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*National Renewable Energy Laboratory*

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

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## List of Abbreviations and Acronyms

ASTM	ASTM International
B100	neat biodiesel
°C	degrees Celsius
°C/min	degrees Celsius per minute
C <sub>XX:Y</sub>	XX is the number of carbon atoms, and Y is the degree of unsaturation in either fatty acid methyl esters or monoglycerides
Ca+Mg	calcium plus magnesium
CP	cloud point
CSFT	cold soak filterability test
FAME	fatty acid methyl esters
GC	gas chromatograph
hr	hour
LC	liquid chromatograph
mgKOH/g	milligrams potassium hydroxide per gram
SMG	saturated monoglycerides
µL	microliters
MAG	monoglycerides
max	maximum
min	minutes
Na+K	sodium plus potassium
NREL	National Renewable Energy Laboratory
psi	pounds per square inch
ppm	parts per million
r	interlaboratory precision in an ASTM test method
sec	seconds
TQD	triple quadrupole detector
UPLC	ultra-high pressure liquid chromatography
vol%	percent by volume
wt%	percent by mass (weight)

## Executive Summary

Samples of B100 from producers and terminals in 2011 were tested for critical properties: free and total glycerin, flash point, cloud point, oxidation stability, cold soak filterability, and metals. Failure rates for cold soak filterability and oxidation stability were below 5%. A single flash point failure due to excess methanol content was observed. One sample failed multiple properties, including oxidation stability and metal content. Overall, 95% of the samples surveyed met biodiesel specification ASTM 6751. Metals analysis showed calcium above the method detection limit in nearly half the samples otherwise meeting the specification. Feedstock analysis revealed half of the biodiesel was produced from soy and half from mixed feedstocks. The B100 saturated fatty acid methyl ester concentrations were compared to the saturated monoglyceride concentration as a percent of total monoglycerides. Real-world correlation was very good. A novel liquid chromatography method for measurement of monoglycerides was developed and compared to ASTM method results. Agreement was good, particularly for total monoglycerides and unsaturated monoglycerides. Due to the very low levels of saturated monoglycerides measured, the two methods had more variability; the correlation was still acceptable.

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# 1 Introduction

A significant incentive for biodiesel production in the United States came in 2004 as part of the American Jobs Creation Act, which established a tax incentive for biodiesel production [1]. The industry grew from 27.9 million gallons in 2004 to 678 million gallons in 2008, dropping to 515 million gallons in 2009 when the tax credit was allowed to expire [2]. The tax credit was reinstated for 2011, coupled with volume mandates in the Renewable Fuels Standard [3], and U.S. production increased to 967 million gallons of B100 in 2011 and 780 million gallons through September 2012, the last numbers available [2].

To ensure the quality of B100, ASTM International (ASTM) published the first B100 quality specification, D6751, in 2002 [4]. Although ASTM does not enforce fuel quality, its specifications are frequently adopted by state and local agencies to ensure acceptable quality and promote commerce. Between 2002 and January 2013, the D6751 specification for biodiesel has undergone 17 updates to continually improve biodiesel quality.

The most recent update to D6751 was the addition of a No. 1-B grade for biodiesel in an effort to eliminate cold weather operability problems experienced with biodiesel blends. The No. 1-B grade limits total monoglycerides (MAGs) to 0.40 weight percent (wt%) maximum and requires a cold soak filterability test (CSFT) of 200 seconds (sec) or less, while all other properties are unchanged. Biodiesel producers have the option of meeting the No. 1-B grade biodiesel standard limits or the less stringent standard limits for the D6751 No. 2-B grade.

The rapid growth in the market has not been problem free, as various surveys by the National Renewable Energy Laboratory (NREL) and other groups have shown quality issues over the years [5-10]. In the first B100 quality survey, in 2004, NREL sampled B100 directly from terminals around the United States, compared the samples to the then current D6751 specification, and found 85% of the samples were on-specification [5]. Major conclusions from this study were that the terminals relied almost exclusively on the biodiesel producer to ensure product quality, oxidation stability (measured by Rancimat), though not part of the specification, was typically below 1 hour, and samples not meeting the D6751 specification typically failed several properties.

A follow-up B100 survey was conducted at U.S. terminals in 2006 [6]. In this survey, 59% of the samples collected did not meet the D6751 specification. Samples most often exceeded the total glycerin (33% failure rate) or flash point (30% failure rate) requirements. Although D6751 did not include an oxidation stability specification at the time of the survey, 10 samples were selected for testing. The average oxidation stability was 1.6 hours for these samples.

