



National Renewable Energy Laboratory

A national laboratory of the U.S. Department of Energy
Office of Energy Efficiency & Renewable Energy

Innovation for Our Energy Future

Analysis of Biodiesel Blend Samples Collected in the United States in 2008

T.A. Alleman, L. Fouts, and R.L. McCormick

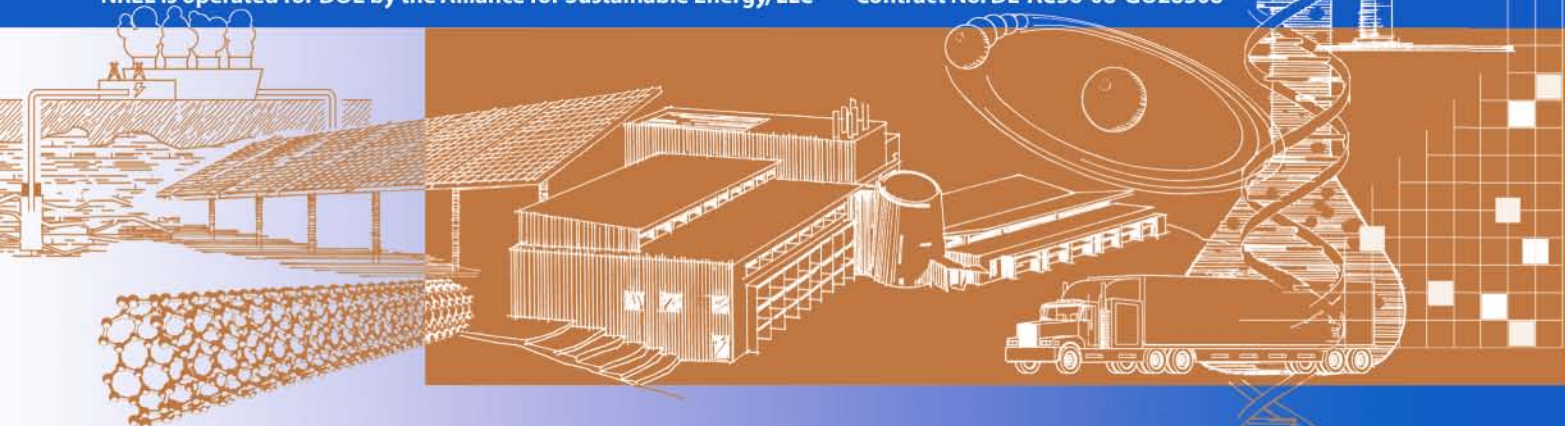
Technical Report

NREL/TP-540-46592

March 2010

NREL is operated for DOE by the Alliance for Sustainable Energy, LLC

Contract No. DE-AC36-08-GO28308



Analysis of Biodiesel Blend Samples Collected in the United States in 2008

T.A. Alleman, L. Fouts, and R.L. McCormick

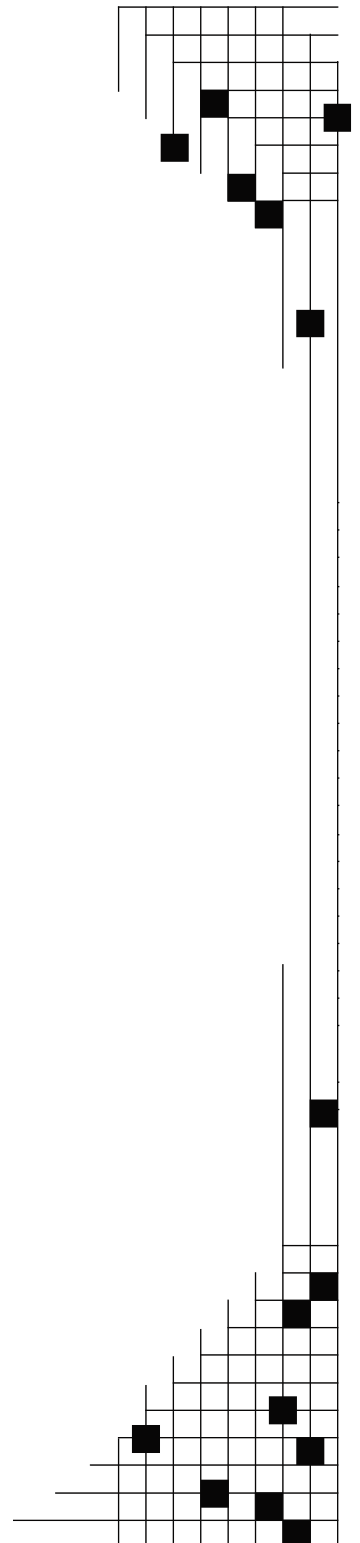
Prepared under Task No. FC08.9400

Technical Report
NREL/TP-540-46592
March 2010

National Renewable Energy Laboratory
1617 Cole Boulevard, Golden, Colorado 80401-3393
303-275-3000 • www.nrel.gov

NREL is a national laboratory of the U.S. Department of Energy
Office of Energy Efficiency and Renewable Energy
Operated by the Alliance for Sustainable Energy, LLC

Contract No. DE-AC36-08-GO28308



NOTICE

This report was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or any agency thereof.

Available electronically at <http://www.osti.gov/bridge>

Available for a processing fee to U.S. Department of Energy
and its contractors, in paper, from:

U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831-0062
phone: 865.576.8401
fax: 865.576.5728
email: <mailto:reports@adonis.osti.gov>

Available for sale to the public, in paper, from:

U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
phone: 800.553.6847
fax: 703.605.6900
email: orders@ntis.fedworld.gov
online ordering: <http://www.ntis.gov/ordering.htm>



Printed on paper containing at least 50% wastepaper, including 20% postconsumer waste

Acknowledgments

The authors thank the U.S. Department of Energy Vehicle Technologies Program and the National Biodiesel Board for funding and support of this project.

Executive Summary

In the summer of 2008, NREL conducted a nationwide survey of the quality of B20, a blended fuel consisting of about 20 volume percent (vol%) biodiesel and 80 vol% petroleum diesel. Thirty-three samples were collected prior to the announcement of a new ASTM specification, D7467, for B6–B20. The B20 samples were tested against multiple properties—those included in the eventual D7467 specification and other properties of interest. Because this study preceded the announcement of the specification, the samples could not be termed “on” or “off” specification.

Previous NREL surveys have shown that biodiesel blending has been problematic, because the samples have been almost evenly distributed above and below B20. In this survey, only 60% of the samples were nominally B20 (i.e., B18–B22), and the majority of the rest of the samples contained less biodiesel, typically B2, B5, and B10. Two samples contained over 20 vol% biodiesel, likely the result of poor blending.

The induction period (IP) stability and acid value (AV) are key parameters in the quality of a Bxx blend. Although the D7467 specification was not applicable at the time of sample collection, 25% of the samples were below the 6-hour proposed limit. It is noteworthy that the average IP, 8.4 hours, was well above the 6-hour limit. Every sample but one met the proposed AV specification of 0.3 mgKOH/g, a low failure rate similar to that of previous NREL surveys.

The minimum flash point of Bxx blends is allowed to vary depending on the type of diesel fuel used and the cloud point of the blend. The average cloud point was -12.6°C, and the samples all readily met the flash point minimum of 38°C. The B20 samples all met the sulfur limit of 15 ppm, except for one sample that was likely contaminated. The range of cetane number for the blends was 46 to 52.

The current specification contains a combined water and sediment value, although there is interest in separating these parameters into Karl Fisher water and particulate contamination. As expected by its polar nature, biodiesel will have a higher water saturation point than that of diesel fuel. The average Karl Fisher water content of the B20 samples was 130 ppm, about 30% higher than that of conventional diesel fuel. Almost all the samples showed very low particulate contamination except one, which was likely contaminated during collection. The metal content of the blends was also low, although the amount of sodium in one sample would not have allowed the B100 to meet the D6751 specification.

