Fuel 89 (2010) 3662–3667

Contents lists available at ScienceDirect

Fuel

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

# 2009 Quality survey of retail biodiesel blends in Michigan

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ARTICLE INFO

*Article history:*
Received 2 February 2010
Received in revised form 21 July 2010
Accepted 21 July 2010
Available online 4 August 2010

*Keywords:*
Biodiesel blends
Quality survey
Retail stations

ABSTRACT

A fuel quality survey of biodiesel blends collected in June 2009 from 26 Michigan retail stations was performed, 8 months after the publication of ASTM D7467. Measured blend levels were not consistent in stations where pump labels indicate specific biodiesel blend levels. Fatty acid methyl ester (FAME) analyses revealed that majority of the samples are soybean oil-based (SBO) biodiesel. Full compliance with the ASTM D7467 requirements for kinematic viscosity and flash point (FP) were observed with the biodiesel blends; all but one for cetane number (CN). Barely half of the samples were able satisfy the total acid number (TAN) specification with select samples reflecting as high as 1.6 mg KOH/g. The most pressing is that only 45% were able to meet the 6 h induction period (IP) requirement; out of those that did not qualify 42% are even low blends hinting the degraded quality of the biodiesel component. Inconsistencies on the expected correlations of the tested properties were evident, suggesting that additives may be present in many samples. When compared with results from a similar survey in 2007, the properties of the 2009 samples are even poorer, indicating poor observance of fuel standards by the producers.



## 1. Introduction

Due to its renewability and applicability to existing compression–ignition (diesel) engine technologies [1], biodiesel has gained considerable attention as an alternative fuel, offering improved lubricity and exhaust emissions [2,3]. However, despite these advantages over traditional diesel, biodiesel's inherent structure introduces significant problems with oxidative stability and cold flow properties (CFP). These two major factors coupled with improving the lubricity of ultra low sulfur diesel (ULSD) and the overall exhaust emissions [4] are the main reasons why biodiesel currently is marketed as a blend rather than a standalone fuel. Blending at a 20% level with ULSD (B20) has been shown to overcome the CFP [5] and oxidative stability concerns, since ULSD performs better in cold temperatures and is more stable.

In our 2007 survey [6] to assess the quality of biodiesel in Michigan retail outlets, poor oxidative stability and fuel blending were observed in a large number of samples, indicating a serious need for quality oversight. In 2008, the ASTM International Committee D02 (Petroleum Products and Lubricants) published the ASTM D7467 (Standard Specification for Diesel Fuel Oil, Biodiesel Blend) in an effort to standardize biodiesel blend quality [7]. The standard covers the fuel property requirements and test methods of biodiesel blends from B6 to B20 as stated in Table 1. In order to determine if the retail biodiesel fuel quality had improved since these events, the National Biofuels Energy Laboratory (NBEL, Detroit, MI) has conducted another survey on the current status of the biodiesel quality for fuel blends sold in retail stations across the state of Michigan in 2009. Additional properties such as, the total acid number (TAN), kinematic viscosity, cetane number (CN) and flash point (FP) were also evaluated in this quality survey study.

## 2. Experimental procedures

### 2.1. Survey methodology

A list of MI biodiesel retailers was generated from the National Biodiesel Board website and shortlisted based on proximity and business operation. Twenty-six (26) retailers were sampled as well as given a paper questionnaire (Supplementary material) over the period of June 8–10, 2009. The questionnaires were given to retailers' manager or officer-in-charge who could answer the survey most accurately. Table 2 summarizes the pump biodiesel blend level labels and number of the samples. ULSD samples were also gathered from the stations and analyzed for comparison and verification purposes of the survey. Fuel samples were tested at NBEL facilities within 2 weeks of sampling to limit compositional and property changes.

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0016-2361/$ - see front matter 
doi:10.1016/j.fuel.2010.07.035

**Table 1**
ASTM D7467 requirements for various fuel properties.

| Property | Test method | Unit | ASTM D7467 Requirement | Test performed |
|---|---|---|---|---|
| Acid number | D664 | mg KOH/g | 0.3 (max) | Yes |
| Viscosity at 40 °C | D445 | $mm^2/s$ | 1.9–4.1 | Yes |
| Cetane number | D613 | CN | 40 (min) | Yes |
| Flash point | D93 | °C | 52 (min) | Yes |
| Oxidation stability | EN 14112 | h | 6 (min) | Yes |
| Cloud point | D2500, D4539, D6371 | °C | Report | Yes |
| Sulfur content | D2622 | μg/g | – (S15) | No |
| Distillation temperature | D86 | °C | 90% vol recovered (max) | No |
| Carbon residue on 10% bottoms | D524 | Mass% | 0.35 (max) | No |
| Ash content | D462 | Mass% | 0.01 (max) | No |
| Water and sediment | D2709 | Volume% | 0.05 (max) | No |
| Copper corrosion | D130 | – | No. 3 (chart) | No |
| Biodiesel content | D7371 | % (v/v) | 6–20 | No |
| Lubricity | D6079 | μm | 520 (max) | No |