In 2008, NREL published a B100 production volume-weighted quality survey based on new samples collected in 2007 [7]. NREL and the National Biodiesel Board collaborated to bin producers based on actual production volumes. The biodiesel market was estimated at 394 million gallons at the time of the survey. Samples were collected from 52% of the producers in the United States at that time and represented nearly 70% of the total biodiesel production in the United States, or approximately 287 million gallons. In this survey, samples from large producers met the D6751 specifications nearly 95% of the time. Samples from small and medium-size producers had more difficulties meeting the specification. Although failure rates

were high for oxidation stability in this survey and the small producers were disproportionately out of compliance, the volume-weighted failure rate was less than 10 million gallons. Failures on other properties were estimated at less than 2 million gallons.

The current study sampled B100 from both producers and multiple terminals around the United States. A sample was requested from each of the top 50 producers and every BQ-9000 (the biodiesel industry voluntary quality program) producer [11]. Terminal samples were collected from the East and West coasts, the Rocky Mountain region, and the Midwest. Fifty-three samples were collected directly from producers, and 14 samples were collected from terminals.

## 2 Experimental

Every sample was tested for critical operability properties using ASTM methods. Table 1 lists the properties, methods, and applicable D6751 limits.

**Table 1. Properties Tested for B100 Samples, Including Method and Applicable D6751 Limit**

Property	Method <sup>a</sup>	D6751 Limit	D6751 No. 1-B grade requirements
Flash point, °C	D93	93, min	Same
Alcohol control, meet one of the following:			Same
Methanol content, wt%	EN 14110	0.2, max	
Flash point, °C	D93	130, min	
Acid number, mgKOH/g	D664	0.50, max	Same
CSFT, sec	D7501	360, max <sup>b</sup>	200, max
Free glycerin, wt%	D6584	0.020, max	Same
Total glycerin, wt%	D6584	0.240, max	Same
Monoglycerides, wt%			0.40, max
Diglycerides, wt%	D6584	Report <sup>c</sup>	Report
Triglycerides, wt%			Report
SMG, wt%	Modified D6584	None	None
	In-house UPLC		None
CP, °C	D5773 <sup>d</sup>	Report	Report
Calcium and magnesium, ppm	D7111 <sup>e</sup>	5, max	Same
Sodium and potassium, ppm	D7111 <sup>e</sup>	5, max	Same
Oxidation stability, hrs	EN15751	3, min	Same
FAME profile	In-house	None	None

<sup>a</sup> Methods are ASTM unless otherwise noted.

<sup>b</sup> B100 blended in diesel fuel for an end use of -12°C or lower shall meet a 200-sec limit.

<sup>c</sup> Although glycerin species are not required to be reported in D6751, method D6584 reports the values for these species.

<sup>d</sup> D2500 is the referee cloud point (CP) method.

<sup>e</sup> EN14538 is the referee method for metals.

*Flash point and alcohol control*—The flash point is the temperature where the vapor above the fuel reaches the lower flammability limit and will ignite under a given set of test conditions specified in ASTM D93. Samples with a flash point below 130°C were tested for methanol content by EN14110.

*Acid number*—The acid number was measured using a Metrohm 809 Titrand via the ASTM D664 method.

*CSFT*—The CSFT followed the D7501 method. Sample preheating and cooling in the CSFT method was performed in a Test Equity 1000 series environmental chamber with temperature precision to  $\pm 0.1^\circ\text{C}$ . After cold soak, the samples were heated to room temperature using a circulating water bath with a 50:50 mixture of water and ethylene glycol.

*Free and total glycerin and speciated glycerides*—The D6584 method, as written, allows for a wide variety of chromatographic conditions. In this study, a Restek MXT Biodiesel column (14 m x 0.53  $\mu\text{m}$  x 0.16  $\mu\text{m}$ ) with an integrated guard column was used. The method was run with helium as a carrier gas at 3 mL/min in constant flow mode. The temperature program followed the D6584 method. 1,2,4-Butanetriol (Supelco 44896-U) and tricaprins (Supelco 44897-U) were used as internal standards. A five-point calibration curve was generated using standards purchased from Supelco (parts 44899-U, 44914-U, 44915-U, 44916-U, 44917-U), with an  $r^2$  of 0.999.