Typically, little or no information is known about the parent fuels to provide complete information about the source of the biodiesel used in Bxx blends. However, advanced analytical techniques have helped to overcome this hurdle. The B100 feedstock can be determined by using multi-dimensional gas chromatography. The blends in this study were produced mainly from soybean-derived B100, although a significant number of animal-fat-derived B100 samples were also found.

Another critical B100 parameter is the glycerin content, which is impossible to reliably determine for Bxx because of method limitations. A novel ion chromatography technique was used to extract and analyze the glycerin in the biodiesel portion of the blend. Overall, the biodiesel was typically on-specification for glycerin.

Table of Contents

Introduction	1
Materials and Methods	1
Results and Discussion.....	4
Standard Tests	4
Biodiesel Content of Blends	4
Induction Period Stability	5
Acid Value	6
Flash Point	8
Cloud Point	8
Other Properties from D7467.....	9
Nonstandard Tests.....	9
Karl Fisher Moisture	9
Particulate Contamination.....	10
Interfacial Tension	11
Free and Total Glycerin	11
Group I and II Metals.....	12
Feedstock Analysis	13
Conclusions.....	14
References	16

List of Figures

Figure 1.	The 2008 B20 sample collection sites	2
Figure 2.	Typical MDGC/FID chromatograms for B20; top: diesel component, bottom: biodiesel component	4
Figure 3.	Blend percentage results for B20 samples collected in 2008	5
Figure 4.	Induction period stability for the 2008 B20 survey	6
Figure 5.	Acid value results for the 2008 B20 survey	7
Figure 6.	B20 samples analyzed by modified D664 method	7
Figure 7.	Flash point results for the 2008 B20 survey	8
Figure 8.	Cloud point results for the 2008 B20 survey	9
Figure 9.	Karl Fisher moisture results for the 2008 B20 survey	10
Figure 10.	Particulate contamination results for the 2008 B20 survey, using D6217 or D7321 ..	11
Figure 11.	Water interfacial tension results for the 2008 B20 survey.....	12
Figure 12.	Free and total glycerin by ion chromatography for 2008 B20 survey samples; results extrapolated to B100 properties.....	13
Figure 13.	Feedstocks used in the blends collected in the 2008 B20 survey	14

List of Tables

Table 1.	ASTM D7467-08 Specifications and Methods for the 2008 B20 Quality Survey	2
Table 2.	Nonspecification Test Performed on 2008 B20 Survey Samples.....	3
Table 3.	Chromatographic Conditions for MDGC/FID Method	3
Table 4.	Average and Minimum and Maximum Group I and II Metal Content of B20 Samples (ppb).....	13

Introduction

Biodiesel has considerable potential to displace traditional petroleum in the transportation sector. Biodiesel production in the United States grew from 25 million gallons in 2003 to 683 million gallons in 2008 [1]. The vast majority of biodiesel used as a blendstock in the United States is blended with petroleum diesel fuel and signified “Bxx” (e.g., B20), where xx is the volume percent of the biodiesel content in the fuel.

Minnesota has mandated B2, and Illinois encourages the use of B11 by waiving a sales tax [2]. Although these and other mandates exist, no Bxx fuel specifications existed until October 2008. At that time, ASTM International adopted specifications for up to 5 volume percent (vol%) biodiesel in diesel fuel (D975) and a stand-alone specification for 6 vol% to 20 vol% biodiesel (B6-B20, D7467). These specifications allow regulatory agencies to ensure the quality of biodiesel blends.

Surveys of B100 and B20 to determine quality have been conducted since 2004, providing part of the data necessary for ASTM to establish blend specifications. The first National Renewable Energy Laboratory (NREL) quality survey was conducted in 2004 on B100 and B20 [3]. A significant issue with blend percentage was noted; in fact, 18 of 33 presumably samples that were presumably of B20 were outside the accepted B18 to B22 window for biodiesel content. In addition, results for induction period stability showed that a majority of the blends were below 2.5 hours. In a spring 2007 survey of retail stations selling B20 at unspecified locations, researchers at Wayne State University also found very low stability for biodiesel blends [4]. Subsequent NREL surveys focused on B100 rather than the finished blends [5, 6].

Here we report the results of a B20 survey conducted in summer 2008. The B20 samples were purchased from retail stations or obtained from fleets throughout the United States. Analyses included properties in the D7467 specification, which had not yet taken effect when samples were collected, and other properties of interest. The feedstock used in each blend was also determined from the fatty acid methyl ester (FAME) profile measured by multidimensional gas chromatography (MDGC), and the free and total glycerin content of the parent biodiesel was determined through ion chromatography (IC).

Materials and Methods

The B20 samples were collected at retail stations and from fleets throughout the United States (Figure 1). Samples were collected only from pumps that were either labeled as dispensing B20 or stated to be dispensing B20 by on-site staff. These locations were identified by selecting pumps with voluntary B20 labeling or by polling station staff. One gallon of each fuel was collected and stored in metal fuel cans in cold storage until sampled for analysis. Aliquots were taken from these cans into 1-L glass jars for additional analysis. The bulk samples were tested for properties thought to immediately impact engine operability and proposed specification properties for future versions of D7467 (Table 1). The D7467 specification limits presented in Table 1 were not in effect at the time of sample collection, so samples cannot be judged as “on-specification” or “off-specification.” All testing was performed per the methods without deviation.



Figure 1. The 2008 B20 sample collection sites

Table 1. ASTM D7467-08 Specifications and Methods for the 2008 B20 Quality Survey^a

Property	Test Method, ASTM unless otherwise noted	D7467-08 Specification	Notes
Acid number (mgKOH/g), max	D664, D02.06 modifications	0.3	Tested on all samples
Viscosity (mm ² /s at 40°C)	D445	1.9-4.1 ^b	Not tested
Flash point (°C), min	D93	52 ^c	Tested on all samples
Cloud point (°C)	D2500, D4539, D6371	Report ^d	Tested on all samples
Sulfur (ppm), max	D5453	15 ^e	Tested on all samples
Distillation temperature (°C), 90% recovered, max	D86	343	Not tested
Ramsbottom carbon residue, 10% bottoms (mass%), max	D524	0.35	Not tested
Cetane number, min	D613	40	Tested using ASTM D6890, all samples
One of the following:			
Cetane index, min	D976	40	Not tested
Aromatics (vol%), max	D1319	35	Not tested
Ash content (mass%), max	D483	0.01	Not tested
Water and sediment (vol%), max	D2709	0.05	Not tested
Biodiesel content (vol%)	D7371	6.-20.	Tested on all samples
Copper corrosion (3 h at 50°C), max	D130	No. 3	Not tested
Oxidation stability (h), min	EN14112	6	Tested on all samples
Lubricity (HFRR at 60°C, μm), max	D6079	520 ^f	Not tested

^a D7467 limits are given for reference but were not in effect at the time of the survey.

^b If No.1 diesel fuel is used in the blend, minimum viscosity shall be 1.3 mm²/s.

^c If No.1 diesel fuel is used in the blend or a cloud point of less than -12°C is specified, the flash point minimum is 38°C.

^d Cloud point is based on operability limits and time of year where the blend will be used.

^e All samples were on-road and must meet the 15-ppm maximum sulfur limit.

^f If diesel fuel meets D975 lubricity requirements, it is not necessary to test the lubricity of the blend.

Several tests that are not part of the D7467 specification were also performed (Table 2). ASTM tests were performed without deviation from the method. Free and total glycerin was measured by ion chromatography (IC). In this method, samples were separated by a high-efficiency anion exchange separator column (Metrohm CARB1 150 mm x 4.0 mm, part number 6.1013.010) with an electrochemical detector. The mobile phase was 0.10 M sodium hydroxide solution at 1.0 mL/min. The sample loop was 10 μ L. The IC method required two separate injections, one for free glycerin and one for total glycerin. Five grams of the sample were extracted with approximately 35 g of water in the free glycerin determination. The glycerin was quantitatively extracted into the aqueous layer, which was removed and injected directly on the IC. The total glycerin is composed of free glycerin plus glycerin in mono-, di-, and tri-glycerides. To measure total glycerin, the glycerides must first be reduced to free glycerin and soap before aqueous extraction and analysis. To accomplish this, 2.5 g of Bxx was mixed with ca. 6 mL 1.0 M potassium hydroxide and heated to 95°C for 1 hour while stirred at 400 rpm. The sample was allowed to cool to room temperature, and glycerin was water-extracted with three 20-g water washes. The aqueous solution from these extractions was composited and injected into the IC.

