

# 2006 B100 Quality Survey Results

## Milestone Report

T.L. Alleman, R.L. McCormick, and S. Deutch

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**NREL/TP-540-41549**

**May 2007**

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Prepared under Task No. FC079400

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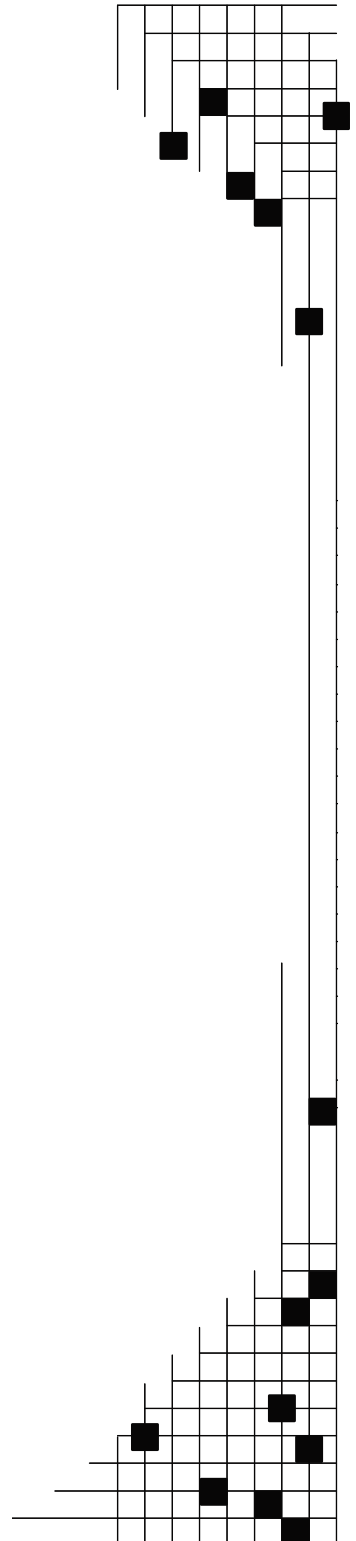
May 2007

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1617 Cole Boulevard, Golden, Colorado 80401-3393  
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Contract No. DE-AC36-99-GO10337



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## **Acknowledgments**

The authors thank the U.S. Department of Energy's Office of FreedomCAR & Vehicle Technologies for funding support, Scott Fenwick at Archer Daniels Midland for conducting the methanol analysis, Tom Livingston of Robert Bosch for the Rancimat analysis, and Tom Carter at Eastman for oil stability index analysis.

## Executive Summary

In 2006, the National Renewable Energy Laboratory conducted a nationwide quality survey of pure biodiesel (B100) intended to be used as a blendstock. The study collected random samples throughout the United States and analyzed them for quality against the current and proposed ASTM D6751 fuel quality specifications.

This report documents completion of the National Renewable Energy Laboratory's Fiscal Year 2007 Annual Operating Plan Milestone 10.2. This milestone supports the U.S. Department of Energy, Fuels Technologies Program Multiyear Program Plan Goal of identifying fuels that can displace 5% of petroleum diesel by 2010.

Samples were randomly collected from terminals throughout the Petroleum Area Defense Districts (PADDDs), with a higher concentration of fuels collected in the Midwest, where biodiesel production is highest. The samples were sent to a subcontracted analytical laboratory for analysis. The same methodology was used to analyze all samples.

Results of a telephone survey of the distributors revealed that most samples were soy derived. The sample set contained a few animal fat-derived samples, and one derived from palm stearin. Samples were typically stored at the distributors in aboveground tanks.

The survey revealed the increasing prevalence of B99.9 in the marketplace, 6 of 37 U.S. samples were B99.9 rather than B100. As a group, the samples had a failure rate of 59% compared to the specifications. The B100 samples as a subset had an identical failure rate. Most often, the samples failed by exceeding the allowable total glycerin or by not meeting the minimum flash point specification. Several samples failed to meet requirements for multiple properties. The individual failure rates for total glycerin and flash point were 33% and 30%, respectively. The results of this study were not production volume weighted, but do show a significant fuel quality concern for B100 produced and distributed during 2006.

## Acronyms and Abbreviations

|                         |  |
|-------------------------|--|
| <b>AET</b>              | atmospheric equivalent temperature                       |
| <b>ASTM</b>             | ASTM International                                       |
| <b>B</b>                | boron  |
| <b>Bxx</b>              | Biodiesel blend composed of xx% biodiesel in diesel fuel |
| <b>Ca</b>               | calcium  |
| <b>°C</b>               | degrees Celsius  |
| <b>Cu</b>               | copper   |
| <b>EN</b>               | European Normalization                                   |
| <b>EPA</b>              | U.S. Environmental Protection Agency                     |
| <b>FAME</b>             | fatty acid methyl ester                                  |
| <b>Fe</b>               | iron   |
| <b>GC</b>               | gas chromatography                                       |
| <b>GC-MS</b>            | gas chromatography-mass spectrometry                     |
| <b>h</b>                | hour, hours  |
| <b>ICP-AES</b>          | Inductively coupled plasma atomic emission spectroscopy  |
| <b>K</b>                | potassium  |
| <b>mass%</b>            | percent by mass  |
| <b>max</b>              | maximum  |
| <b>Mg</b>               | magnesium  |
| <b>mgKOH/g</b>          | milligrams potassium hydroxide per gram                  |
| <b>min</b>              | minimum  |
| <b>mm<sup>2</sup>/s</b> | millimeters squared per second                           |
| <b>MSTFA</b>            | N-methylN-trimethylsilyltrifluoroacetamide               |
| <b>Na</b>               | sodium   |
| <b>NREL</b>             | National Renewable Energy Laboratory                     |
| <b>OSI</b>              | oil stability index                                      |
| <b>PADD</b>             | Petroleum Area Defense District                          |
| <b>ppm</b>              | parts per million  |
| <b>S</b>                | sulfur   |
| <b>S15</b>              | 15 ppm sulfur  |
| <b>S500</b>             | 500 ppm sulfur   |
| <b>Si</b>               | silicon  |
| <b>UOP</b>              | Universal Oil Products                                   |
| <b>Zn</b>               | zinc   |

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## Introduction

In 2004 the U.S. Jobs Creation Act set forth credits for biodiesel to encourage the domestic biodiesel market. A blender's tax credit of \$1.00/gal for agri-biodiesel and \$0.50/gal for biodiesel from recycled oils went into effect January 1, 2005.<sup>1,2</sup> The Internal Revenue Service rule governing the tax credit states that blending one gallon of diesel fuel with 999 gallons of biodiesel classifies as a "blending event." Thus, many biodiesel producers sell B99.9 and claim the tax credit. As a result of these credits and industry growth, biodiesel production in the United States reached 75 million gallons in 2005 and about 250 million gallons in 2006.<sup>3</sup> Producers must ensure that the biodiesel meets the ASTM D6751 specifications for neat biodiesel to meet U.S. Environmental Protection Agency fuel registration requirements and to obtain the tax credit.

As part of an effort to help the biodiesel industry achieve engine manufacturer warranty approval for the use of biodiesel blends, the National Renewable Energy Laboratory (NREL), for the U.S. Department of Energy, has conducted nationwide surveys of biodiesel quality. NREL conducted a B100 quality survey in 2004, the results of which showed that approximately 85% of the samples met the quality standards of ASTM D6751-03a, the version of D6751 that was in effect at the time.<sup>4</sup> Beginning in late 2005 and continuing through mid-2006, NREL conducted a second nationwide B100 quality survey, which is the subject of this report.

## Methodology

B100 samples were collected from distributors throughout the 48 contiguous states. A contractor contacted each distributor to obtain a B100 sample. The contractor was constrained to obtain a certain number of samples within each Petroleum Area Defense District (PADD). The samples were collected from random points of distribution. Thus, the samples may not be wholly representative on a volume basis of biodiesel in use in the United States today.

After the samples were collected, the contractor was instructed to conduct a telephone survey of the distributors, who were asked what the biodiesel feedstock was, how recently the load sampled had been delivered, the storage conditions, if any additives were in use, and if so, which ones.

The samples were tested for a variety of properties, including those that make up the ASTM D6751 specification as well as other properties that were proposed for inclusion or are otherwise of interest. The samples were collected between November 2005 and July 2006. During this period, the ASTM fuel property specification for biodiesel was modified. The first set of samples was collected under ASTM D6751-03a (Table 1). An update to D6751 was published in May 2006 as D6751-06. Table 2 lists the relevant modifications made in D6751-06 relative to D6751-03a. Properties not listed are identical for both versions of the standard. The impact of these changes to the fuel quality specifications will be discussed as appropriate. Other properties for which testing was also performed are listed in Table 3. Several of these properties and limits have been included in subsequent versions of D6751 but were not in effect at the time of this study.

**Table 1. Fuel Property Specifications for B100 Samples under ASTM D6751-03a**

| Property   | ASTM Method | S15 Limits | S500 Limits |
|--|-------------|------------|-------------|
| Flash point, closed cup, °C                      | D93         | 130.0 min  | 130.0 min   |
| Water and sediment, vol%                         | D2709       | 0.050 max  | 0.050 max   |
| Kinematic viscosity, 40°C, mm <sup>2</sup> /s    | D445        | 1.9-6.0    | 1.9-6.0     |
| Sulfated ash, mass%                              | D874        | 0.020 max  | 0.020 max   |
| Sulfur, ppm                                      | D5453       | 0.0015 max | 0.0500 max  |
| Cetane number                                    | D613        | 47 min     | 47 min      |
| Cloud point, °C                                  | D2500       | Report     | Report      |
| Carbon residue, mass%                            | D4530       | 0.050 max  | 0.050 max   |
| Acid number, mg KOH/g                            | D664        | 0.80 max   | 0.80 max    |
| Free glycerin, mass%                             | D6584       | 0.020 max  | 0.020 max   |
| Total glycerin, mass%                            | D6584       | 0.240 max  | 0.240 max   |
| Phosphorus content, mass%                        | D4951       | 0.001 max  | 0.001 max   |
| Distillation temperature, AET, 90% recovered, °C | D1160       | 360 max    | 360 max     |

**Table 2. Changes to D6751 in 2006 (D6751-06e1)**

| Property                          | Test Method | S15 Limits | S500 Limits |
|-----------------------------------|-------------|------------|-------------|
| Acid number, mg KOH/g             | D664        | 0.50 max   | 0.50 max    |
| Sodium + potassium, combined, ppm | UOP 391     | 5 max      | 5 max       |

**Table 3. Other Properties Tested**

| <b>Property</b>                                 | <b>Method</b> | <b>Limit if Proposed for Inclusion in D6751</b>        |
|---|---------------|--|
| Oxidation stability, h <sup>a</sup>             | EN14112       | 3 min  |
| Calcium + magnesium, combined, ppm <sup>a</sup> | EN14538       | 5 max  |
| Methanol content, mass% <sup>a</sup>            | EN14110       | 0.20 max <sup>b</sup>                                  |
| Karl Fisher water, ppm                          | D6304         | 500 max  |
| Particulate contamination, mg/L                 | D6271         | 24 max   |
| Peroxide content, ppm                           | D3703         | Not proposed for inclusion in D6751, no proposed limit |

<sup>a</sup> Incorporated into D6751-07. Additionally, the test method for sodium+potassium was changed from UOP391 to EN14538.

<sup>b</sup> Incorporated into D6751-07 with a minimum flash point of 93°C as an alternative to the 130°C minimum flash point requirement.

## Sample Collection and Telephone Survey

The goal of the sample collection was to include samples from every PADD, with an emphasis in areas where biodiesel use and/or production is highest. A total of 37 samples were collected from 23 of the 48 contiguous states. For comparison, two additional samples were included in the survey from outside the United States, one each from Canada and Germany. Figure 1 shows the collection location for each U.S. sample.