The current emphasis on MAGs in biodiesel led to the modification of the D6584 method to quantify saturated monoglycerides (SMGs) in addition to total monoglycerides. The D6584 method does not resolve the unsaturated MAGs (USMGs), which co-elute as a single peak. The SMG analysis was limited to monopalmitin (C16:0) and monostearin (C18:0), which were assumed to be the only SMGs in these samples for the gas chromatograph (GC) analysis. Standards of C16:0 and C18:0 were purchased from Nu-Chek Prep, Elysian, Minnesota (parts N-16-M and N-18-M, respectively), prepared at the desired concentrations in heptane, and derivatized following the D6584 method procedure. A three-point calibration curve was generated, with a linearity of 0.999.

*Monoglycerides by Liquid Chromatography*—With the increased industry scrutiny on monoglycerides, a novel method for MAG determination was developed based on liquid chromatography (LC). The analysis was performed on a Waters Acquity ultra-high performance liquid chromatograph (UPLC) with a triple quad detector (TQD). The TQD was used to monitor the parent ions from the target MAGs. The UPLC-TQD analysis was based on a biodiesel analytical method developed by Waters Corporation [12]. One advantage to this novel method is the separation of all MAGs present in the biodiesel sample. The D6584 method separates the SMGs but is unable to separate USMGs. The UPLC/TQD method was able to achieve adequate resolution of these compounds.

Prior to analysis on the UPLC-TQD, the MAGs were removed from the biodiesel through solid phase extraction. This step allowed for an increased concentration of monoglycerides. The solid phase extraction cartridges selected for this work were Waters Sep Pak Silica [3 cc] Vac gel columns, selected for their affinity for polar components. Yang and coworkers [13] used a similar procedure to determine the polar impurities in biodiesel by GC-mass spectrometry. Each cartridge was preconditioned with 15 mL of reagent grade n-hexane prior to sample loading. Approximately 200 mg of sample and 50  $\mu\text{L}$  of monotridecanoin, C13:1 (Nu-Chek part U-35M, Elysian, Minnesota), as an internal standard, were added. The cartridge was rinsed with 20 mL methylene chloride to remove the fatty acid methyl ester (FAME) portion followed by 10 mL of methanol to remove the polar components. The polar fraction was dried under nitrogen gas and

reconstituted with 2 mL of methanol. Samples were diluted 1:100 or 1:200 to target a MAG concentration of 10 µg/mL prior to analysis.

An Acquity UPLC HSS T3 2.1-mm x 150-mm x 1.8-µm column was chosen, and the column temperature was maintained at 55°C with a flow rate of 0.4 mL/minute. Mobile phase A was 60:40 water:acetonitrile (vol/vol), and mobile phase B was 90:10 (vol/vol) isopropanol:acetonitrile. Both mobile phases contained 10 mM ammonium acetate to enhance ionization of the MAGs [14]. Table 2 shows the final gradient program used to provide optimal separation of the desired MAGs. A five-point calibration curve, from 2.5 µg/mL to 12.5 µg/mL, was generated using monopalmitin, monostearin, monoolein, monolinolein, and monolinolenin in methanol to evaluate linearity. Because linearity was demonstrated over the target range, a single-point calibration was used for quantitation of the MAGs.

**Table 2. UPLC-TQD Gradient Table**

<b>Time (Minutes)</b>	<b>% Mobile Phase A</b>	<b>% Mobile Phase B</b>	<b>Curve</b>
Initial	75	25	0
1.0	75	25	6
4.0	55	45	6
6.0	55	45	6
11.0	0	100	6
14.0	0	100	6
14.5	75	25	6
17.5	75	25	6

Mass spectral conditions were optimized using Intellistart in Waters MassLynx software and by directly infusing each MAG to determine optimal cone voltages in ES+ mode. Desolvation and source temperatures were then varied to ensure that no loss of sensitivity was occurring. Final mass spectral conditions are listed in Table 3, and compound masses and cone voltages used for analysis are listed in Table 4. All compounds had a dwell time of 0.05 sec.

**Table 3. Mass Spectral Conditions**

<b>Parameter</b>	<b>Value</b>
Mode	Selective ion response from 2 minutes to 10 minutes
Source Temperature	150°C
Desolvation Temperature	400°C
Cone Gas Flow	20 L/hr
Desolvation Gas Flow	800 L/hr
Capillary	3.1 kV

**Table 4. Compound Masses and Cone Voltages Used**

Compound	Mass Monitored, g/mol	Cone Voltage, kV
Internal Standard	306.3	12
Monomyristin	320.3	14
Monopalmitin	348.3	14
Monolinolenin	370.3	14
Monolinolein	372.3	16
Monoolein	374.3	14
Monostearin	376.3	16

*Cloud point*—An automatic mini-method (D5773) was used for this study. Testing was conducted using a PhaseTek 70X automatic cloud point (CP) instrument.