Table 2. Nonspecification Test Performed on 2008 B20 Survey Samples

Property	ASTM Test Method (unless otherwise noted)	Notes
Group I and II metals (ppm)	D7111	Tested on all samples
Karl Fisher (ppm)	D6304	Tested on all samples
Particulate contamination (mg/L)	D6217 or D7321	Tested on all samples
Interfacial tension (mN/m)	D971	Tested on all samples
Free and total glycerin (mass%)	In-house method	Tested on all samples

The B20 samples were analyzed for biodiesel feedstock using MDGC with flame ionization detection (FID). The MDGC/FID method uses a Deans switch to separate the B100 blendstock from the diesel fuel in the mixture. The B100 blendstock is quantified on a highly polar column that separates individual FAMES in a method developed by Agilent [7]. Chromatographic conditions are listed in Table 3. Each Bxx sample was accurately weighed to 0.25 g and mixed with 1 mL high-performance liquid chromatography-grade hexane before injection. Figure 2 illustrates a typical chromatogram of a B20 using this method.

Table 3. Chromatographic Conditions for MDGC/FID Method

Primary column	HP-5ms, 15 m x 0.25 mm x 0.1 μ m
Secondary column	HP-INNOWAX, 30 m x 0.25 mm x 0.5 μ m
Deans restrictor	Deactivated fused silica, 0.77 m x 0.1 mm
Injection	Split, 200:1
Injector temperature	250°C
EPC pressure	33.86 psi, He, constant pressure
Injection volume	0.5 μ L
HP-5 ms column flow	1.5 mL/min
PCM	30.7 psi He, constant pressure
HP-INNOWAX column flow	3.5 mL/min
FID temperatures	275°C
Oven program	
Initial temperature	50°C for 0 min
Ramp 1	20°C/min to 210°C for 18 min
Ramp 2	20°C/min to 230°C for 13 min
Cut times	Depend on specific chromatographic system

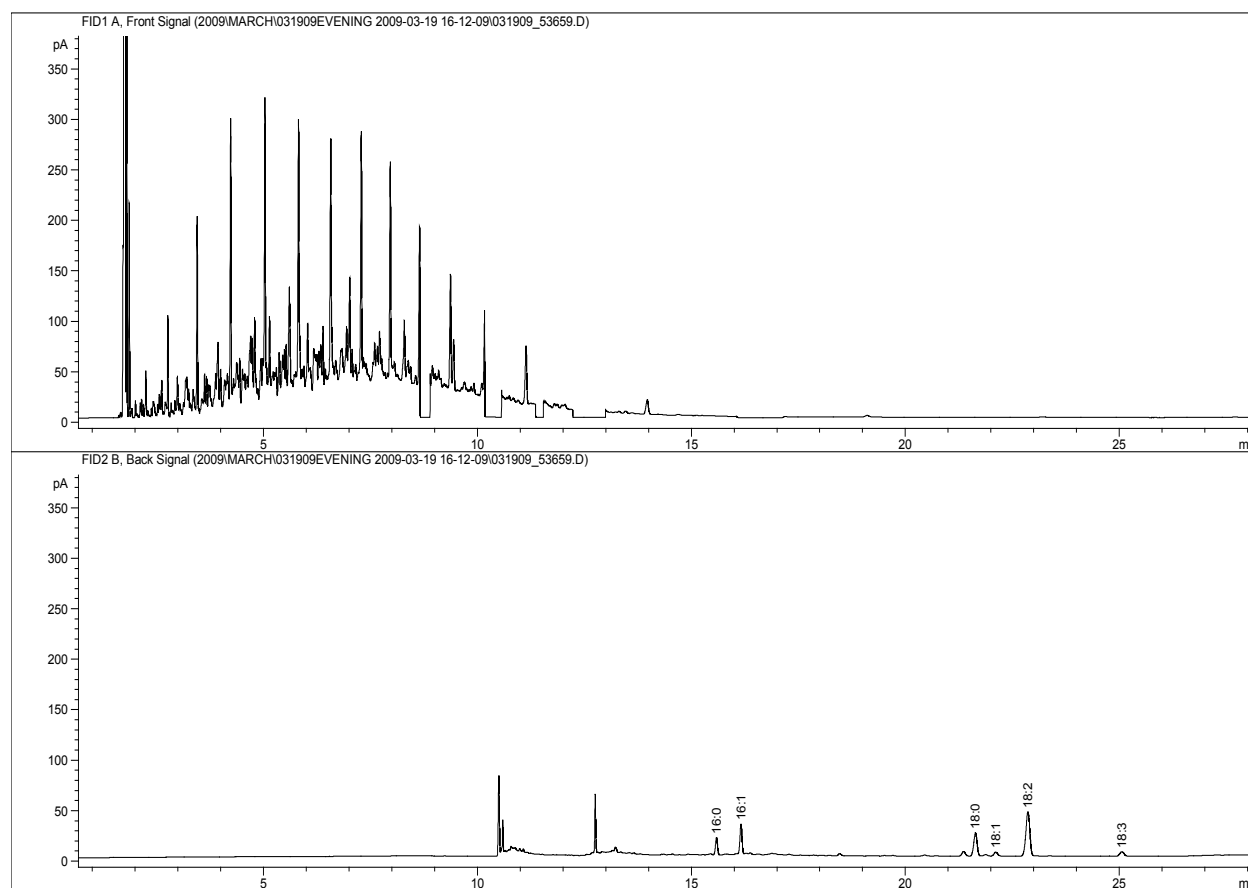


Figure 2. Typical MDGC/FID chromatograms for B20; top: diesel component, bottom: biodiesel component

Results and Discussion

Standard Tests

Biodiesel Content of Blends

Twenty-six samples came from public pumps and seven came from fleets with on-site fueling. Figure 3 shows the biodiesel content measured in each sample. Each sample was considered to be nominally B20 if the measured biodiesel content was between 18 and 22 vol%, and 57% of samples were in this range. The majority of non-B20 samples contained lower percentages of biodiesel—typically, B2, B5, and B11. Six of the seven fleet samples were nominally B20, the seventh had slightly low biodiesel content (17 vol%). Only two samples had extremely high biodiesel content (B55 and B90), suggesting that the blend had been prepared without adequate mixing so that when the sample was pumped from the tank bottom it contained a higher level of the more dense biodiesel.

In 2004, half the non-B20 samples were high in biodiesel content and half were low. This was attributed to poor blending practices. In the 2008 survey, however, it is likely that the low-biodiesel-content samples were blended accurately to lower levels but then mistakenly sold from a pump labeled B20.