The feedstock of the samples was predominantly soy (31 of the 39 samples). These results are similar to the results of the 2004 survey, showing that the United States still produces most of its biodiesel from soy. Animal fats composed four of the samples and there was one sample each of palm stearin and unknown origin. The two non-U.S. samples were produced from canola (Canada) and rapeseed (Germany).

The distributors held the biodiesel in a variety of storage containers and locations. Table 4 lists the storage conditions encountered and the frequency of each condition, along with applicable notes. Most of these samples were stored outside in aboveground tanks. No information was collected about whether these tanks were heated during the winter; however, outdoor B100 tanks are commonly heated to temperatures in the range of 10°C to 15°C. In most cases, the distributors did not report additive usage in the biodiesel. Two distributors reported use of additives: an additive described as Sure Flo in one sample, and additives described as Power Service Products plus an unspecified biodiesel antigel additive in the other. No specific product information or treat rates were given.

**Table 4. Storage Location Information for Biodiesel Samples**

| <b>Storage Type</b>   | <b>Frequency</b> | <b>Notes</b>                    |
|-----------------------|------------------|---------------------------------|
| Aboveground, outdoors | 27               |                                 |
| Aboveground, indoors  | 4                |                                 |
| Underground           | 2                |                                 |
| Other                 | 1                | Fuel stored in 5-gal containers |

The sample collection contractor was specifically instructed to collect B100 samples. However, a number of biodiesel blends were collected. Of the 37 U.S. samples, six were B99.9 blends and one (sample #28) was a B50 blend. These samples were identified as B99.9 during the D6584 glycerin analysis, as discussed in the glycerin section. Fourier transform infrared spectroscopy with an attenuated total reflectance cell was used to measure the biodiesel content of the B50 sample. This method for blend level quantification was developed at ASTM by a work group under the D02.04.F subcommittee on Adsorption Spectroscopy. The number of samples collected that were B99.9 rather than B100 for the 2005–2006 survey contrasts with the 2004 survey, where no B99.9 was encountered. The fact that several distributors submitted B99.9 instead of B100 indicates a lack of specificity in differentiating between these products in the marketplace.

### **ASTM D6751 Specification Results**

Samples 1–24 were collected under the D6751-03a fuel property specification from November 2005 to March 2006 and were tested for all the properties listed in Table 1. Samples 25–39 were collected after D6751-06 was published in May 2006, and were tested against the properties listed in Table 1 plus additional properties or limits listed in Table 2. Based on the results of the 2004 B100 quality survey (where every sample met the water and sediment, copper corrosion, and cetane limits) these tests were not performed in the current survey.<sup>4</sup>

Results from the D6751 properties are listed in Table 5. The results in **boldface type** failed to meet the D6751 standard in effect at the time of sample collection. Excluding the samples from outside the United States, the failure rate of the samples collected in this survey is 59%. The failure rate is the same regardless of whether the B99.9 samples are included with the B100 samples (assuming that all the B99.9 samples met the glycerin standards). The failure rates for individual test methods vary and will be discussed in the subsequent sections; the highest single failure rate was observed for total glycerin; 10 of 30 B100 samples did not meet the specifications (33% failure rate). The next most significant test method in terms of failure rate is the flash point, with an 18% failure rate for the B100 samples and a combined

failure rate (B100 and B99.9) of 30%. For the other requirements failure rates were much lower.

### **Flash Point**

Flash point is the temperature to which a fuel must be heated to produce a fuel/air mixture that is ignitable by a flame. It is an important safety and handling parameter for fuels. The flash point of biodiesel was required to be  $>130^{\circ}\text{C}$  during the period of sample collection for this study. This limit ensures that residual alcohol, typically methanol, from the production process is below 0.20 mass% in the finished fuel. The current specification, D6751-07 includes two options for limiting methanol content. In the first option, the flash point must be  $>130^{\circ}\text{C}$  as before. In the second option, the flash point must be  $>93^{\circ}\text{C}$  and methanol content  $<0.20$  mass%. The methanol content is measured by EN14110, a gas chromatography (GC) method that employs head-space sampling, meaning the vapors above the fuel are sampled under specified conditions and analyzed chromatographically. This second option was not available at the time these samples were collected.

Figure 2 shows the flash point of the B100 samples and indicates a 30% failure rate compared to the standard of  $>130^{\circ}\text{C}$ . Three of the samples with low flash points were analyzed for methanol content by EN14110. All three contained residual methanol in excess of 0.20 mass% and would not meet the updated flash point specification.

Compared to the 2004 survey, where no samples failed the flash point specification, the greatly increased failure is noteworthy. Methanol in biodiesel is a remnant of the production process, indicating that a significant fraction of fuels entering the marketplace are not being postprocessed adequately to meet the current specifications.

Five of six B99.9 blends had flash point below the  $130^{\circ}\text{C}$  limit. Blending with such a small amount of diesel fuel would be unlikely to reduce the flash point of biodiesel below the  $130^{\circ}\text{C}$  limit. This is illustrated within the data set by sample #36, a B99.9 blend that readily met the  $130^{\circ}\text{C}$  flash point minimum and by the blend flash point study results shown in the Appendix. More likely possibilities are that the B99.9 failed because of high methanol content in the B100 or because of cross contamination with other, more volatile products (such as gasoline or ethanol) at the distributor. These low boiling products could significantly reduce the flash point of biodiesel.

**Table 5. Fuel Property Test Results from B100 Quality Survey**  
**(boldface type indicates the sample failed the property specification in effect at the time of sample collection)**

| Sample ID | Feedstock    | Date Collected | Sample Age, days | Comments                       | Cloud Point,<br>D2500, °C | Flash Point,<br>D93, °C | Sulfated Ash,<br>D874, mass% | Sulfur,<br>D5453, ppm | Carbon Residue,<br>D524, mass% | Acid Number,<br>D664, mg KOH/g | Rancimat,<br>EN14112, h | Viscosity,<br>D445, mm <sup>2</sup> /s | Free Glycerin,<br>D6584, mass% | Total Glycerin,<br>D6584, mass% | P, D5185, ppm | Na+K,<br>D5185, ppm | Ca+Mg,<br>D5185, ppm |
|-----------|--------------|----------------|------------------|--------------------------------|---------------------------|-------------------------|------------------------------|-----------------------|--------------------------------|--------------------------------|-------------------------|--|--------------------------------|---------------------------------|---------------|---------------------|----------------------|
| 1         | Soy          | 11/10/2005     | 1                |                                | 0                         | 130                     | <0.001                       | 6.9                   | 0.03                           | 0.14                           | 3.12                    | 4.131                                  | 0.002                          | <b>0.274</b>                    | <1            | 5.6                 | 1                    |
| 2         | Soy          | 11/10/2005     | 35               |                                | -1                        | 146                     | <0.001                       | 4.4                   | 0.04                           | 0.57                           | 2.09                    | 4.119                                  | 0.002                          | 0.176                           | <1            | 5                   | 0                    |
| 3         | Soy          | 11/10/2005     | 8                |                                | -1                        | 159                     | <0.001                       | 1.8                   | 0.04                           | 0.47                           | 0.43                    | 4.107                                  | 0.002                          | 0.184                           | <1            | 5                   | 0                    |
| 4         | Soy          | 11/10/2005     | 54               |                                | -1                        | 141                     | <0.001                       | 7.1                   | 0.05                           | 0.31                           | 0.53                    | 4.118                                  | 0.004                          | 0.172                           | <1            | 5.6                 | 0                    |
| 5         | Soy          | 11/11/2005     | 18               |                                | 0                         | 150                     | <0.001                       | 7                     | <0.01                          | 0.57                           | 0.52                    | 4.173                                  | 0.001                          | <b>0.271</b>                    | 1             | 1.8                 | 0                    |
| 6         | Soy          | 11/10/2005     | 86               |                                | 0                         | 166                     | <0.001                       | 16.1                  | 0.03                           | 0.39                           | 1.08                    | 4.27                                   | 0.003                          | <b>0.275</b>                    | 2             | 2                   | 0                    |
| 7         | Soy          | 11/15/2005     | 0                |                                | -1                        | 138                     | <0.001                       | 1.1                   | 0.05                           | 0.14                           | 0.80                    | 4.099                                  | 0.003                          | 0.212                           | <1            | 0                   | 0                    |
| 8         | Soy          | 11/13/2005     | 6                |                                | 0                         | 168                     | 0.02                         | 8.3                   | <b>0.08</b>                    | <0.05                          | 4.26                    | 4.377                                  | <b>0.074</b>                   | <b>0.627</b>                    | <1            | 82                  | 0                    |
| 9         | Soy          | 11/15/2005     | 1                |                                | 0                         | <b>122</b>              | <b>0.03</b>                  | 53.3                  | 0.03                           | 0.58                           | 4.12                    | 4.098                                  | 0.012                          | 0.196                           | <1            | 4                   | 0                    |
| 10        | Soy          | 11/21/2005     | 19               | B99.9,<br>Sure Flo<br>additive | -6                        | <b>93</b>               | <0.001                       | 45.2                  | 0.02                           | 0.07                           | 0.56                    | 3.729                                  | -                              | -                               | <1            | 4.5                 | 0                    |
| 11        | Canola       | 11/29/2005     | U                | Canadian                       | -5                        | 167                     | <0.001                       | 2.2                   | 0.05                           | 0.23                           | -                       | 4.432                                  | 0.009                          | 0.103                           | <1            | 4                   | 0                    |
| 12        | Palm Stearin | 11/29/2005     | U                |                                | 12                        | 151                     | <0.001                       | 0.5                   | 0.02                           | 0.69                           | -                       | 4.672                                  | <0.001                         | 0.121                           | <1            | 2                   | 0                    |
| 13        | Rapeseed     | 12/16/2005     | U                | European                       | -3                        | 165                     | <0.001                       | 2.2                   | 0.04                           | 0.08                           | -                       | 4.480                                  | <0.001                         | 0.161                           | <1            | 3                   | 0                    |
| 14        | Animal fat   | 12/20/2005     | U                |                                | 10                        | 183                     | <0.001                       | 34.7                  | 0.03                           | 0.41                           | -                       | 4.731                                  | <0.001                         | 0.081                           | <1            | 16                  | 0                    |
| 15        | Soy          | 2/10/2006      | 101              |                                | -2                        | <b>58</b>               | <0.001                       | 8.4                   | 0.05                           | <b>0.94</b>                    | -                       | 4.081                                  | 0.003                          | <b>0.418</b>                    | <1            | 10.7                | 1                    |
| 16        | Soy          | 2/10/2006      | 9                |                                | -3                        | 136                     | <0.001                       | 3.1                   | 0.05                           | 0.39                           | -                       | 4.160                                  | <0.001                         | <b>0.280</b>                    | <1            | 6.8                 | 3                    |
| 17        | Animal fat   | 2/7/2006       | 7                |                                | 9                         | 176                     | <0.001                       | 17.2                  | <b>0.06</b>                    | 0.53                           | -                       | 4.712                                  | 0.007                          | 0.201                           | <1            | 2                   | 3                    |
| 18        | Soy          | 2/3/2006       | 33               |                                | -2                        | 161                     | <0.001                       | 0.7                   | 0.04                           | 0.08                           | -                       | 4.099                                  | 0.009                          | 0.215                           | <1            | 5                   | 0                    |
| 19        | Soy          | 2/9/2006       | 9                | Power<br>Service<br>additive   | 0                         | 193                     | <0.001                       | 5.6                   | 0.02                           | 0.11                           | -                       | 4.182                                  | 0.001                          | 0.230                           | <1            | 1                   | 1                    |
| 20        | Animal fat   | 2/20/2006      | U                |                                | 0                         | 172                     | <0.001                       | 0.7                   | 0.02                           | 0.22                           | -                       | 3.991                                  | 0.011                          | 0.076                           | <1            | 6                   | 0                    |