**Table 2**
Number of samples collected per blend label on the given survey dates.

| Sampling date/blend label | Number of collected samples | | | | | |
|---|---|---|---|---|---|---|
| | BXX | B5 | B10 | B5–20 | B20 | ULSD |
| 8 Jun 2009 | 1 | 3 | – | – | 3 | 6 |
| 9 Jun 2009 | 2 | 1 | 3 | 3 | 2 | 7 |
| 10 Jun 2009 | – | 1 | 1 | 4 | 4 | 9 |
| Total | 3 | 5 | 4 | 7 | 9 | 22 |

### *2.2. Composition and fuel property test methodologies*

#### *2.2.1. FAME profile and blend concentration*

The fatty acid methyl ester (FAME) composition of the biodiesel blend samples was determined using a Perkin–Elmer (Shelton, CT) Clarus 500 GC–MS with a split automatic injector and a Rtx-WAX (Restek, Bellefonte, PA) column (length: 60 m; ID: 0.25 mm, coating: 0.25 μm). Five milliliters of heptane was used to dissolve 15 mg of the sample and 20 μL of ethyl arachidate (C20:0) was added as the internal standard. The mixture was injected into the column using an auto sampler where it was held at 120 °C for a minute and then ramped to 240 °C at a rate of 20 °C/min, and finally held at 240 °C for 13 min. The transfer line was kept at 240 °C. The system used Helium (99.9999%, Cryogenic Gases, Detroit, MI) as the carrier gas with a flow rate of 1.5 mL/min. Total ion count (TIC) was used for the quantification of each component. Details of the procedures have been described elsewhere [6,8].

#### *2.2.2. Total acid number, kinematic viscosity, derived cetane number and flash point*

Total acid number (TAN) is a parameter that indicates free fatty acid as well as other acids (e.g., residual catalyst) in the fuel. TAN also suggests the level of degradation of the blend, increasing as the blend degrades. The ASTM D664 [9] method using a Brinkman Metrohm 809 Titrando instrument (Riverview, FL) was utilized to measure the TAN values. The kinematic viscosity was determined according to ASTM D445 [10] by measuring the time for a volume of liquid to flow under gravity through a calibrated capillary viscometer at 40 °C. The test method was done using a Rheotek AKV8000 automated kinematic viscometer (Poulten Selfe & Lee Ltd., Essex, England).

The CN measures ignition delay from the time the fuel is injected to the start of combustion as a measure of the fuel quality. The CN was determined using an Ignition Quality Tester (IQT™, Advanced Engineering Technology, Inc., Ottawa, Canada) using the ASTM D6890 [11] test method. Details of the derivation of the CN using the IQT™ are described elsewhere [12]. The FP of the fuel samples is the lowest temperature at which its vapor can produce an ignitable mixture with air. FP measurements according to ASTM D93 [13] were performed using a Herzog HFP 339 Pensky–Martens Flash Point Analyzer (Houston, TX) by automatic heating of the samples at 0.5 °C increments until ignition was obtained inside the closed cup.

#### *2.2.3. Oxidative stability*

The oxidative stability was determined using a Metrohm 743 Rancimat (Herisau, Switzerland) based on EN14112 [14]. Dry air at a rate of 10 L/h is bubbled into 7.5 g of biodiesel (based on ASTM D7467) maintained at 110 °C. The accelerated oxidation process produces volatile products, mainly formic acids [15], that are carried through the detector chamber containing deionized water. Conductivity increase is recorded every 36 s and the induction period (IP) is obtained based on the maximal increase in conductivity as a function of time.

#### *2.2.4. Cold flow properties*

Biodiesel cold flow properties (Cloud Point: CP, Pour Point: PP and Cold Filter Plugging Point: CFPP) were determined using a Lawler DR-34H automated cold properties analyzer (Edison, NJ). Test sample temperature was lowered by 3 (CP and PP), and 1 °C (CFPP) increments until the end-point measurements are determined. ASTM standards D2500 [16], D97 [17], and D6371 [18] were used as test methods for CP, PP and CFPP, respectively.

Results were reported as mean values of triplicate runs with values (errors are within ±5%) compliant with the repeatability limits of their respective standard method.

## **3. Results and discussion**

### *3.1. Written survey responses*

The responses from the written survey gave an overview of the status of retail biodiesel blends in Michigan. According to 60% of the responders, biodiesel supply arrives monthly, receiving around 10,000 gallons per shipment. Typical customers are light duty vehicles ranging from cars to sport utility vehicles (SUVs). One fourth of the sampled stations served as truck refueling stations and these stations would get daily supply of biodiesel typically exceeding 40,000 gallons per load, the rest are low volume retailers that get supplies irregularly based on availability/supply and demand. The majority of the fuel blends are either splash blended within the fuel tankers or inside the storage tank. A small number of the responders receive either pre-blended fuel from the biodiesel producer or blending is conducted through an in-line blending facility in their station. Both local and national biodiesel producers were equally represented as sources of fuel for those stations sampled in the survey. Similarly, half of the stations reported receiving test analysis certifications of the delivered biodiesel and ULSD fuel. B20 blends are offered at almost all of the stations. B2, B5 and B10 blends are then present in 25% of the retailers. The majority of the fuel blends are soybean oil based-biodiesel (SBO) confirmed via the SBO pump label and/or producer certifications; a small part of the samples are identified by the producers to contain both SBO and animal fat-based biodiesel (AF). The majority of customer complaints reported by the survey respondents are low temperature related problems in higher biodiesel blends such as sluggish