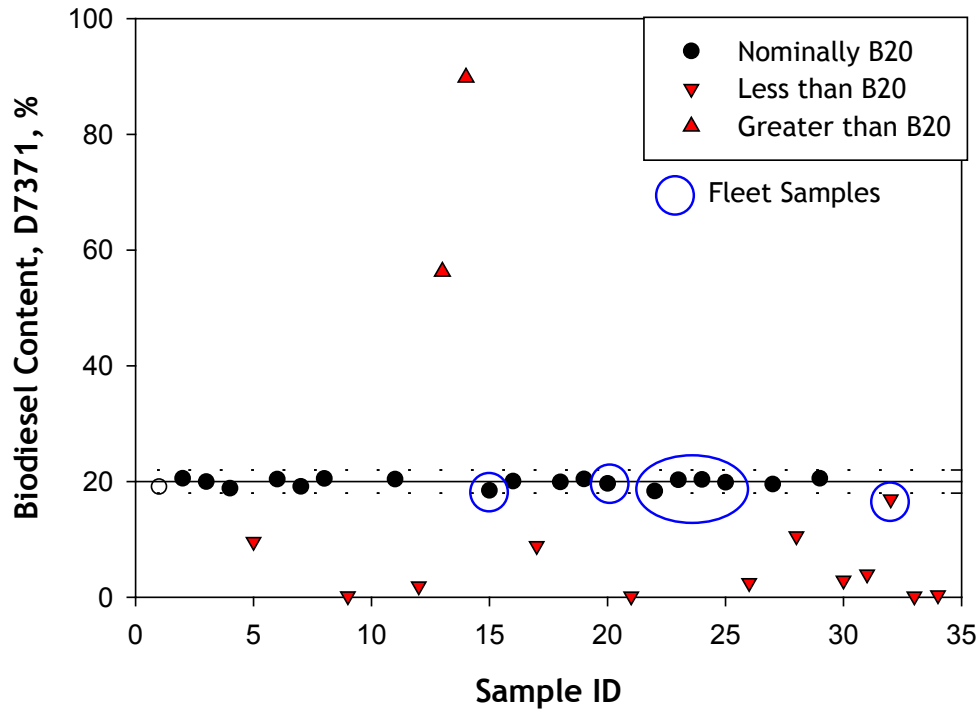


Figure 3. Blend percentage results for B20 samples collected in 2008

Induction Period Stability

The induction period (IP) stability, sometimes called the Rancimat or Oil Stability Index (OSI), is an indicator of the oxidative stability of fuels. The IP for neat diesel fuel is well over 24 hours [8, 9]. Previous work has shown the IP of biodiesel and biodiesel blends to be significantly less than that of diesel fuel unless treated with a synthetic antioxidant [10]. ASTM D6751, the specification for B100 as a blendstock, sets the IP at a minimum of 3 hours. This is intended to ensure an IP of 6 hours, minimum, for B6 to B20 as required by D7467.

The IP results are presented in Figure 4. The IP testing was stopped after 12 hours. These samples were artificially assigned a value of 12 hours. No information was collected on the amount of time these fuels spent in storage before sample collection.

The average B20 IP was 8.4 hours, well above the limit set in D7467. Three fleet samples were at or just below the 6-hour limit for D7467. For all samples with an IP of less than 6 hours, it was impossible to determine if the samples were “fresh” or “aged.” In “aged” Bxx blends, the IP begins to drop as the fuel ages [11]. Using the current specification, 75% of the B20 samples would be on-specification.

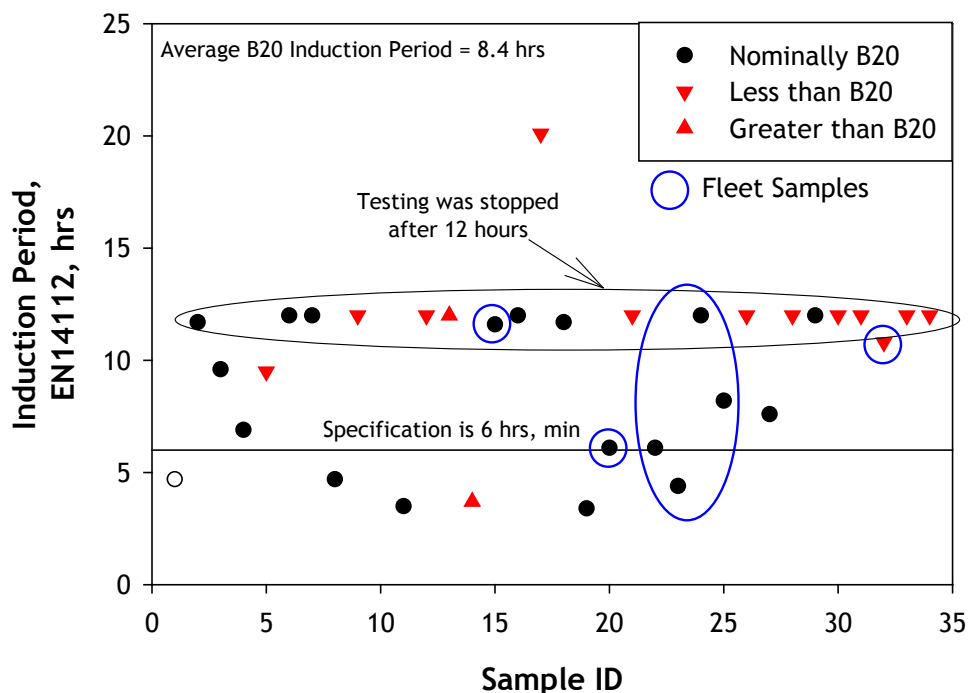


Figure 4. Induction period stability for the 2008 B20 survey

Acid Value

The acid value (AV) measures the amount of acids present in the fuel. These acids can be formed as the fuel begins to age and degrade. As with the IP, it is not possible to determine if aging had begun prior to sampling and impacted the AV. However, a majority of the sample AVs were below the detection limit of 0.05 mgKOH/g (Figure 5). Only one of the 33 samples was higher than the proposed D7467 AV specification level of 0.5 mgKOH/g. The 2007 B100 survey showed almost all the B100 to be on-specification for AV with very low failure rates [6], which was also seen in the 2008 B20 survey.

Several modifications to the AV method have been proposed through ASTM to improve detection limits. These modifications, including a smaller sample size and more dilute reagents, are included in the newest version of the AV test method, D664, which will decrease the detection limit from 0.05 mgKOH/g to 0.01 mgKOH/g. To illustrate the impact of these changes, the samples were tested with the current D664 method and with the proposed modifications. Figure 6 compares results for both methods. Samples that were below the detection limit using the traditional method were assigned a value of 0.05 mgKOH/g. A slight bias was observed between the current and modified method—the result of a delay between initial testing conducted using D664 and subsequent testing conducted using the modified method. Efforts were made to minimize the delay, but in some cases, several weeks elapsed between testing; thus, the fuel continued to age and the AV increased. The improvements in the D664 acid value test method allow greater precision at very low acid values, providing a better understanding of the critical fuel property.

Flash Point

The flash point is an important measure for ensuring the safe handling of fuels. A minimum flash point for fuels typically is set to avoid a flammable fuel/air mixture in normal use. The flash point of a mixture is dominated by the lowest flash component in that mixture. Thus, for Bxx blends, the flash point temperature is dominated by the diesel fuel, which has a significantly lower flash point than that of B100. For this reason, the flash point specification for Bxx blends is identical to that for diesel fuels set in D975. The minimum allowable flash point for Bxx blends composed of No. 2 diesel fuel is 52°C, while any blend containing No. 1 diesel fuel or any blend with a cloud point below -12°C can have a flash point as low as 38°C. For this survey, all samples had a flash point above 38°C. No information was available about the diesel fuel used in the Bxx blends. Of the four samples with flash point below 52°C, only one had a cloud point (CP in Figure 7) below -12°C.