U: Unknown sample age



Table 5. Fuel Property Test Results from B100 Quality Survey (continued)

| Sample ID | Feedstock  | Date Collected | Sample Age, days | Comments | Cloud Point, D250, °C | Flash Point, D93, °C | Sulfated Ash, D874, mass% | Sulfur, D5453, ppm | Carbon Residue, D524, mass% | Acid Number, D664, mg KOH/g | Viscosity, D445, mm <sup>2</sup> /s | Free Glycerin, D6584, mass% | Total Glycerin, D6584, mass% | P, D5185, ppm | Na+K, D5185, ppm | Ca+Mg, D5185, ppm |
|-----------|------------|----------------|------------------|----------|-----------------------|----------------------|---------------------------|--------------------|-----------------------------|-----------------------------|-------------------------------------|-----------------------------|------------------------------|---------------|------------------|-------------------|
| 21        | Soy        | 2/8/2006       | 102              |          | 1                     | 169                  | <0.001                    | 6.4                | 0.05                        | 0.24                        | 4.153                               | 0.008                       | <b>0.325</b>                 | <1            | 1                | 0                 |
| 22        | Soy        | 2/7/2006       | 98               | B99.9    | -5                    | <b>103</b>           | <0.001                    | 74.4               | 0.05                        | 0.19                        | 3.922                               | -                           | -                            | <1            | 0                | 0                 |
| 23        | Soy        | 2/10/2006      | 40               |          | -4                    | 157                  | <b>0.04</b>               | 1.0                | 0.04                        | 0.34                        | 4.061                               | 0.001                       | 0.012                        | <1            | 2                | 0                 |
| 24        | Soy        | 3/16/2006      | 2                |          | 0                     | <b>113</b>           | <0.001                    | 2.1                | <b>0.06</b>                 | 0.22                        | 4.163                               | 0.004                       | 0.219                        | <1            | 1                | 0                 |
| 25        | Soy        | 6/16/2006      | <b>U</b>         |          | -3                    | <b>119</b>           | <0.001                    | 15.2               | 0.03                        | 0.46                        | 4.082                               | 0.004                       | 0.180                        | <1            | 0                | 0                 |
| 26        | Soy        | 6/15/2006      | 0                |          | 3                     | 171                  | <0.001                    | 5.7                | 0.03                        | 0.12                        | 4.115                               | 0.004                       | 0.187                        | <1            | 0                | 0                 |
| 27        | Soy        | 6/6/2006       | 0                |          | 0                     | 169                  | <0.001                    | 5.7                | 0.05                        | 0.46                        | 4.24                                | 0.002                       | 0.151                        | <1            | 0                | 2                 |
| 28        | Soy        | 7/18/06        | 290              | B50      | -1                    | 126                  | <0.001                    | 101.5              | 0.04                        | 0.27                        | 4.085                               | -                           | -                            | 2             | 2                | 0                 |
| 29        | Soy        | 7/18/2006      | 1                |          | 0                     | 138                  | <0.001                    | 0.4                | 0.03                        | 0.13                        | 4.08                                | 0.002                       | 0.095                        | <1            | 3                | 0                 |
| 30        | Soy        | 7/19/2006      | 171              |          | 2                     | 155                  | <0.001                    | 0.8                | 0.03                        | 0.17                        | 2.855                               | 0.012                       | <b>0.242</b>                 | <1            | 0                | 0                 |
| 31        | Unknown    | 7/19/2006      | 2                | B99.9    | 3                     | <b>105</b>           | <0.001                    | 26.8               | 0.03                        | 0.11                        | 4.027                               | -                           | -                            | <1            | 0                | 1                 |
| 32        | Soy        | 7/18/2006      | 43               | B99.9    | 1                     | <b>100</b>           | <0.001                    | 15.3               | 0.03                        | 0.16                        | 4.088                               | 0.004 <sup>a</sup>          | 0.166 <sup>a</sup>           | <1            | 0                | 0                 |
| 33        | Soy        | 7/20/2006      | 0                |          | 0                     | 172                  | <0.001                    | 1.3                | 0.04                        | <b>0.55</b>                 | 4.153                               | 0.016                       | <b>0.251</b>                 | <1            | 0                | 0                 |
| 34        | Soy        | 7/19/2006      | 5                |          | 0                     | 163                  | <0.001                    | 1.4                | 0.03                        | 0.05                        | 4.125                               | 0.014                       | 0.229                        | <1            | 0                | 0                 |
| 35        | Soy        | 7/20/2006      | 1                | B99.9    | -2                    | <b>84</b>            | 0.008                     | 51.1               | 0.04                        | 0.34                        | 4.061                               | 0.014 <sup>a</sup>          | 0.192 <sup>a</sup>           | 10            | 0                | 17                |
| 36        | Soy        | 7/21/2006      | <b>U</b>         | B99.9    | 2                     | 160                  | <0.001                    | 13.6               | 0.03                        | 0.32                        | 4.183                               | 0.009 <sup>a</sup>          | 0.231 <sup>a</sup>           | <1            | 0                | 0                 |
| 37        | Animal fat | 7/19/2006      | 1                |          | -2                    | 161                  | <0.001                    | 5.4                | 0.03                        | 0.07                        | 4.293                               | 0.002                       | 0.041                        | <1            | 0                | 0                 |
| 38        | Soy        | 7/24/2006      |                  |          | -1                    | <b>122</b>           | <0.01                     | 2.7                | 0.03                        | 0.34                        | 4.089                               | 0.002                       | 0.162                        | <1            | 0                | 0                 |
| 39        | Soy        | 7/28/2006      | 12               |          | 0                     | <b>90</b>            | <0.001                    | 0.7                | 0.05                        | 0.26                        | 4.131                               | 0.019                       | <b>0.274</b>                 | <1            | 3                | 2                 |

U: Unknown sample age

a: Estimated (discussed below)

### Kinematic Viscosity

Kinematic viscosity is determined by the D445 method, which measures the time required for a given volume of fuel to flow through a capillary tube viscometer under force of gravity at a fixed temperature. For biodiesel the kinematic viscosity is limited to 1.9-6.0 mm<sup>2</sup>/s. This limit is set to ensure adequate lubrication without causing either leakage in metal-to-metal contact regions or excessively high resistance to flow during cold temperature operation. All samples met this limit, with an average for the set of 4.18 mm<sup>2</sup>/s. One outlier (sample #30) exhibited viscosity of 2.855 mm<sup>2</sup>/s and had a slightly elevated total glycerin content (0.242 mass%, failing to meet the specification), but met all the other property specifications.

### Sulfated Ash

The sulfated ash, measured by D874, determines the amount of ash, soluble metallic soaps, and residual catalyst in the biodiesel. In this test the sample is burned to form ash, which is then treated with sulfuric acid to form metal sulfates. These components can lead to deposits, wear, and filter plugging. Only two of the 37 U.S. samples did not meet the sulfated ash specification of <0.02 mass%. One of the failing samples did not meet multiple properties; the other failed to meet only the D874 sulfated ash content.

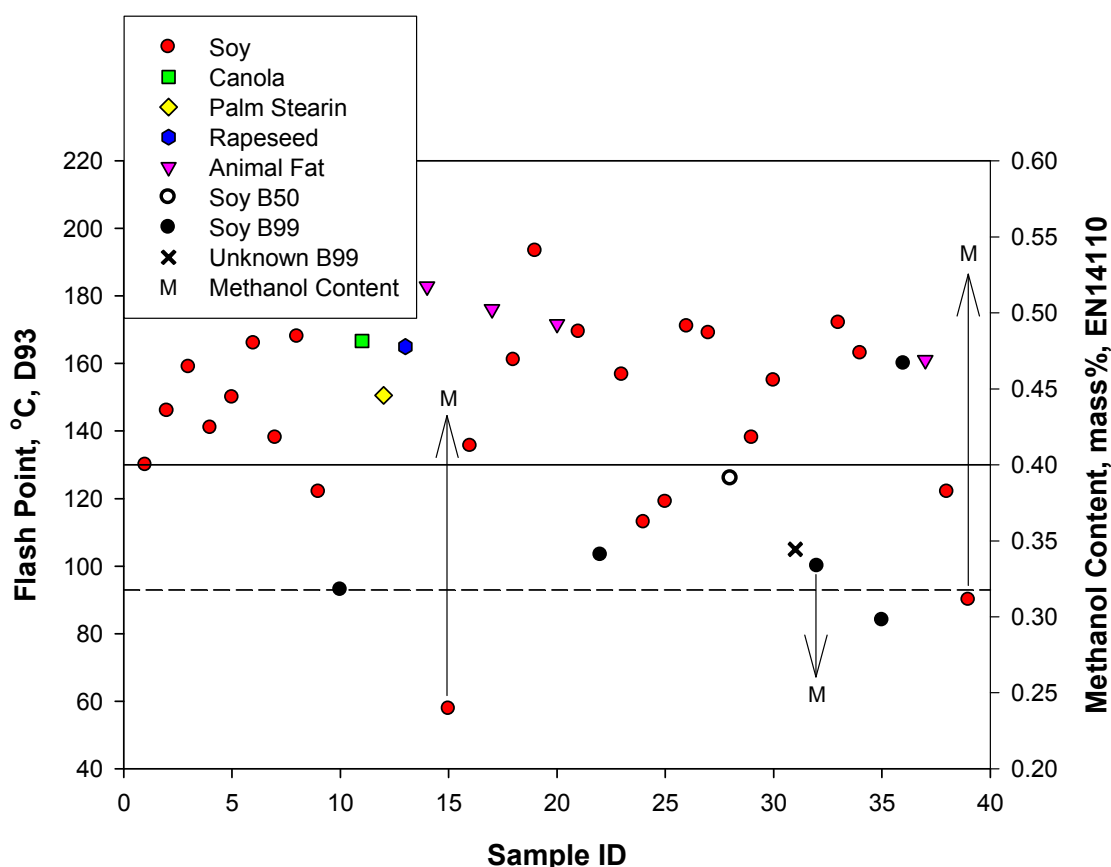


Figure 2. Flash point of B100 quality survey samples. Methanol content has been measured for selected samples and shown on the right hand axis.

### Sulfur Content

The sulfur content of biodiesel produced from virgin oils is expected to be inherently low because these oils naturally contain few sulfur compounds. Recycled cooking oils can

acquire sulfur from the foods fried in them and thus may have significant sulfur content (higher than 15 ppm). In these cases, the sulfur must be removed during production to allow the finished fuel to meet the specifications for on-highway diesel in effect today. However, at the time these samples were collected (before October 2006), 15 ppm sulfur was not required for on-highway diesel fuel. The sulfur content of the sample was not specified when the samples were collected. Thus, any sample meeting the on-highway requirement of 500 ppm in effect at that time is regarded as meeting the specification. Sulfur is determined by method D5453, where the sample is burned in a high temperature oven and the sulfur dioxide formed is quantified by ultraviolet fluorescence.

Figure 3 shows the results obtained for sulfur content of the samples collected in this study. The significant sulfur content of several of the B100 samples is not readily explained, but seems most likely to have been caused by contamination during handling and storage and will need to be addressed as the 15 ppm sulfur limit has come into effect.

