunity provider and employer.

* Tel.: +1 309 681 6511; fax: +1 309 681 6524.
E-mail address: Bryan.Moser@ars.usda.gov

0016-2361/$ - see front matter Published by Elsevier Ltd.
http://dx.doi.org/10.1016/j.fuel.2012.04.050

Table 1
Selected specifications from biodiesel and ULSD fuel standards.

	Units	Biodiesel		ULSD		
		ASTM D6751	EN 14214	ASTM D975	ASTM D7467	EN 590
FAME content	vol%	–[a]	96.5 min[b]	0–5	6–20	0–7
AV	mg KOHg^{-1}	0.50 max	0.50 max	–[a]	0.30 max	–[a]
Glycerol content:	mass%					
Free glycerol		0.020 max	0.020 max	–[a]	–[a]	–[a]
Total glycerol		0.240 max	0.250 max	–[a]	–[a]	–[a]
Low temperature:	°C					
CP		Report	–[a]	–[c]	–[c]	–[a]
PP		–[a]	–[a]	–[a]	–[a]	–[a]
CFPP		–[a]	Variable[d]	–[c]	–[c]	–[a]
Sulfur	ppm	15 max	10 max	15 max	15 max	10 max
SG, 15.6 °C		–[a]	–[a]	–[a]	–[a]	–[a]
KV, 40 °C	mm^2 s^{-1}	1.9–6.0	3.5–5.0	1.9–4.1	1.9–4.1	2.0–4.5

[a] Not specified.
[b] mass%.
[c] Guidance is provided.
[d] Variable by location and time of year.

containing high sulfur content [7,8]. Concern over these issues led the US EPA to mandate a sulfur content reduction in on-road diesel fuels from 500 to 15 ppm. The process by which ultra-low sulfur (<15 ppm) diesel (ULSD) fuel is produced from petroleum oil distillate is referred to as hydrotreatment and involves high-pressure, high-temperature hydrodesulfurization (HDS) in which chemically bound sulfur is converted into H_2S [7–9–11]. A two-stage HDS unit is typically employed whereby a Co–Mo/Al_2O_3 catalyst is first used followed by Ni–Mo/Al_2O_3 (or Ni–W/Al_2O_3). HDS over Co–Mo primarily removes sulfur from aliphatic hydrocarbons. The more active Ni–Mo facilitates hydrogenation of aromatic sulfur as well as saturation of aromatic hydrocarbons. The two-stage deep desulfurization needed to produce ULSD has caused changes to the chemical composition of ULSD relative to its low sulfur (<500 ppm) diesel (LSD) fuel predecessor, which was historically prepared in only one HDS stage utilizing a Co–Mo catalyst. The resulting ULSD fuel contains fewer aromatics and heteroatom-containing hydrocarbons relative to LSD. Such modifications to chemical composition have resulted in changes to exhaust emissions as well as to fuel properties such as cetane number, cloud point (CP) and kinematic viscosity (KV) [12–14]. As a result, previous data on LSD-biodiesel blends is not relevant to ULSD-biodiesel blends.

The actual volumetric blend ratio of biodiesel to petrodiesel (V_{BD}) sold at retail stations in some cases varies significantly from the advertized V_{BD} [15,16]. Such variability along with the need to know V_{BD} has catalyzed the search for facile methods to quickly and accurately determine V_{BD}. Spectroscopic techniques such as infrared and nuclear magnetic resonance have been reported [17–20]. However, such methods require significant capital investment along with specialized expertise for their successful implementation. Proposed is an alternative approach in which easily determined fuel properties are leveraged to predict V_{BD}. Several previous studies reported the fuel properties of biodiesel–petrodiesel blends, but none have used this data to determine V_{BD} [21–34]. Two studies developed blending equations for prediction of fuel properties from known V_{BD} [21,22]. A recent study measured CP, refractive index, specific gravity (SG) and KV of biodiesel blended (B0–B20) with ULSD and determined that SG data after least-squares statistical regression provided the highest coefficients of correlation ($R^2 > 0.9992$) [23]. The principal objective of the current study was to test the hypothesis that predictive equations based on SG data can accurately determine V_{BD}.

2. Experimental

2.1. Materials

Soybean oil methyl esters (SME) were supplied by two commercial biodiesel producers, designated SME-1 and SME-2. Palm oil methyl esters (PME), chicken fat methyl esters (CFME), rapeseed oil methyl esters (RME), ULSD-A, ULSD-B and ULSD-C were also donated by commercial entities to wish to remain anonymous. With the exception of conductivity and corrosion inhibitor additives, none of the ULSDs contained performance-enhancing additives. FA methyl ester (FAME) standards were purchased from Nu-Chek Prep, Inc. (Elysian, MN). All other reagents were obtained from Sigma–Aldrich Corp (St. Louis, MO) and used as received.

2.2. Fatty acid composition

FAMEs were identified using an HP 5890 Series II GC (Palo Alto, CA) equipped with an FID, an HP series 7673 auto sampler/injector and an SP2380 column (30 m × 0.25 mm i.d., 0.20 μm film thickness). Carrier gas was He at 1.0 mL min^{-1}. The temperature program was: 170–190 °C at 4 °C min^{-1}, increase to 265 °C at 30 °C min^{-1}, hold for 2.5 min. The injector and detector temperatures were 250 °C. Peaks were identified (triplicates, means reported) by comparison to the retention times of reference standards.

2.3. Preparation of biodiesel–petrodiesel blends

Blends were prepared at room temperature (22–24 °C) by pipetting precisely measured volumes followed by agitation of the contents to ensure homogeneity. Properties were measured at B0, B1, B2, B3, B4, B5, B8, B12, B16, B20 and B100. ULSD-A and ULSD-B blends included CFME, PME, RME, SME-1, and SME-2. Only CFME, SME-1 and SME-2 were blended with ULSD-C due to lack of sample availability.

2.4. Fuel properties

Free and total glycerol (mass%) were measured following ASTM D6584 with an Agilent (Santa Clara, CA, USA) 7890A GC-FID equipped with a model 7683B injector and an Agilent D8-5HT (15 m × 0.32 mm i.d., 0.10 μm film thickness) column.