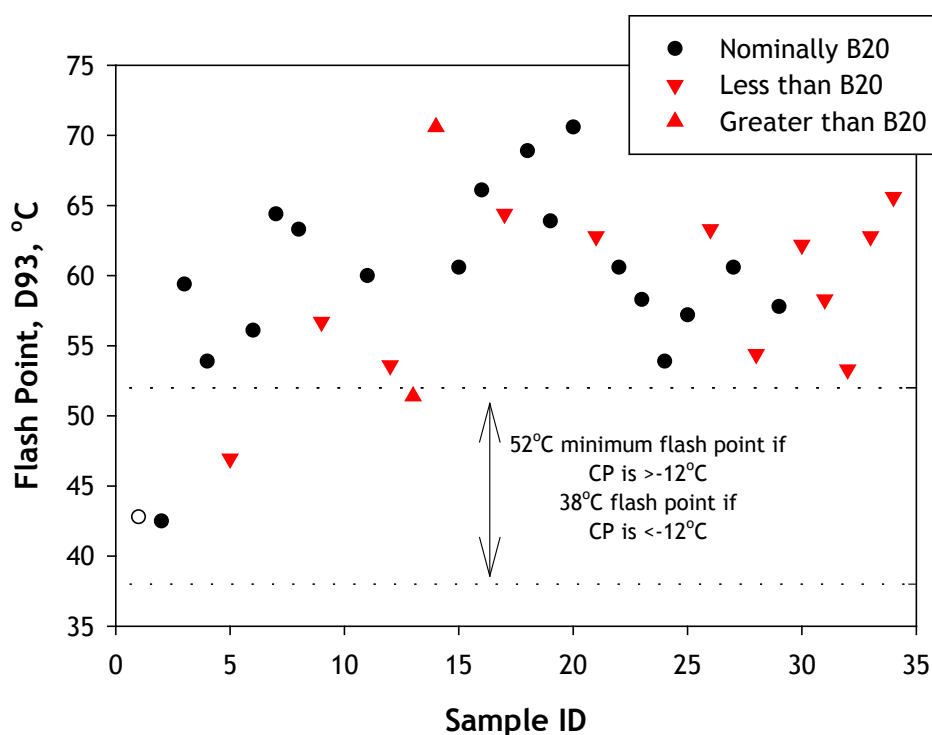


Figure 7. Flash point results for the 2008 B20 survey

Cloud Point

The cloud point is an important parameter for cold weather operability and is the temperature at which the first crystals appear in a fuel upon cooling under specified conditions. Cloud point is not specified but rather given as a report value. The cloud point needed to ensure appropriate cold weather operability depends on several factors, including geography and time of year. Figure 8 reports the cloud point for the fuels collected in this survey. The cloud point ranged from -7°C to -25°C. The average B20 cloud point was -12.6°C, and the median was -11.3°C.

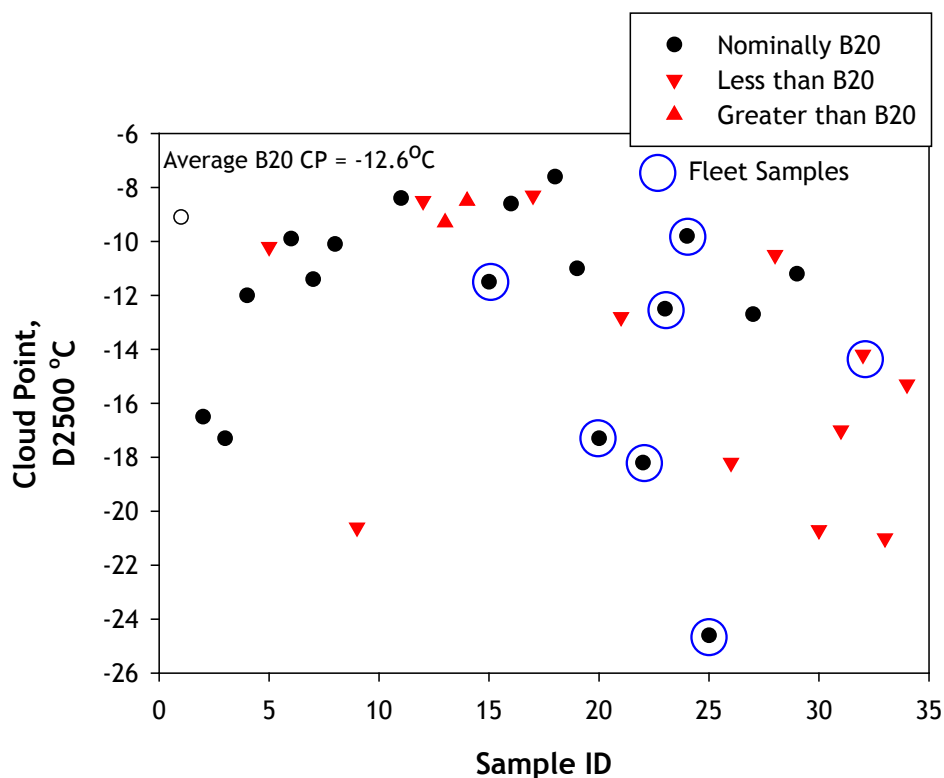


Figure 8. Cloud point results for the 2008 B20 survey

Other Properties from D7467

Three additional properties from the D7467 specification were tested. These properties were sulfur, cetane number, and ash. The sulfur content of the blends was tested with D5453. For samples that were nominally B20, the average sulfur content was 7.3 ppm, with a minimum of 3.7 ppm and a maximum of 16.2 ppm. Previous survey work has never found samples that do not meet the on-highway sulfur specification of 15 ppm, so the 16.2 ppm sample was unusual. This sample also had high particulate contamination (as discussed later in the report) and may have been contaminated during collection at the fleet. Samples that contained less than 20 vol% biodiesel had a slightly lower average sulfur content of 5.7 ppm and ranged from 3.5 ppm to 8.2 ppm. The two samples with greater than 20 vol% biodiesel had less than 4.5 ppm sulfur. The derived cetane number (a measure of ignition delay) of the Bxx blends was tested using D6890. The cetane numbers of the samples ranged from 45 to 56. All Bxx blends were below detection limits on the D482 ash content test.

Nonstandard Tests

Additional testing was performed on the Bxx blends to further characterize the fuels in the marketplace.

Karl Fisher Moisture

Currently, biodiesel blends are required to meet a combined free water and sediment limit of 0.050 vol% by D2709, a centrifuge test. Previous survey work has shown that biodiesel and

biodiesel blends rarely fail the water and sediment requirement. Free water is present once fuels become water-saturated. Any water in fuels below the saturation level is soluble. At room temperature, the water saturation level of B100 is between 1,200 and 1,500 ppm and may be a function of impurity levels and degree of oxidation [12]. Typical ultra-low-sulfur No. 2 diesel (ULSD) fuel will be saturated between 50 and 100 ppm water [13]. The soluble water was measured by coulometric Karl Fisher (KF, ASTM D6304). Figure 9 shows soluble water levels for the Bxx survey samples. The average KF titration (KF, ASTM D6304, Procedure B) for the B20 samples was 130 ppm, about 30% higher than expected for ULSD based on limited data from Stanfel [13].

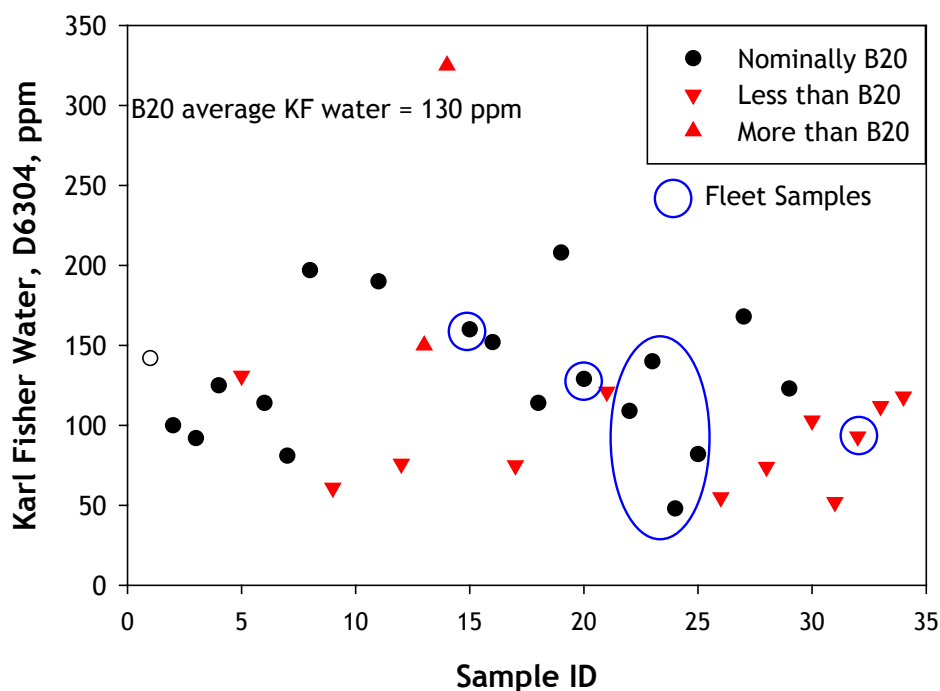


Figure 9. Karl Fisher moisture results for the 2008 B20 survey

Particulate Contamination

Particulate contamination is a concern for any diesel fuel because fine particles may damage modern, very high pressure fuel injection systems. A majority of the samples collected in this study were tested using the diesel method, D6217, which at the time of the survey was the only particulate contamination method for distillate fuels. That method does not cover biodiesel or biodiesel blends. A new method specific to biodiesel and biodiesel blends (D7321) was adopted in the middle of the survey, and the final seven samples were tested using the new method. Only small differences can be noted between these two highly similar methods.