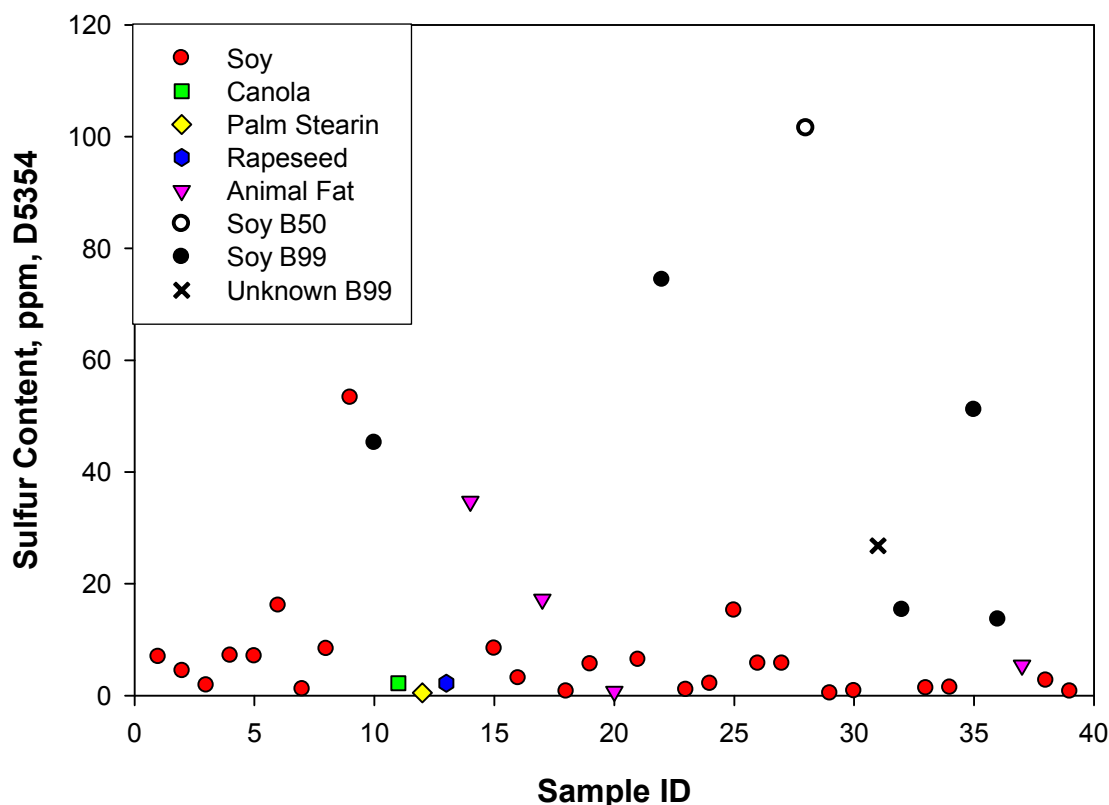


Figure 3. Sulfur content for B100 quality survey samples

### Cloud Point

The cloud point by method D2500, wherein the sample is cooled at a specified rate and the temperature at which crystals first begin to form, is measured. Cloud point is used as a predictor of the low temperature performance of biodiesel in a blend and for the samples included in this study ranged from  $-6^{\circ}\text{C}$  to  $12^{\circ}\text{C}$  (see Figure 4), with the highest cloud point

recorded for palm stearin-derived biodiesel. The average soy biodiesel cloud point was  $-0.8^{\circ}\text{C}$ . The animal fat derived biodiesels had a higher average cloud point,  $4^{\circ}\text{C}$ .

The cold weather operability of biodiesel is influenced by the cloud point, although very little biodiesel is used as B100. The impact of cold weather operability of blends is more important because of the differences between petroleum diesel and biodiesel properties at low temperatures.

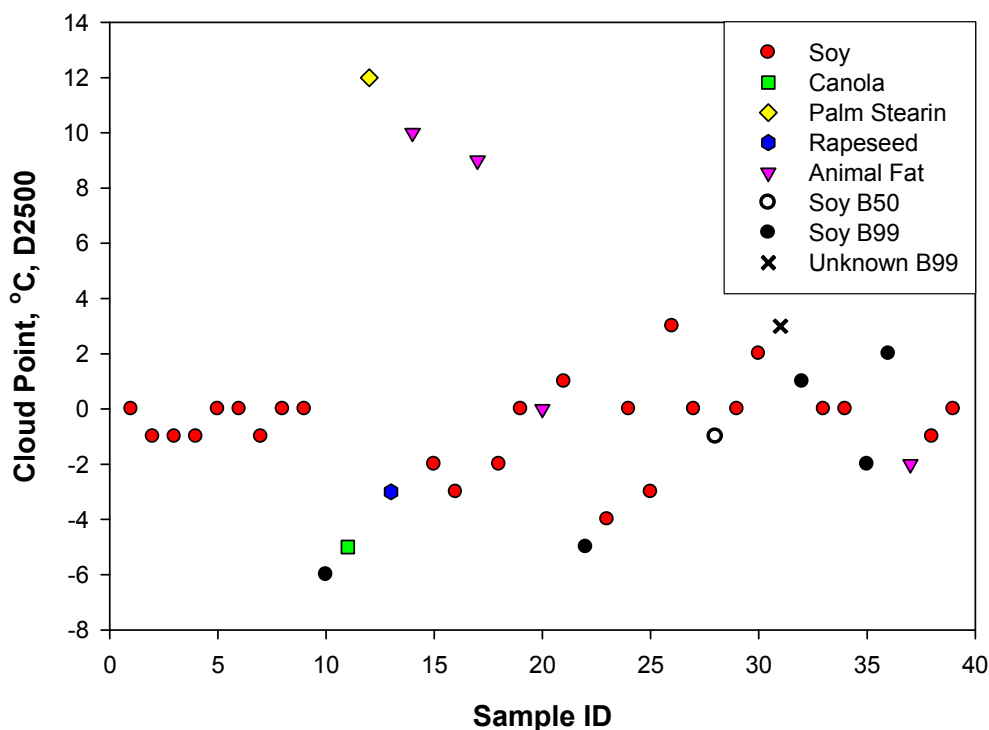


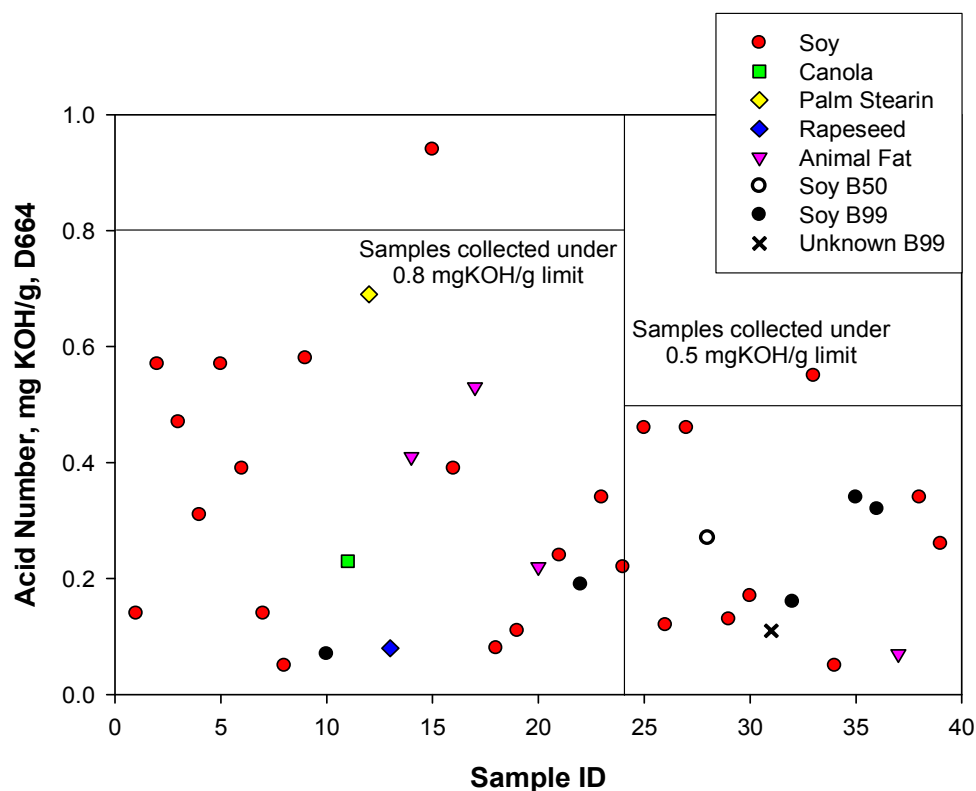
Figure 4. Cloud point of biodiesel quality survey samples

### Carbon Residue

D524, the carbon residue indicates the carbon deposit-forming potential of a fuel in the combustion chamber. It is measured by heating the biodiesel to a high temperature to drive off volatiles and volatile pyrolysis products. A high carbon residue may lead to combustion chamber deposits. Three of the samples failed to meet this specification; two of these also failed on at least one other property.

### Acid Number

Acid number is measured by method D664 using potentiometric titration. Figure 5 shows the results of the acid number determination for the samples. In the left half of the figure, the samples were collected when D6751-03a was in effect with a limit of 0.80 mg KOH/g. On the right half of the figure, the acid number limit was 0.50 mg KOH/g under D6751-06. Only two samples failed to meet the appropriate standard at the time of collection.



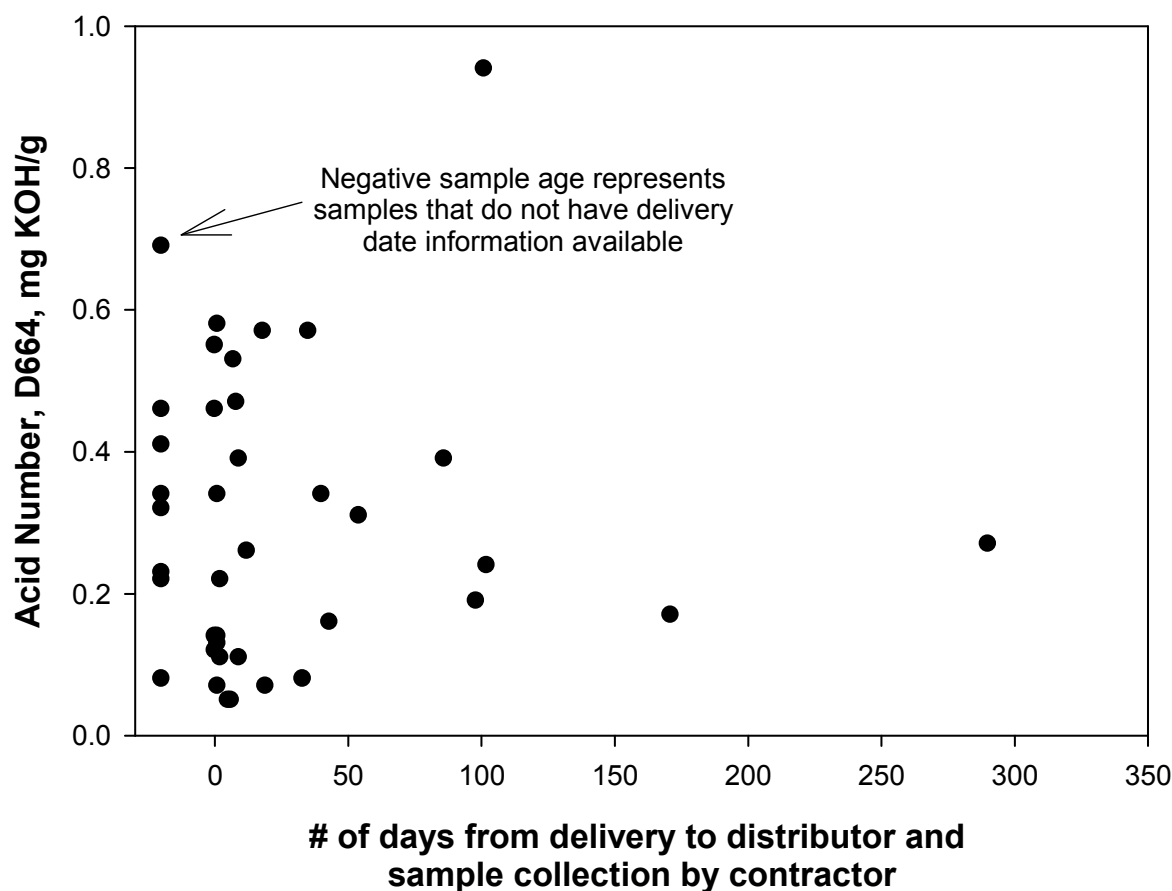
**Figure 5. Acid number for B100 samples**

Acid number is one of the first parameters to increase as biodiesel begins to oxidize and age. During the telephone survey, the distributors were asked when the biodiesel being sampled was delivered. Property analysis was completed within weeks of sample receipt to ensure the accuracy of the analyses. There is no relationship between sample age, as given by the fuel distributor, and acid number (Figure 6). The samples with an unknown age have been shown as a negative value to artificially separate the data in the figure.