*FAME profile*—The FAME profile was measured by GC with the instrument conditions described in Table 5. A five-point calibration curve was generated with a standard FAME mixture (Nu-Chek part GLC-744, Elysian, Minnesota). Each sample was prepared in n-heptane, by mass, using C13:1 as an internal standard.

**Table 5. GC Instrument Conditions to Measure FAME Profile in Biodiesel**

Column	Varian Select FAME 100 m x 0.25 mm x 0.25 $\mu$ m
Injection volume	1 $\mu$ L
Injector temperature	250°C
Split ratio	100:1
Head pressure	44.695 psi
Flow	1.3164 mL/min Constant flow mode
Oven Profile	
Initial temperature	140°C
Hold time	5 min
Ramp 1	3°C/min to 190°C
Hold time	10 min
Ramp 2	4°C/min to 210°C
Hold time	5 min
Ramp 3	4°C/min to 240°C
Hold time	4 min
Detector	Flame Ionization Detector
Detector temperature	250°C

*Group I and II metals*—The metal content analysis was subcontracted to Southwest Research Institute of San Antonio, Texas, and analyzed by ASTM D7111.

*Oxidation stability*—A Metrohm 873 Rancimat instrument was used to measure the oxidation stability by the EN15751 method.

## 3 Results and Discussion

### 3.1 Sample Identification

Samples were given a unique numeric identifier to keep the biodiesel producers and terminals anonymous. All B100 samples from producers are illustrated as circles on the following figures, while the B100 samples from terminals are shown as squares.

### 3.2 Significant Figures and Error Bars

As illustrated in Table 1, there is no consistent use of significant figures in D6751. Although at first this may appear to be an oversight, the use, or lack of use, of significant figures is deliberate in ASTM methods. For properties such as flash point that are limited to 93°C, the precision of the test method is such that any additional significant figures are not meaningful. However, in the D6584 method for glycerin, the reported value is calculated and a potentially infinite number of significant figures could be reported. To standardize reporting, the limit for total glycerin is 0.240 wt%. Rules for rounding measurements to determine compliance with specifications are described in ASTM E-29.

The error bars presented in this study were determined by the reported interlaboratory precision in the ASTM method, except as noted below for SMG. This precision is known as reproducibility or R. Data reported by EN methods follow the same convention. Each error bar is +/- R. Because there is no published precision for SMG by D6584, the error bars are the intralaboratory precision (repeatability, or r).

### 3.3 Flash Point and Alcohol Control

The volatility of biodiesel is extremely low, and properly produced biodiesel presents minimal risk for handling and safety. To ensure safe handling of biodiesel, a minimum flash point of 130°C is set to limit residual methanol. The flash points of the samples are shown in Figure 1, with only four samples having a flash point below 130°C. Certain feedstocks and process conditions may result in slightly lower flash points, and the methanol content of these samples needed to be tested. The samples with flash points below 130°C (without taking the error bars into consideration) were sent for methanol analysis. Three of the four samples with a flash point below 130°C met the methanol content requirement. The final sample had excess methanol content and failed both requirements.