Each method determines the particulate contamination as the mass collected on a standard filter after a set volume of fuel is filtered. To compare the methods, five samples were tested using both D6217 and D7321. Results showed some variation between methods, but overall trends were similar and there was no consistent bias for this small sample set (Figure 10). Except for

one sample, the particulate contamination results are typically below 10 mg/L, a level cited as acceptable by engine manufacturers [14].

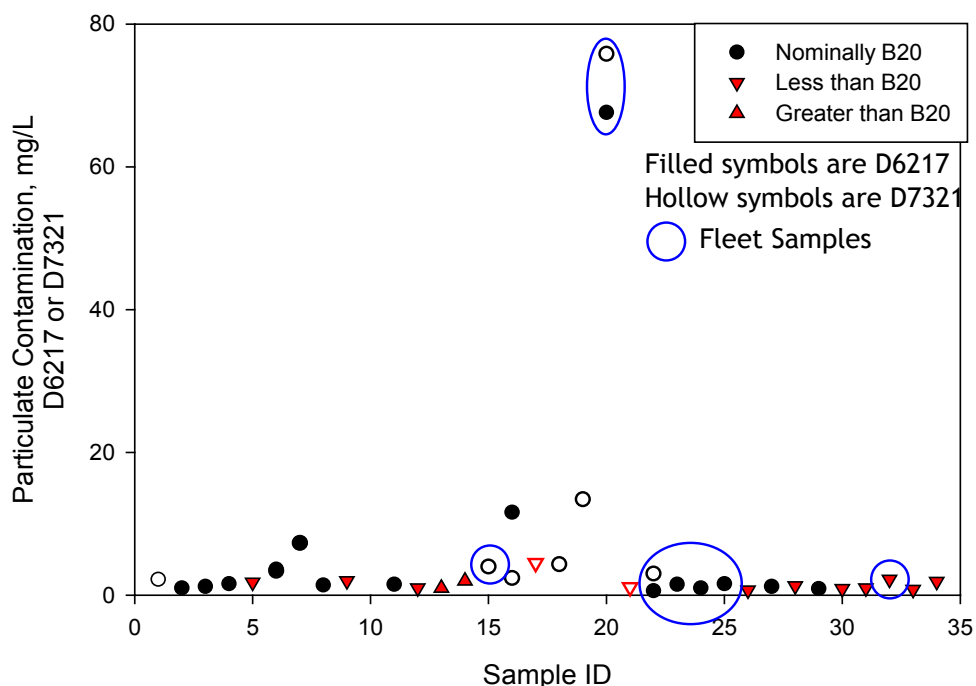


Figure 10. Particulate contamination results for the 2008 B20 survey, using D6217 or D7321

Interfacial Tension

Water interfacial tension (IFT) can indicate how effective coalescing water separator filters will be at removing free water from fuels that will be introduced into an engine. One measure of interfacial tension is the DuNuoy ring method, ASTM D971. Figure 11 shows the interfacial tension of the Bxx survey samples. The average IFT is 12.3 mN/m, slightly lower than that observed in the 2004 survey; however, the range of IFT values was significantly less in this survey. The IFT of diesel fuel has dropped since ULSD fuel was introduced to 9–25 mN/m, likely as a result of increased surfactancy from lubricity and other additives [13]. The IFT values of Bxx blends collected in this survey were similar to those of U.S. ULSD samples, but at the lower end of the range.

Free and Total Glycerin

One assumption for Bxx blends is that if the B100 and diesel fuel are on-specification, the Bxx blend will be on-specification. At the time of this survey, before the B6-B20 specification was adopted, this was the only metric used to assess Bxx quality. An important parameter for B100 is the free and total glycerin content measured by ASTM D6584. One of the significant drawbacks to this method is the extreme sensitivity to even trace amounts of diesel fuel. Therefore, for Bxx blends, it is not possible to use D6584 to extract the glycerin information about the B100 used for blending unless the parent B100 is available. Excess free and total glycerin can impact engine operability by causing injector deposits and plugging fuel filters; it could also impact cold weather operability.

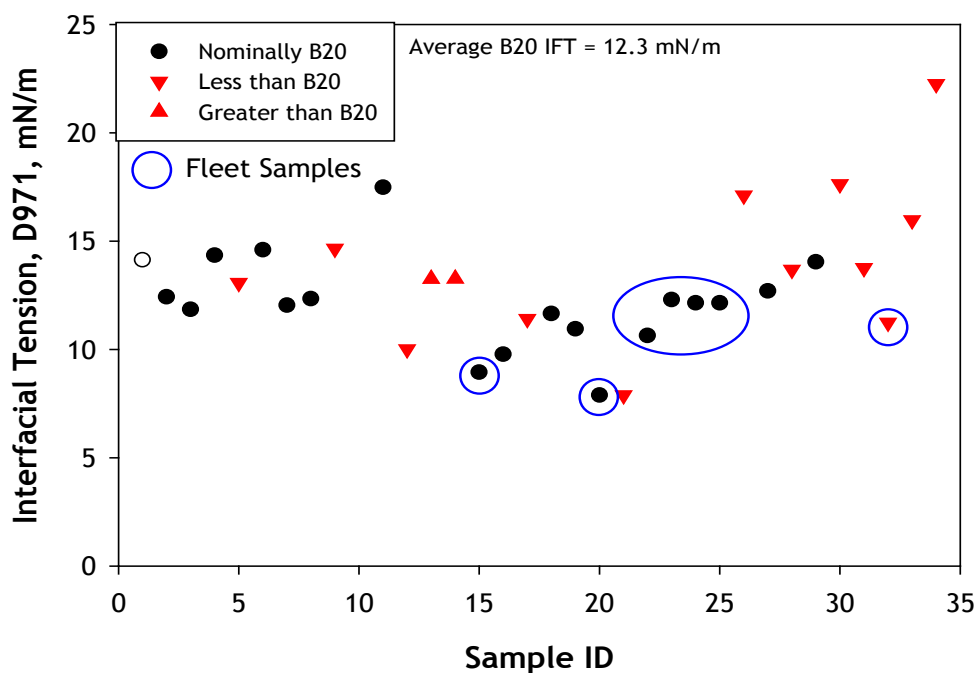


Figure 11. Water interfacial tension results for the 2008 B20 survey

A new IC-based method has been developed that can determine the free and total glycerin content of Bxx blends and, by inference, that of the parent B100. The samples in this survey were tested using the IC method to determine the B100 free and total glycerin content. Figure 12 shows the free and total glycerin results calculated using the exact biodiesel concentration of the B100 used in these blends. Thus, for a B20 sample, the free and total glycerin was multiplied by 5 to allow comparison with the ASTM D6751 specification for B100. All of the samples collected met the B100 specifications for free and total glycerin.