### **Free and Total Glycerin**

Samples with high free glycerin can result in fuel separation and materials compatibility issues. High total glycerin, measured as the sum of free glycerin and glycerin in unreacted and partially reacted fats, are high boiling compounds that can lead to deposit formation and fuel filter plugging.

The free and total glycerin are measured with GC per ASTM D6584, which is a significantly more complex test to implement than any of the others required by the D6751 specification. The free hydroxyl groups in the mixture are derivitized with N-methyl N-(trimethylsilyl) trifluoroacetamide (MSTFA). The derivitized sample mixture is separated using GC. The free glycerin is measured directly, and the mono-, di-, and triglycerides are determined with conversion factors to internal standards.

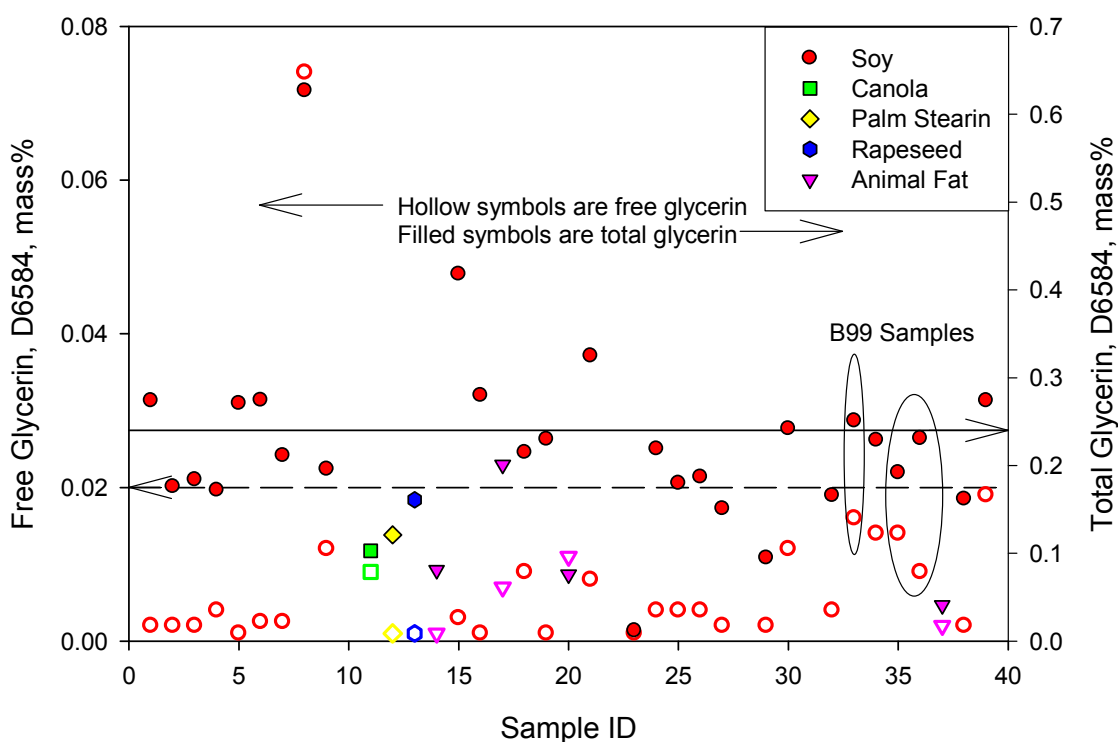


**Figure 6. Relationship between acid number and sample age. Samples with no data on time at distributor are shown as a negative value.**

One of the major shortcomings of the D6584 method is its sensitivity to diesel fuel. Diesel fuel components react differently on the column used in the GC—they make determination of free glycerin very difficult and damage the column. Thus, free and total glycerin cannot be determined in samples with even small amounts of diesel fuel, such as B99.9.

Seven of the 39 samples contained at least small amounts of diesel fuel. Currently, many commercial laboratories do not report free and total glycerin results for biodiesel blends. For the purposes of this study, three of these blends were analyzed by D6584 but, because of the interference of diesel fuel with the free glycerin peak in the chromatogram, the results for free glycerin in these samples are not quantitative.

All but one of the 30 U.S. B100 samples passed the free glycerin specification of <0.02 mass% (Figure 7). For the total glycerin, a much higher percentage of B100 samples (33%) failed to meet the <0.240 mass% limit. Seven of the 11 failing samples also did not meet other quality requirements.



**Figure 7. Free and total glycerin results for biodiesel samples. Hollow symbols are total glycerin using the left axis and the filled symbols are total glycerin using the right axis.**

### **Phosphorus**

In this study phosphorus was determined by D5185, a method that uses inductively coupled plasma-atomic emission spectrometry for elemental analysis. Phosphorus must be limited to protect the particle filters and catalysts that are important components of advanced emission control systems. All samples met the limit of 10 ppm maximum. One sample was right at the limit, containing 10 ppm of phosphorus. This sample (#35) also had high Ca, Zn, and S, indicating possible contamination and/or poor purification after processing.

### **Distillation T90**

Biodiesel, being essentially a pure component, has a distillation “curve” that is very different than a typical petroleum diesel fuel. The temperature at which 90% of the sample has been distilled, the T90, is measured by a reduced pressure distillation with method D1160. The distillation requirement ensures that the fuel is pure biodiesel and has not been contaminated with other high boiling compounds.

The D1160 distillation method was not developed for biodiesel, and appropriate modifications for reproducibility and repeatability have not been developed; however, D1160 was the best method available for distillation at the time D6751 was adopted. ASTM is working to determine whether a simulated distillation, per D2887, is appropriate for biodiesel. The results from this study illustrate the difficulty with the D1160 test method. The first 10 samples of the survey were analyzed for T90 by two test laboratories. Table 6 shows the results from these laboratories for these 10 samples.

**Table 6. T90 Comparison of 10 Biodiesel Samples**

| <b>Sample #</b> | <b>T90, °C, Laboratory A</b> | <b>T90, °C, Laboratory B</b> |
|-----------------|------------------------------|------------------------------|
| 1               | 368                          | 352                          |
| 2               | 365                          | 351                          |
| 3               | 367                          | 351                          |
| 4               | 367                          | 352                          |
| 5               | 367                          | 354                          |
| 6               | 368                          | 355                          |
| 7               | 367                          | 351                          |
| 8               | 366                          | 371                          |
| 9               | 366                          | 355                          |
| 10              | 365                          | 351                          |

In every case but one, Laboratory A recorded higher T90 temperatures than Laboratory B. Laboratory A found the samples to fail this requirement and Laboratory B found the samples to pass. The differences reported between these laboratories show that a more reliable method needs to be considered. Because of this discrepancy in testing results, we do not include T90 in the evaluation of percent of samples passing or failing the standard.

### ***Sodium and Potassium***

The sodium and potassium (Na+K) standard went into effect in May 2006 in the middle of the sample collection period. Sodium and potassium come from the hydroxide catalyst used in the reaction to convert fats and oils into biodiesel. High levels of these metals can lead to the formation of deposits, poison advanced emission control equipment, or act as catalysts in the formation of undesired products.

The samples in this study were analyzed for Na+K using D5185 instead of Universal Oil Products (UOP) 391, which is rarely used. Both methods use inductively coupled plasma atomic emission spectroscopy (ICP-AES). The D5185 method uses the same techniques to introduce and analyze samples as the UOP 391 method and with an appropriate calibration for the low levels of metals in biodiesel, so the results from D5185 reported in this study are reliable and accurate.

The field samples collected before the 5 ppm limit was included in D6751 have a wide range of Na+K contents (Figure 8). In particular, sample #8, with extremely high Na+K (82 ppm) failed multiple other properties and is an example of a fuel with a serious quality problem. With the inclusion of the Na+K specification in D6751 (samples 25–39), all fuels met the <5 ppm standard.