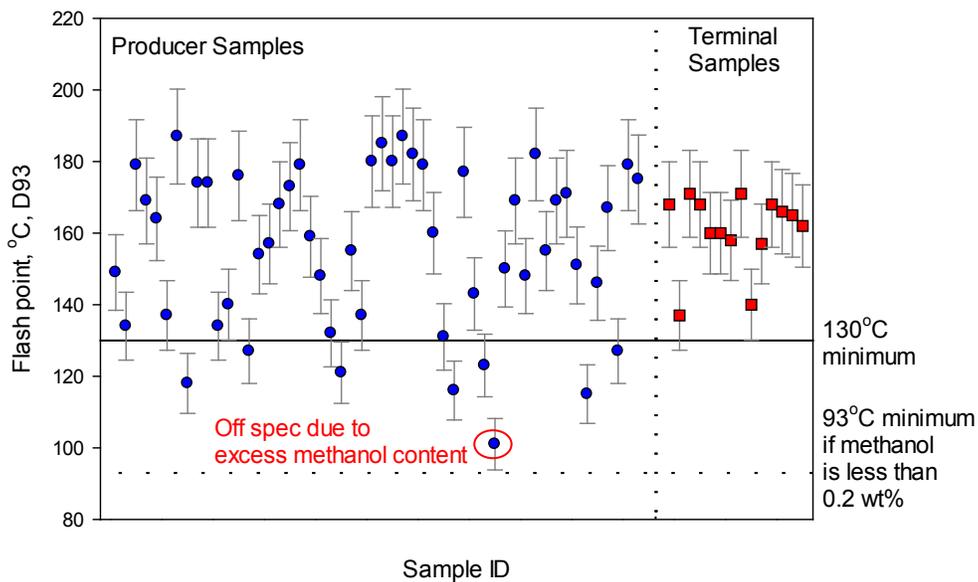


Figure 1. Results from flash point and alcohol control testing of B100 survey samples

### 3.4 Acid Number

The acid number of biodiesel should be low to ensure no residual free fatty acids or processing acids are present in the fuel. The presence of excess acids can lead to corrosion and deposits in fuel systems. Previous surveys have shown few failures on acid value [6, 7], and the current survey shows no failures for acid number (Figure 2). The average acid number of these samples was 0.24 mgKOH/g, approximately half of the specification limit. One sample was close to the specification limit, at 0.48 mgKOH/g and was the highest value recorded in this survey.

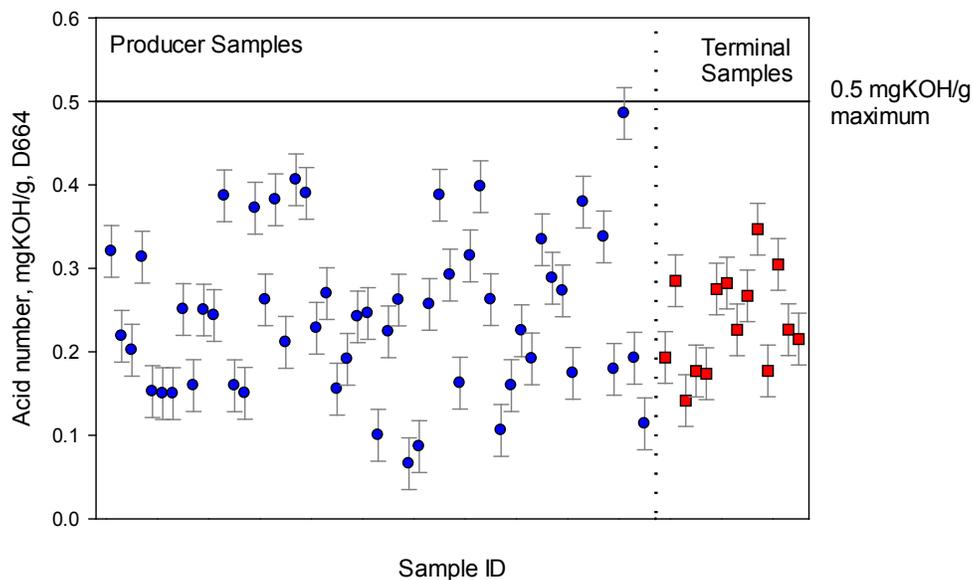


Figure 2. Acid number results

### 3.5 Cold Soak Filtration

Previously, biodiesel users experienced many cold weather operability problems with biodiesel blends [15]. In an effort to combat the impact of minor components not measured in D6751, the CSFT was added as an annex in 2008. The annex was converted into a full ASTM test method, D7501, in 2010. Reports of problems in cold weather have been significantly reduced since the addition of the CSFT.

Immediately after the adoption of the CSFT into D6751, over 50 biodiesel samples from different feedstocks and processes were tested, with the results being bimodal; the biodiesel samples either passed or failed the test [16]. Failure of the CSFT was not correlated to biodiesel feedstock.

The CSFT has an upper limit of 360 sec; however, if the biodiesel is being blended into diesel fuel that will be used in  $-12^{\circ}\text{C}$  environments or colder, a 200-sec upper limit applies. This 200-sec upper limit has sometimes been referred to as the “wintertime” limit of the CSFT and has been adopted into the wintertime No. 1-B grade in the newest version of D6751.

In this study, only one sample failed to meet the CSFT year-round limit of 360 sec (Figure 3). This sample also failed other properties in D6751 and clearly was of poor quality overall. One sample was right at the 360-sec limit, technically on specification, but was much higher than any of the other samples. This sample readily met all the other properties tested.