Group I and II Metals

The Bxx blend samples were also tested for Group I and II metal content: Na, K, Mg, and Ca. Biodiesel might contain Group I and II metals if contaminated during the production process. These metals can cause oxidation and soaps to form or might negatively impact the durability of emission control catalysts and filters. The samples were tested using ASTM D7111. Table 4 lists the minimum, maximum, and average metal content for the samples. For Mg and K, all samples were below the detection limit. Low levels of Ca were observed in a few samples. Only one sample showed elevated Na content in the blend; it was so high (2,000 ppb) that the B100 would likely be off-specification.

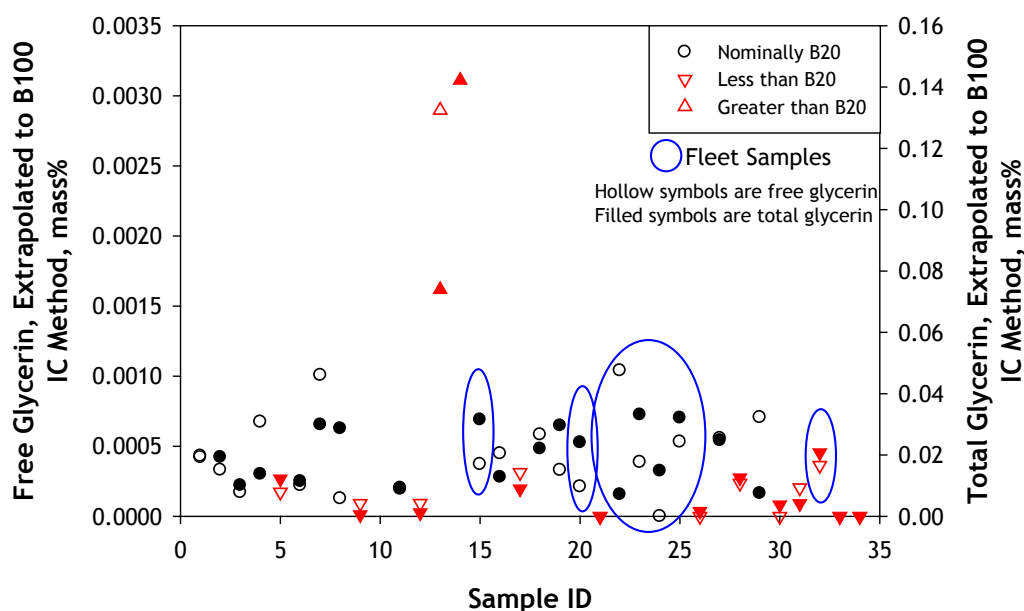


Figure 12. Free and total glycerin by ion chromatography for 2008 B20 survey samples; results extrapolated to B100 properties

Table 4. Average and Minimum and Maximum Group I and II Metal Content of B20 Samples (ppb)

Metal ^a	Minimum	Maximum	Average
Mg	BDL(100) ^b	BDL(100)	BDL(100)
K	BDL(100)	BDL(100)	BDL(100)
Ca	BDL(100)	652	219
Na	BDL(500) ^c	2,000 ^d	606

^a All samples were measured using ASTM D7111.

^b BDL(100) is below the detection limit of 100 ppb.

^c BDL(500) is below the detection limit of 500 ppb.

^d Sample would be off-specification for Na+K in B100.

Feedstock Analysis

The FAME profile of biodiesel can be used to determine the parent fat or oil used in production. For example, the FAME profile of soy-derived biodiesel is approximately 10% methyl palmitate, up to 5% methyl stearate, about 25% methyl oleate, 50% methyl linolenate, and less than 10% methyl linoleate [15]. Although the profile changes slightly with changes in such factors as ambient growing temperature and rainfall, this typical FAME profile can be compared with measured FAME profiles to identify the parent fat or oil.

Each Bxx sample was analyzed using MDGC/FID to determine the source of the B100. Soybean-derived biodiesel was the most common source in these blends and accounted for 78% of the samples (Figure 13). Of the remaining samples, 21% of the Bxx blends were made from

biodiesel produced from mixed feedstock sources such as soybean oil and animal fat. Only two samples were made from neat animal-fat-derived biodiesel. The B100 feedstock could not be identified for one sample, a B2. The MDGC/FID method readily identifies the feedstock for B5 and greater samples. FAME recovery from these samples was in excess of 90%. For blend samples lower than B5, FAME recovery dropped significantly as biodiesel content dropped, although the FAME profile appeared to be intact.

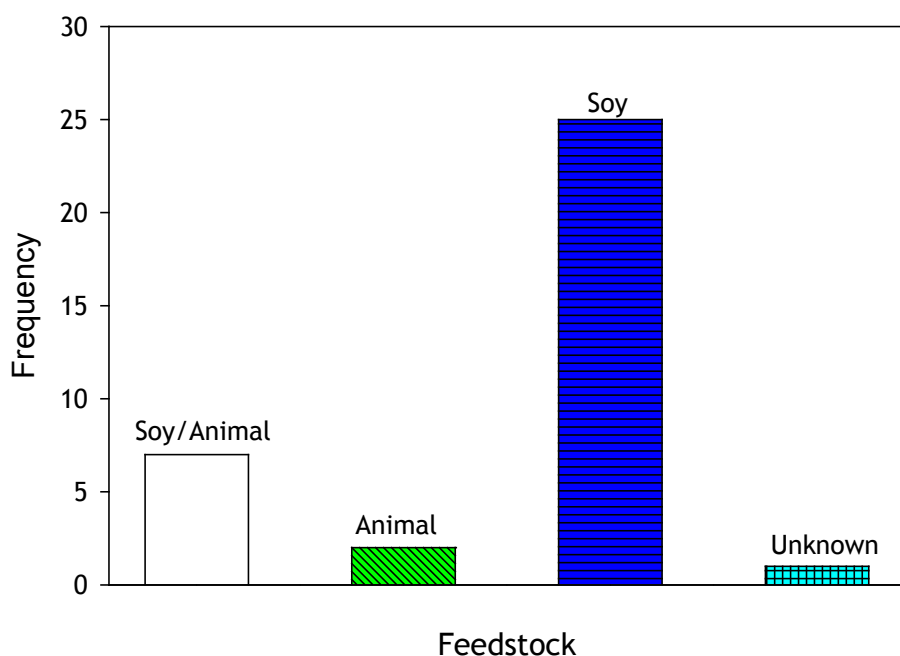


Figure 13. Feedstocks used in the blends collected in the 2008 B20 survey

To further validate this technique, hand blends were produced from a B100 with a known FAME content and a certification diesel fuel. The B2 blend was mixed volumetrically and analyzed with the MDGC/FID. The FAME recovery was better than that for the real-world samples, but still less than the recovery from higher blends. Although the recovery was low, the FAME profile was intact and the source could be positively identified, confirming the results from the real-world samples.

Conclusions

Biodiesel blend samples were collected from around the United States in the summer of 2008. These samples were tested against the D7467 specification for B6-B20, which was adopted in October 2008. Sixty percent of the samples collected were nominally B20. The rest of the samples had lower biodiesel content, such as ~B10, B5, and B2. This is in contrast to NREL's previous B20 survey, in which the biodiesel samples were evenly distributed above and below B20. Twenty-five percent of the samples failed to meet the proposed induction period stability specification of 6 hours, although on average the induction period was well above this level. The

samples readily met the other proposed specification properties, with one sample with high AV and one sample having high sulfur, likely the result of contamination. No failures on flash point were noted. Although part of the specification, cloud point is a report value. For the 2008 B20 survey, the average cloud point was -12.6°C, with a range from -7°C to -25°C.

Although not in the specification, several other properties of interest were measured. The water content of fuels, an important parameter for handling, was measured by Karl Fisher. The B20 blends had an average water content of 130 ppm, about 30% higher than that of conventional diesel fuel. One method of quantifying the particles in fuel is to measure the particulate contamination. For these fuels, particulate levels were low, and only one fuel had levels above 20 mg/L.

Interfacial tension, a measure of the efficacy of water separator filters to remove water from fuels, was similar to ULSD for the B20 samples. Industry-wide, the IFT for diesel fuels has been decreasing and this survey showed the same trend. IFT for the B20 blends was slightly below 2004 levels, but within the range of ULSD samples.