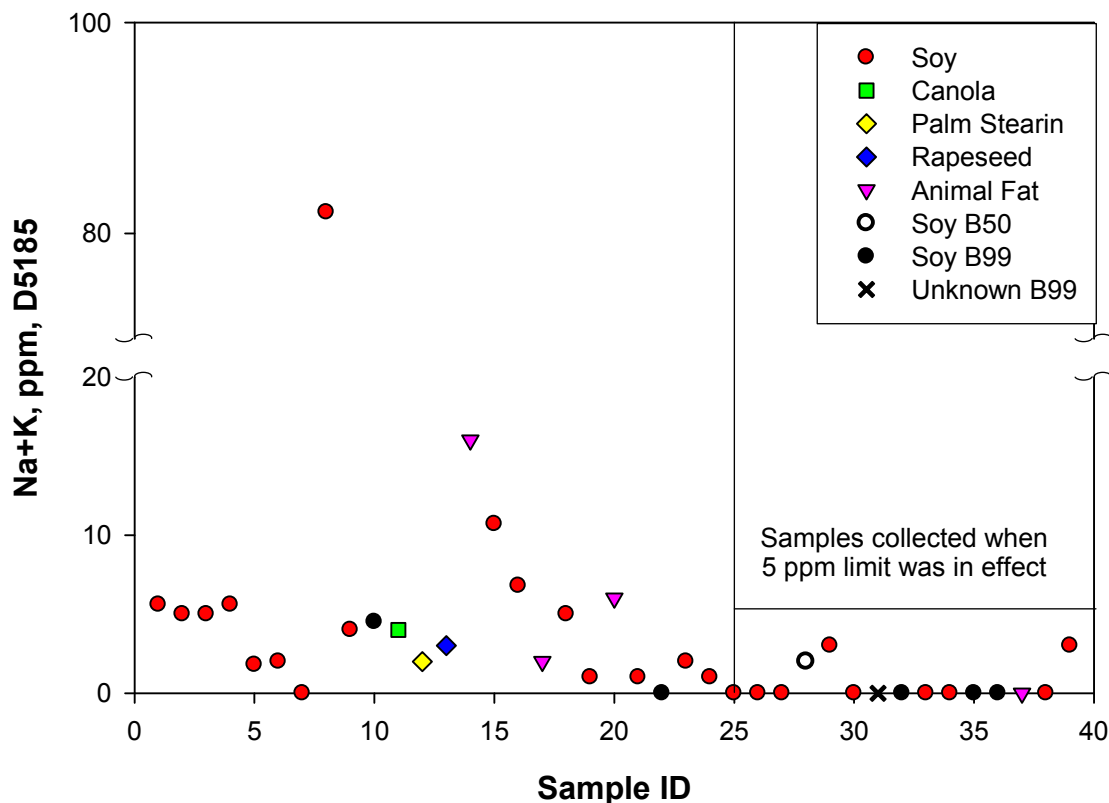


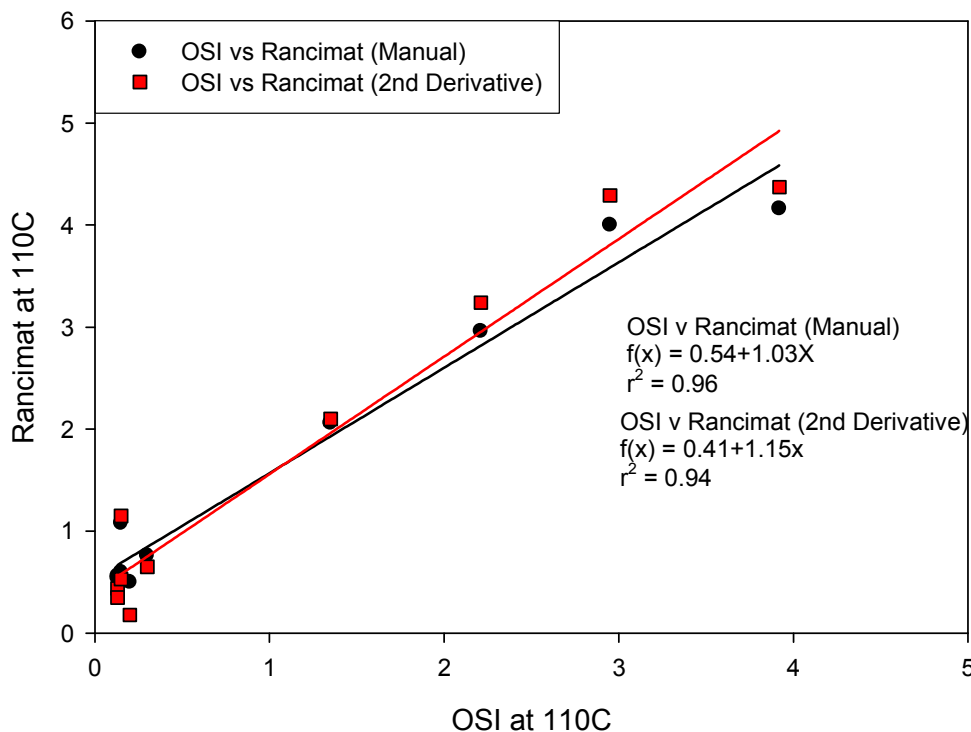
Figure 8. Na+K results from B100 quality survey

## Results for Requirements Recently Included in ASTM D6751

### ***Oxidation Stability***

When the samples were collected, a limit on oxidation stability by Rancimat (EN14112) was not yet included in D6751. Because of a larger stability study already underway,<sup>5</sup> oxidation stability was not measured for all of the samples collected for this study. However, the first 10 samples collected (Samples 1-10) were analyzed for the Rancimat induction period and oil stability index (OSI) at 110°C. The Rancimat and OSI are instruments from two different manufacturers that perform essentially the same experiment. Nevertheless, there has been concern that these instruments will not produce identical results. The Rancimat results are the average of four measurements—two automatic and two manual—and the OSI results are the average of two measurements. The results show slightly shorter induction times with the OSI than with Rancimat, although this might be due to differences in the age of samples when they were tested and slight differences between methods, such as a larger sample size with the OSI.

The range of Rancimat induction period in these samples was 0.43 to 4.26 h and the OSI induction period was 0.13 to 3.92 h (Figure 9). The correlation between OSI and Rancimat is 0.95. At the time of this writing, ASTM D6751-07 includes an oxidation stability standard of 3 h minimum on the Rancimat or OSI test performed at 110°C.



**Figure 9. Rancimat and OSI induction period results for a subset of the B100 quality survey samples**

### ***Calcium and Magnesium***

Calcium and magnesium (Ca+Mg) contamination in biodiesel can also lead to deposits, poison emission control systems, and catalyze side reactions. Calcium and magnesium in biodiesel occur from washing with hard water or contamination from adsorbents used to remove polar compounds during product purification. ASTM D6751-07 currently limits Ca+Mg to a maximum of 5 ppm.

Only one sample from this study did not meet the 5 ppm combined limit for Ca+Mg (Sample #39). This limit was not in effect at the time these samples were collected. This sample was a B99.9 that also failed to meet the phosphorus and flash point specifications. The failure of this sample to meet the specifications suggests possible contamination from other products.

### **Nonspecification Test Results**

In addition to the ASTM D6751 properties that were tested, other properties not part of the specification were included in the analysis. These properties included dissolved water content, particulate contamination, peroxide number, and other metals (Zn, Fe, and Cu). Results from testing are presented in Table 7.

**Table 7. ASTM Test Results for Properties Not Covered in D6751  
(samples in *italics* are biodiesel blends)**

| Sample ID | Water Content<br>D6304, ppm | Particulate Contamination,<br>D6217, mg/L | Peroxide Number,<br>D3703, ppm | Fe, D5185,<br>ppm | Cu, D5185,<br>ppm | Zn, D5185,<br>ppm |
|-----------|-----------------------------|---|--------------------------------|-------------------|-------------------|-------------------|
| 1         | 1238                        | 4.1                                       | 160.                           | <1                | <1                | <1                |
| 2         | 776                         | 2.8                                       | 223                            | <1                | <1                | <1                |
| 3         | 636                         | 0.6                                       | 40                             | <1                | <1                | <1                |
| 4         | 585                         | 5.1                                       | 25                             | <1                | 1                 | <1                |
| 5         | 691                         | 2   | 264                            | <1                | <1                | <1                |
| 6         | 596                         | 2.9                                       | 215                            | <1                | <1                | 1                 |
| 7         | 204                         | 13.9                                      | 64                             | <1                | <1                | <1                |
| 8         | 276                         | 4.4                                       | 64                             | <1                | <1                | <1                |
| 9         | 255                         | 2.5                                       | 127                            | <1                | <1                | <1                |
| 10        | 252                         | 3   | 280                            | <1                | <1                | <1                |
| 11        | 78                          | 3.6                                       | 217                            | <1                | <1                | <1                |
| 12        | 162                         | 6.4                                       | 105                            | <1                | <1                | <1                |
| 13        | 185                         | 6.5                                       | 55                             | <1                | <1                | <1                |
| 14        | 85                          | 93.2                                      | 9                              | <1                | <1                | <1                |
| 15        | 1096                        | 2.1                                       | 199                            | <1                | <1                | 2                 |
| 16        | 1706                        | 5.2                                       | 134                            | <1                | <1                | <1                |
| 17        | 536                         | 6.3                                       | 56                             | 3                 | <1                | <1                |
| 18        | 1031                        | 5.9                                       | 51                             | <1                | <1                | <1                |
| 19        | 846                         | 1.4                                       | 167                            | <1                | <1                | <1                |
| 20        | 416                         | 6.7                                       | 208                            | <1                | <1                | <1                |
| 21        | 604                         | 6.7                                       | 160                            | <1                | <1                | <1                |
| 22        | 1072                        | 1.0                                       | 136                            | <1                | <1                | <1                |
| 23        | 201                         | 3.4                                       | 127                            | <1                | <1                | <1                |
| 24        | 666                         | 1.2                                       | 274                            | <1                | <1                | <1                |
| 25        | 1857                        | 4.4                                       | 64                             | <1                | <1                | <1                |
| 26        | 781                         | 3.6                                       | 50                             | <1                | <1                | <1                |
| 27        | 199                         | 9.4                                       | 87                             | <1                | <1                | <1                |
| 28        | 789                         | 2.8                                       | 364                            | <1                | <1                | <1                |
| 29        | 133                         | 1.2                                       | 61                             | <1                | <1                | <1                |
| 30        | 627                         | 12.0                                      | 296                            | <1                | <1                | <1                |
| 31        | 1148                        | 3.8                                       | 119                            | <1                | <1                | <1                |
| 32        | 1231                        | 18.0                                      | 218                            | <1                | <1                | 1                 |
| 33        | 934                         | 8.8                                       | 438                            | <1                | <1                | <1                |
| 34        | 738                         | 2.2                                       | 206                            | <1                | <1                | <1                |
| 35        | 1031                        | 23.8                                      | 385                            | <1                | <1                | 9                 |
| 36        | 819                         | 1.4                                       | 103                            | <1                | <1                | <1                |
| 37        | 914                         | 0.8                                       | 38                             | <1                | <1                | <1                |
| 38        | 1117                        | 7.4                                       | 82                             | <1                | <1                | <1                |
| 39        | 1375                        | 2.6                                       | 56                             | <1                | <1                | 3                 |

### Water Content

Water in biodiesel can corrode fuel systems and promote degradation and microbial growth. A 500 ppm limit on dissolved water, measured by the Karl Fisher method (D6304), has been proposed. However, because there is currently no limit for water via D6304 in the specifications, there are no controls within the industry to limit the dissolved water in the fuel. Thus, the fuels collected show a wide range of water content (Figure 10), and less than one-third contain <500 ppm dissolved water. An analysis of the time in storage compared to the water content showed no correlation ( $r^2 = 0.005$ , data not shown). Should this requirement be implemented in a future version of D6751, biodiesel producers and blenders will have to take steps to remove dissolved water during production and maintain a relatively dry environment during handling and storage.

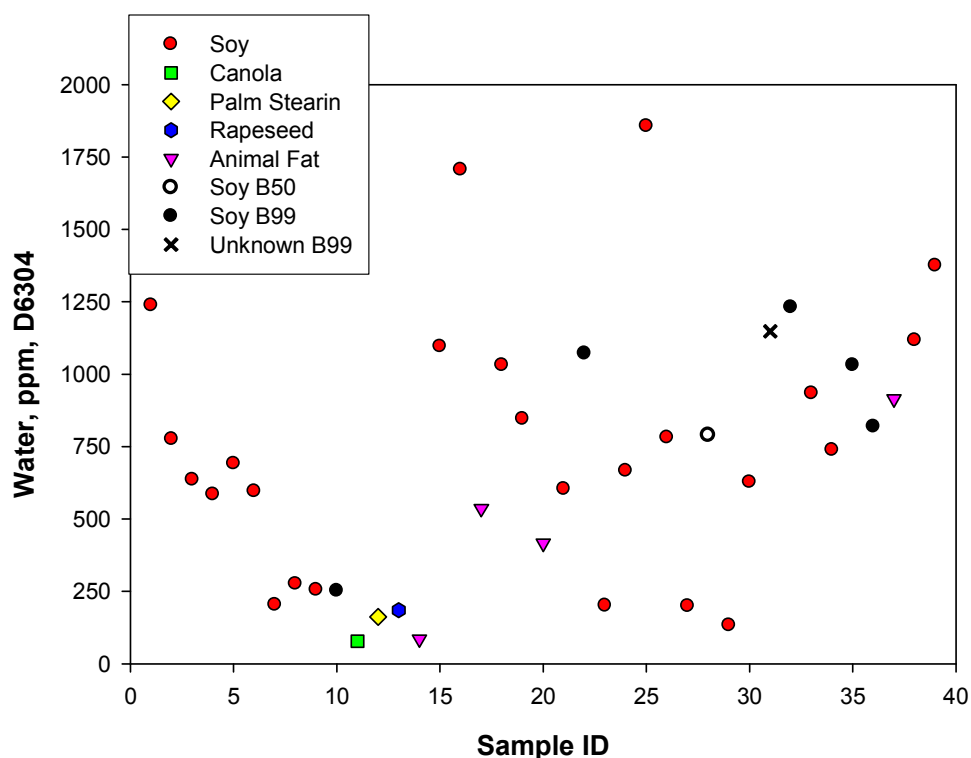


Figure 10. D6304 water content for B100 quality survey samples

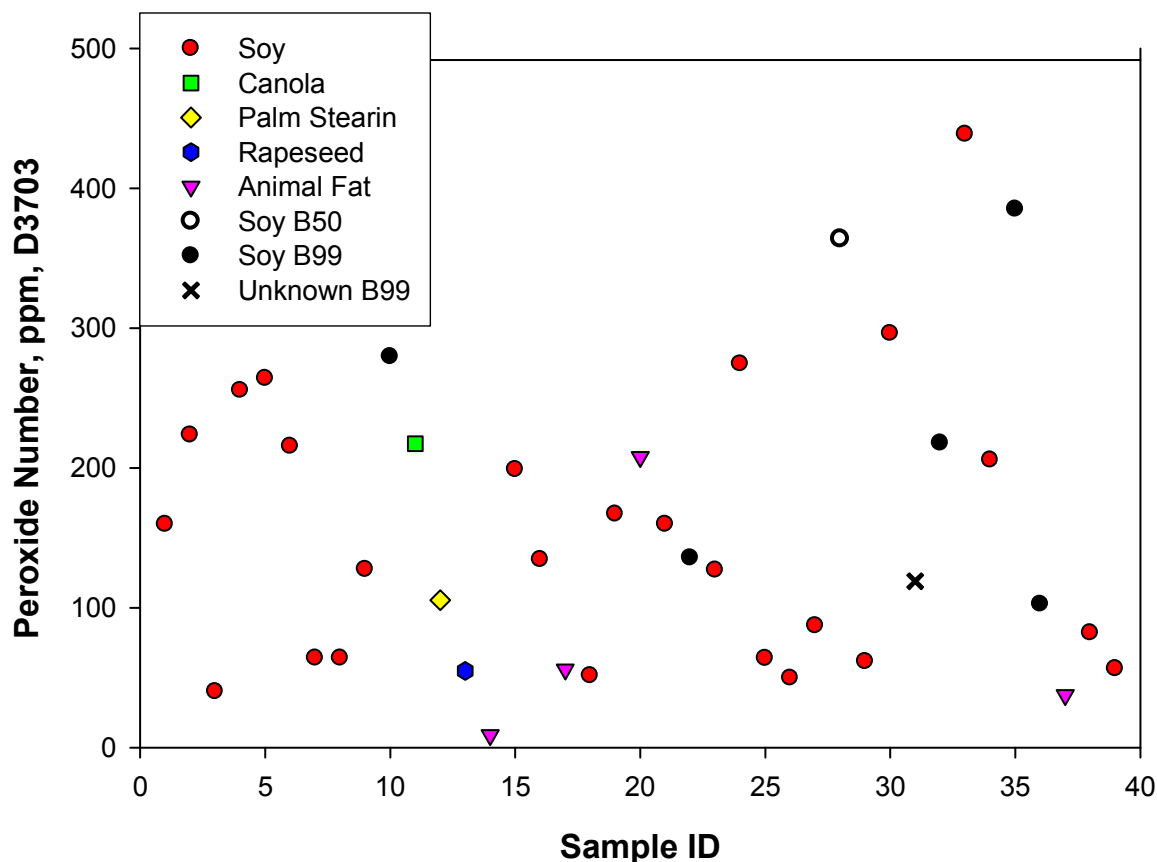
### Particulate Contamination

The particulate contamination was measured via D6217 and is an indicator of the quantity of solids in the biodiesel. The D6217 method measures the mass of particulate (solids) collected on a filter after vacuum filtration at specified conditions. A high mass of particulate can lead to excessive wear of fuel injection equipment because of the mass, type, and number of particles present. All the samples but one passed the proposed limit of 24 ppm. The failing sample had a particulate content almost 4 times greater than the standard and also failed the proposed Na+K limit.

### Peroxide Number

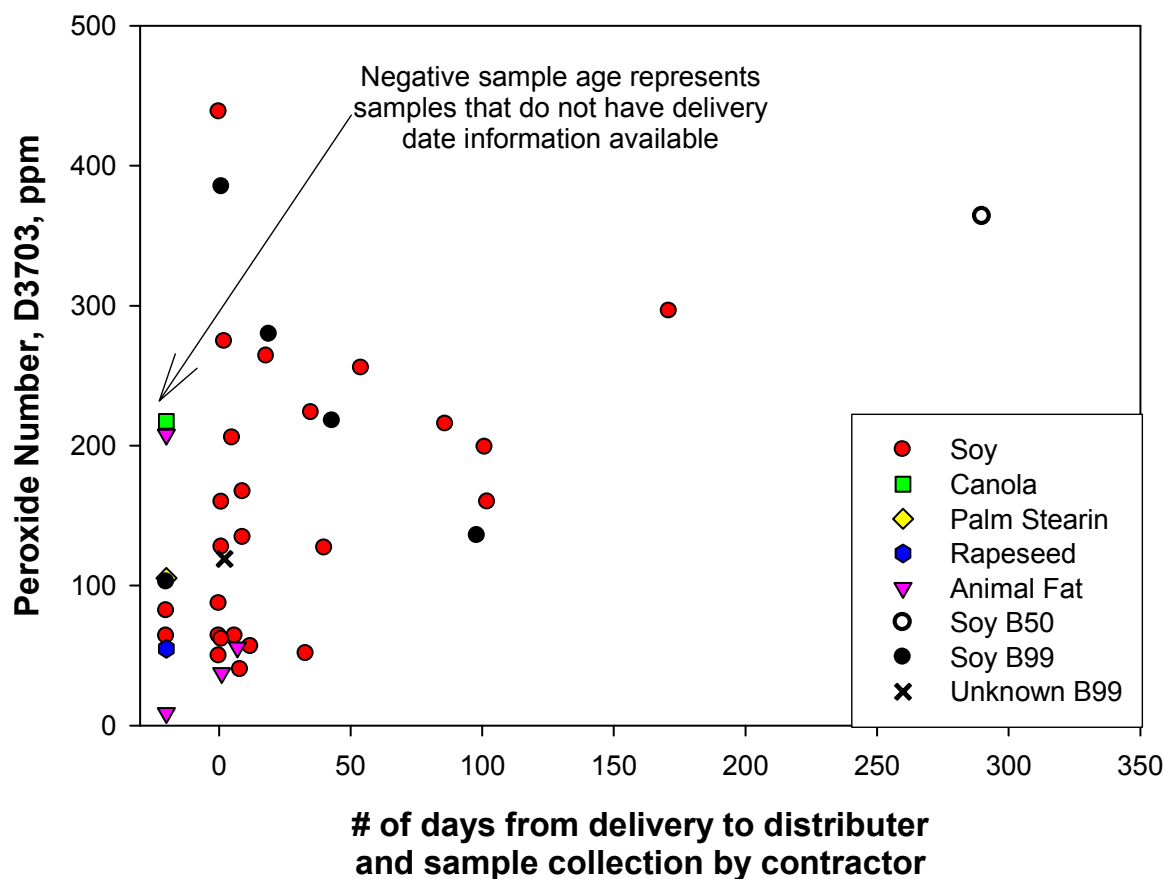
The peroxide content of biodiesel is not limited as part of the quality specifications. The peroxide number is a measure of fuel degradation by oxidation as peroxides are the initial

products formed. These ultimately degrade to acids and aldehydes, or couple to form oligomers that ultimately lead to the formation of gums and deposits. Peroxide is measured through D3703, a method developed for aviation fuels with peroxide contents up to 15 ppm. The D3703 method is therefore not wholly applicable to samples with the high peroxide numbers found in many B100 samples, and an interlaboratory study is underway to determine the applicability of this method to biodiesel. From this study, the average peroxide number for biodiesel is 157 ppm (Figure 11). The B50 sample had a peroxide number of 363 ppm, suggesting that the biodiesel used in the blend had a peroxide number higher than 700 ppm, the highest value observed. When the samples were collected, D6751 had no oxidation stability requirement.



**Figure 11. Peroxide number for B100 quality survey samples**

Figure 12 shows the peroxide number compared to how long the samples were stored at the distributors before collection. There is not a good correlation for time in storage and peroxide number, as measured by D3703. Two of the samples that had been in storage for a long time had high peroxide, but so did several samples that were collected when relatively fresh.



**Figure 12. Relationship between peroxide number and sample age. Note that samples with no data on time at distributor are shown as a negative value.**

### **Other Metals**

In addition to the metals in D6751, the samples were analyzed for Fe, Cu, and Zn. The analysis was performed using the same ICP-AES technique as the other metals. The Fe, Cu, and Zn may come from contamination with lubrication oil or contact with copper or galvanized pipe and containers. These metals can catalyze oxidative degradation of vegetable oils even at below ppm levels. For example, Gordon and Musri report on a rapeseed oil that exhibited a 14.4 h Rancimat induction time (at 100°C). Treating with only 0.05 ppm of  $\text{Cu}^{2+}$  reduced the induction time to 6.4 h.<sup>6</sup> Frankel indicates that as little as 0.01 ppm of Cu can degrade soybean oil.<sup>7</sup> These considerations should also apply to fatty acid methyl esters. The lower detection limit of the method employed here is 1 ppm. All but one sample contained less than 1 ppm of Fe and 1 ppm of Cu. Three samples contained more than 1 ppm of Zn with sample #35, a B99.9 blend exhibiting 9 ppm and having high levels of other metals discussed previously. Notably, this sample also exhibited one of the highest levels of peroxides.

### ***Fatty Acid Methyl Ester Profile***

Each sample was examined by gas chromatography-mass spectrometry (GC-MS) to determine the fatty acid profile. The GC-MS method was developed in-house and details are given in Reference 4. The results from the B100 samples are shown in Table 8. Mass recovery for these samples was only 80%–90%. The chromatographic conditions were such that other components in biodiesel, like the mono-, di-, and triglycerides, were not eluted under these conditions and may contribute to the lost mass. The fatty acid profiles are consistent with the feedstock information collected in the telephone survey and comparison to published literature on the makeup of various feedstocks.<sup>8</sup> The animal fat samples, except #20, are consistent with tallow derived samples. Sample #20, an animal fat derived sample, may be a mixed poultry fat, rather than a straight chicken fat. The fatty acid profile observed in this testing does not exactly match any one poultry fat source (chicken, hen, turkey, or egg).<sup>8</sup>