Analysis of the Group I and II metals revealed very low levels, as expected in biodiesel blends. One sample had Na content sufficiently high that the B100 used in the blend was off-specification for this parameter.

Researchers characterized the B100 used in the blend using novel chromatographic techniques. Typically, information about the parent B100 in a Bxx blend is lost when diesel fuel is added. Ion chromatography is insensitive to diesel fuel, however, allowing the free and total glycerin to be analyzed in the blend. Results show that the parent B100s met the D6751 specification for glycerin. A multidimensional GC technique allowed the feedstock of the parent B100 to be determined. The biodiesel used to blend these samples was produced predominantly from soybean oil, and animal fat was the second most common feedstock.

Although the B6-B20 specification was not applicable in mid-2008 when the B20 samples were collected, a majority of the samples would be meet that specification, with the exception of oxidation stability. The adoption of the specification expands the market for future studies to include all blends between B6 and B20 and another survey is recommended to assess compliance with the specification in the near future.

References

1. Energy Information Administration. August 2009 Monthly Energy Review: Renewable Energy; <http://www.eia.doe.gov/emeu/mer/renew.html>.
2. Alternative & Advanced Fuels–Biodiesel Incentives and Laws; http://www.afdc.energy.gov/afdc/fuels/biodiesel_laws.html.
3. McCormick, R.L.; Alleman, T.L.; Ratcliff, M.; Moens, L.; Lawrence, R. *Survey of the Quality and Stability of Biodiesel and Biodiesel Blends in the United States in 2004*; NREL/TP-540-38836; National Renewable Energy Laboratory: Golden, CO, October 2005; <http://www.nrel.gov/docs/fy06osti/38836.pdf>.
4. Tang, H.; Abunasser, N.; Wang, A.; Clark, B.R.; Wadumesthrige, K.; Zeng, S.; Kim, M.; Salley, S.O.; Hirschlieb, G.; Wilson, J.; Ng, K.Y.S. Quality survey of biodiesel blends sold at retail stations. *Fuel* **2008**, 87, 2951-2955; DOI: 10.1016/j.fuel.2008.04.029.
5. Alleman, T.L.; McCormick, R.L.; Deutch, S. *2006 B100 Quality Survey Results*; NREL/TP-540-41549; National Renewable Energy Laboratory: Golden, CO, May 2007; <http://www.nrel.gov/docs/fy07osti/41549.pdf>.
6. Alleman, T.L.; McCormick, R.L. *Results of the 2007 B100 Quality Survey*; NREL/TP-540-42787; National Renewable Energy Laboratory: Golden, CO, March 2008; <http://www.nrel.gov/docs/fy08osti/42787.pdf>.
7. McCurry, J.D.; Wang, C. *Analysis of Fatty Acid Methyl Ester (FAME) Content and Distribution in Biodiesel Blends Using Heat-cutting 2D Gas Chromatography*; Agilent Technologies publication 5989-8107EN; Agilent Technologies: Santa Clara, CA, March 2008; http://www.chem.agilent.com/en-US/Search/Library/_layouts/Agilent/PublicationSummary.aspx?whid=55043&liid=1873
8. Shiotani, H.; Goto, S. *Studies of Fuel Properties and Oxidation Stability of Biodiesel Fuel*; SAE Technical Paper No. 2007-01-0073; SAE International: Warrendale, PA, January 2007; <http://www.sae.org/technical/papers/2007-01-0073>.
9. Miyata, I.; Takei, Y.; Tsurutani, K.; Okada, M. *Effects of Bio-Fuels on Vehicle Performance: Degradation Mechanism Analysis of Bio-Fuels*; SAE Technical Paper No. 2004-01-3031; SAE International: Warrendale, PA, October 2004; <http://www.sae.org/technical/papers/2004-01-3031>.
10. McCormick, R.L.; Westbrook, S.R. *Empirical Study of the Stability of Biodiesel and Biodiesel Blends*; NREL/TP-540-41619; National Renewable Energy Laboratory: Golden, CO, May 2007; <http://www.nrel.gov/docs/fy07osti/41619.pdf>.
11. McCormick, R.L.; Alleman, T.L.; Waynick, J.A.; Westbrook, S.R.; Porter, S. *Stability of Biodiesel and Biodiesel Blends: Interim Report*; NREL/TP-540-39721; National Renewable Energy Laboratory: Golden, CO, April 2006; <http://www.nrel.gov/docs/fy06osti/39721.pdf>.

12. Routt, D. "Testing Biodiesels' Saturation Properties under the Influence of Variable Temperature, Biodiesel Type and #2 Diesel Concentration"; ASAE Section Meeting Presentation Paper Number PNW05-1014; 2005 Pacific Northwest ASAE Section Meeting, Lethbridge, Alberta, Canada, September 22-24, 2005;
http://asae.frymulti.com/section_meeting.asp?confid=smpnr.
13. Stanfel, C. Fuel filtration: Protecting the diesel engine. *Filtration & Separation* **2009**, 46 (3), 22-25; <http://www.filtsep.com/view/1727/fuel-filtration-protecting-the-diesel-engine/>.
14. *World Wide Fuel Charter, 4th Edition*; European Automobile Manufacturers Association, Alliance of Automobile Manufacturers, Engine Manufacturers Association, and Japan Automobile Manufacturers Association, September 2006;
<http://www.autoalliance.org/index.cfm?objectid=96B9A0F5-1D09-317F-BB2D56C35C3A5F04>).
15. *Physical and Chemical Characteristics of Oils, Fats, and Waxes, 2nd Edition*, American Oil Chemists Society, 2006.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Department of Defense, Executive Services and Communications Directorate (0704-0188). Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ORGANIZATION.

1. REPORT DATE (DD-MM-YYYY) March 2010			2. REPORT TYPE Technical Report		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE Analysis of Biodiesel Blend Samples Collected in the United States in 2008					5a. CONTRACT NUMBER DE-AC36-08-GO28308	
					5b. GRANT NUMBER	
					5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) T.A. Alleman, L. Fouts, and R.L. McCormick					5d. PROJECT NUMBER NREL/TP-540-46592	
					5e. TASK NUMBER FC08.9400	
					5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) National Renewable Energy Laboratory 1617 Cole Blvd. Golden, CO 80401-3393					8. PERFORMING ORGANIZATION REPORT NUMBER NREL/TP-540-46592	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)					10. SPONSOR/MONITOR'S ACRONYM(S) NREL	
					11. SPONSORING/MONITORING AGENCY REPORT NUMBER	
12. DISTRIBUTION AVAILABILITY STATEMENT National Technical Information Service U.S. Department of Commerce 5285 Port Royal Road Springfield, VA 22161						
13. SUPPLEMENTARY NOTES						
14. ABSTRACT (Maximum 200 Words) The quality of B20 (20 vol% biodiesel, 80 vol% petroleum diesel fuel) in the United States was sampled in 2008. Thirty-two samples from retail locations and fleets using B20 were tested against the proposed D7467 B6-B20 specification, which took effect later in 2008. Sixty percent were $\pm 2\%$ (nominally) B20. Twenty-five percent failed the proposed minimum induction period stability of 6 hours; the overall average was 8.4 hours. All B20 samples met proposed specifications for acid value, cetane, and ash. Ion chromatography was used to determine free and total glycerin in B20 blends. Results showed that all the B100 used for blending met D6751 glycerin specifications. Samples were analyzed by multidimensional gas chromatography to determine the B100 feedstock; most was soy-derived; some was animal-derived. The average dissolved water in B20 samples was 130 ppm, 30% higher than the typical saturation level of diesel fuel. Particulate contamination in the B20 was below 20 mg/L in every case but one.						
15. SUBJECT TERMS biodiesel; biodiesel blends; biodiesel quality; biodiesel quality survey; National Renewable Energy Laboratory						
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UL	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON	
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (Include area code)	