**Table 8. FAME Analysis of B100 Samples**

| Sample ID | C8:0  | C10:0 | C12:0 | C14:0 | C16:0  | C16:1 (9) | C18:0  | 18:1(9) | C18:2 (9,12) | C18:3 (9,12,15) | C20:0 | C20:1 (11) | C22:0 | C22:1 (13) | C24:0 |
|-----------|-------|-------|-------|-------|--------|-----------|--------|---------|--------------|-----------------|-------|------------|-------|------------|-------|
| 11        | 0.00% | 0.00% | 0.00% | 0.04% | 4.44%  | 0.15%     | 1.51%  | 46.08%  | 22.38%       | 7.06%           | 0.45% | 0.99%      | 0.26% | 0.22%      | 0.08% |
| 12        | 0.00% | 0.08% | 0.11% | 1.27% | 21.94% | 1.89%     | 11.77% | 33.55%  | 10.88%       | 0.85%           | 0.14% | 0.63%      | 0.00% | 0.00%      | 0.00% |
| 13        | 0.00% | 0.00% | 0.00% | 0.00% | 3.08%  | 0.13%     | 1.37%  | 47.68%  | 19.61%       | 8.79%           | 0.49% | 1.13%      | 0.28% | 0.00%      | 0.09% |
| 14        | 0.00% | 0.00% | 0.00% | 0.00% | 15.54% | 0.00%     | 13.34% | 48.01%  | 9.00%        | 0.60%           | 0.86% | 0.12%      | 0.10% | 0.00%      | 0.08% |
| 15        | 0.00% | 0.00% | 0.00% | 0.06% | 9.35%  | 0.00%     | 3.89%  | 19.14%  | 40.32%       | 5.39%           | 0.26% | 0.12%      | 0.24% | 0.00%      | 0.05% |
| 16        | 0.00% | 0.00% | 0.00% | 0.06% | 10.22% | 0.00%     | 3.74%  | 21.89%  | 44.67%       | 5.50%           | 0.27% | 0.15%      | 0.28% | 0.00%      | 0.08% |
| 17        | 0.00% | 0.06% | 0.11% | 1.23% | 20.91% | 2.03%     | 11.11% | 33.59%  | 10.94%       | 1.17%           | 0.15% | 0.57%      | 0.00% | 0.00%      | 0.00% |
| 18        | 0.00% | 0.00% | 0.00% | 0.06% | 10.35% | 0.00%     | 3.87%  | 20.70%  | 44.95%       | 5.54%           | 0.27% | 0.14%      | 0.27% | 0.00%      | 0.06% |
| 19        | 0.00% | 0.00% | 0.00% | 0.06% | 9.86%  | 0.00%     | 3.77%  | 20.56%  | 43.24%       | 5.70%           | 0.26% | 0.14%      | 0.27% | 0.00%      | 0.07% |
| 20        | 0.00% | 0.00% | 0.00% | 0.06% | 10.36% | 0.00%     | 4.04%  | 21.06%  | 43.50%       | 5.76%           | 0.24% | 0.12%      | 0.09% | 0.00%      | 0.00% |
| 21        | 0.00% | 0.00% | 0.00% | 0.06% | 10.13% | 0.00%     | 3.99%  | 18.83%  | 43.99%       | 7.24%           | 0.26% | 0.11%      | 0.25% | 0.00%      | 0.05% |
| 22        | 0.00% | 0.00% | 0.00% | 0.05% | 8.26%  | 0.00%     | 3.16%  | 16.49%  | 38.33%       | 5.49%           | 0.21% | 0.11%      | 0.21% | 0.00%      | 0.04% |
| 23        | 0.15% | 0.08% | 0.13% | 0.23% | 8.26%  | 0.00%     | 4.28%  | 21.70%  | 42.74%       | 2.04%           | 0.23% | 0.13%      | 0.11% | 0.00%      | 0.00% |
| 24        | 0.00% | 0.00% | 0.00% | 0.06% | 10.31% | 0.00%     | 3.98%  | 20.18%  | 45.03%       | 7.00%           | 0.26% | 0.12%      | 0.23% | 0.00%      | 0.00% |
| 25        | 0.00% | 0.00% | 0.00% | 0.05% | 9.89%  | 0.00%     | 4.01%  | 20.32%  | 44.38%       | 6.15%           | 0.26% | 0.12%      | 0.24% | 0.00%      | 0.00% |
| 26        | 0.00% | 0.00% | 0.00% | 0.06% | 10.38% | 0.00%     | 3.96%  | 20.78%  | 45.55%       | 5.82%           | 0.29% | 0.15%      | 0.29% | 0.00%      | 0.07% |
| 27        | 0.00% | 0.00% | 0.03% | 0.23% | 11.92% | 0.57%     | 4.46%  | 23.31%  | 40.95%       | 5.97%           | 0.23% | 0.14%      | 0.20% | 0.00%      | 0.04% |
| 28        | 0.00% | 0.00% | 0.00% | 0.06% | 9.66%  | 0.00%     | 3.71%  | 18.87%  | 42.84%       | 6.09%           | 0.25% | 0.12%      | 0.24% | 0.00%      | 0.05% |
| 29        | 0.00% | 0.00% | 0.00% | 0.05% | 10.10% | 0.00%     | 3.89%  | 20.90%  | 44.75%       | 7.03%           | 0.26% | 0.11%      | 0.24% | 0.00%      | 0.00% |
| 30        | 0.00% | 0.00% | 0.00% | 0.05% | 10.30% | 0.00%     | 3.94%  | 20.99%  | 45.39%       | 6.65%           | 0.26% | 0.12%      | 0.25% | 0.00%      | 0.05% |
| 31        | 0.00% | 0.00% | 0.00% | 0.05% | 9.57%  | 0.00%     | 3.68%  | 18.75%  | 43.46%       | 5.06%           | 0.25% | 0.13%      | 0.25% | 0.00%      | 0.06% |
| 32        | 0.00% | 0.00% | 0.00% | 0.06% | 10.25% | 0.00%     | 3.80%  | 19.91%  | 44.69%       | 5.77%           | 0.27% | 0.14%      | 0.27% | 0.00%      | 0.06% |
| 33        | 0.00% | 0.00% | 0.00% | 0.06% | 10.54% | 0.00%     | 4.08%  | 21.25%  | 45.95%       | 6.37%           | 0.27% | 0.13%      | 0.26% | 0.00%      | 0.06% |
| 34        | 0.00% | 0.00% | 0.00% | 0.05% | 10.14% | 0.00%     | 4.30%  | 20.04%  | 45.23%       | 5.57%           | 0.30% | 0.13%      | 0.29% | 0.00%      | 0.06% |
| 35        | 0.00% | 0.00% | 0.00% | 0.05% | 9.44%  | 0.00%     | 3.59%  | 18.78%  | 42.12%       | 6.07%           | 0.23% | 0.12%      | 0.22% | 0.00%      | 0.04% |
| 36        | 0.00% | 0.00% | 0.00% | 0.06% | 9.93%  | 0.00%     | 3.82%  | 19.07%  | 43.18%       | 6.59%           | 0.25% | 0.11%      | 0.24% | 0.00%      | 0.05% |
| 37        | 0.00% | 0.00% | 0.13% | 0.61% | 20.86% | 6.13%     | 4.79%  | 37.37%  | 19.08%       | 1.25%           | 0.04% | 0.24%      | 0.00% | 0.00%      | 0.00% |
| 38        | 0.00% | 0.00% | 0.00% | 0.05% | 10.05% | 0.00%     | 4.04%  | 21.12%  | 45.19%       | 6.02%           | 0.26% | 0.12%      | 0.24% | 0.00%      | 0.06% |
| 39        | 0.00% | 0.00% | 0.00% | 0.06% | 10.45% | 0.00%     | 4.03%  | 20.78%  | 45.42%       | 6.16%           | 0.27% | 0.13%      | 0.25% | 0.00%      | 0.06% |



## Summary and Conclusions

In the marketplace, where biodiesel is an emerging fuel, fuels must meet or exceed the prevailing fuel property specifications. Ensuring that biodiesel is of adequate quality is necessary both to comply with federal law (fuel registration and tax credit requirements) and to provide consumers with the reliability that they have come to expect from petroleum products and modern vehicles. The 59% failure rate observed for this study shows significant and serious quality issues at the time these samples were collected. The primary failures were for total glycerin (33%) and flash point (30%). Even considering that the failure rate observed in this study applies only to the samples we collected and is not based on production volume, the results are still alarming. The 2004 study, conducted when biodiesel production was estimated at 25 million gallons, showed only a 15% failure rate.<sup>4</sup>

Ensuring biodiesel quality is critical for the future growth of the biodiesel market. To that end, the National Biodiesel Board has begun to stress fuel quality and has released several informational documents to assist its members in this area.<sup>9</sup>

With the increase of B99.9 blends in the marketplace to take advantage of the tax credit available, the ability to ensure the B100 quality before blending becomes even more important. In particular, with D6584 (Test Method for Determination of Free and Total Glycerin in B-100 Biodiesel Methyl Esters by Chromatography) not being applicable to fuels with diesel content, even at 0.1%, the measurement of glycerin content is clearly an area for concern. The test methods will need to be adapted or new methods developed to allow for determination of glycerin content in B99.9 blended fuels.

## References

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- <sup>8</sup> *Fats and Oils Handbook*, AOCS Press, 1998.
- <sup>9</sup> National Biodiesel Board Web site, Fuel Quality Enforcement Guide, accessed on March 27, 2007, [www.biodiesel.org/resources/fuelqualityguide/](http://www.biodiesel.org/resources/fuelqualityguide/).

## Appendix

To investigate the impact of small amounts of diesel fuel on the flash point of biodiesel blends, a typical No. 2 diesel fuel and biodiesel were used to produce B99 and B99.9 blends. These blends were analyzed for flash point using D93. The results are shown in the table. As the data illustrates, the presence of small amounts of diesel fuel in biodiesel (such as a B99 or B99.9 blend), does not impact the flash point significantly.

| <b>Fuel</b> | <b>Flash point, C</b> |
|-------------|-----------------------|
| Diesel fuel | 72                    |
| B100        | 124                   |
| B99.9       | 124                   |
| B99         | 124                   |

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|---|------------------------------------|-------------------------------------|---|----------------------------|--|--|
| <b>1. REPORT DATE (DD-MM-YYYY)</b><br>May 2007  |                                    |                                     | <b>2. REPORT TYPE</b><br>Milestone Report |                            | <b>3. DATES COVERED (From - To)</b>                                  |  |
| <b>4. TITLE AND SUBTITLE</b><br>2006 B100 Quality Survey Results: Milestone Report  |                                    |                                     |   |                            | <b>5a. CONTRACT NUMBER</b><br>DE-AC36-99-GO10337                     |  |
|   |                                    |                                     |   |                            | <b>5b. GRANT NUMBER</b>  |  |
|   |                                    |                                     |   |                            | <b>5c. PROGRAM ELEMENT NUMBER</b>                                    |  |
| <b>6. AUTHOR(S)</b><br>T.L. Alleman, R.L. McCormick, and S. Deutch  |                                    |                                     |   |                            | <b>5d. PROJECT NUMBER</b><br>NREL/TP-540-41549                       |  |
|   |                                    |                                     |   |                            | <b>5e. TASK NUMBER</b><br>FC079400                                   |  |
|   |                                    |                                     |   |                            | <b>5f. WORK UNIT NUMBER</b>  |  |
| <b>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</b><br>National Renewable Energy Laboratory<br>1617 Cole Blvd.<br>Golden, CO 80401-3393   |                                    |                                     |   |                            | <b>8. PERFORMING ORGANIZATION REPORT NUMBER</b><br>NREL/RP-540-41549 |  |
| <b>9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)</b>  |                                    |                                     |   |                            | <b>10. SPONSOR/MONITOR'S ACRONYM(S)</b><br>NREL                      |  |
|   |                                    |                                     |   |                            | <b>11. SPONSORING/MONITORING AGENCY REPORT NUMBER</b>                |  |
| <b>12. DISTRIBUTION AVAILABILITY STATEMENT</b><br>National Technical Information Service<br>U.S. Department of Commerce<br>5285 Port Royal Road<br>Springfield, VA 22161  |                                    |                                     |   |                            |  |  |
| <b>13. SUPPLEMENTARY NOTES</b>  |                                    |                                     |   |                            |  |  |
| <b>14. ABSTRACT (Maximum 200 Words)</b><br>In 2006, the National Renewable Energy Laboratory conducted a nationwide quality survey of pure biodiesel (B100) intended to be used as a blendstock. The study collected random samples throughout the United States and analyzed them for quality against the current and proposed ASTM D6751 fuel quality specifications. |                                    |                                     |   |                            |  |  |
| <b>15. SUBJECT TERMS</b><br>biodiesel; B100; quality survey; blendstock   |                                    |                                     |   |                            |  |  |
| <b>16. SECURITY CLASSIFICATION OF:</b>  |                                    |                                     | <b>17. LIMITATION OF ABSTRACT</b><br>UL   | <b>18. NUMBER OF PAGES</b> | <b>19a. NAME OF RESPONSIBLE PERSON</b>                               |  |
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