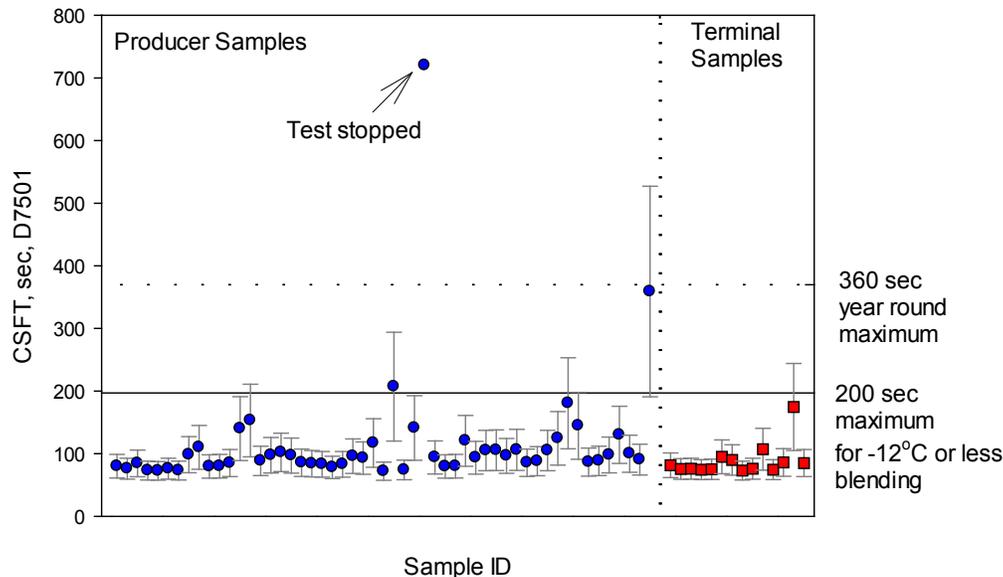


Figure 3. B100 survey CSFT results

### 3.6 Oxidation Stability

Because biodiesel contains polyunsaturated fatty acid chains, it will degrade by the well-known peroxidation mechanism [17]. A large body of work has been conducted on the oxidation and stabilization of biodiesel with synthetic and natural antioxidants [18, 19]. An oxidation stability limit was adopted in D6751 in early 2007. The 2007 survey showed a wide variety of oxidation

stability levels in B100, with 30% of samples collected failing the specification, although this represented only 8.5 million gallons of the nearly 500 million gallons in the market at that time. The current study shows a significant improvement in meeting the oxidation stability limit. Only two samples had oxidation stability results below the 3-hr limit (Figure 4). Two samples were very close to the 3-hr limit but met the limit based on the method variability, as the error bars are over 3 hours. On average, the median value for both the producer samples and terminal samples is around 9.5 hrs.

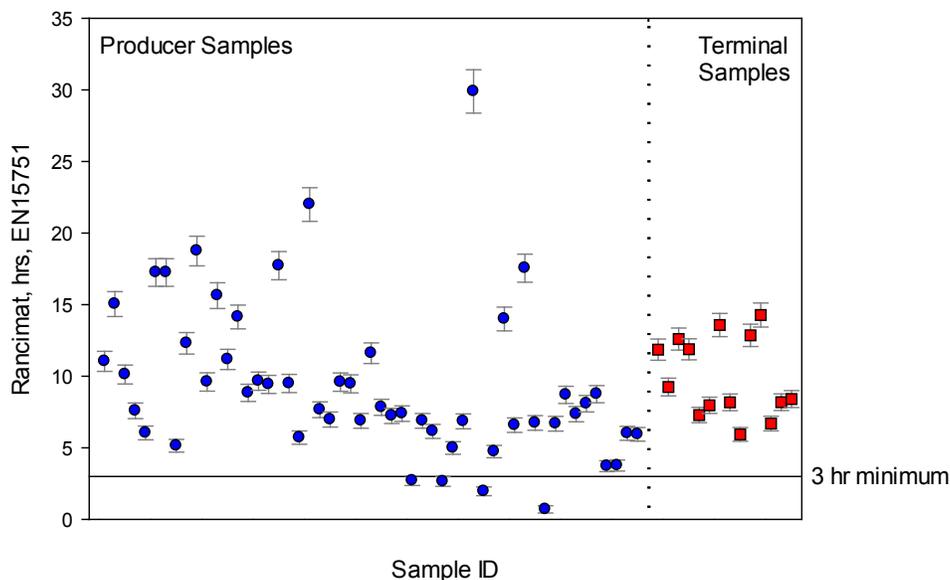
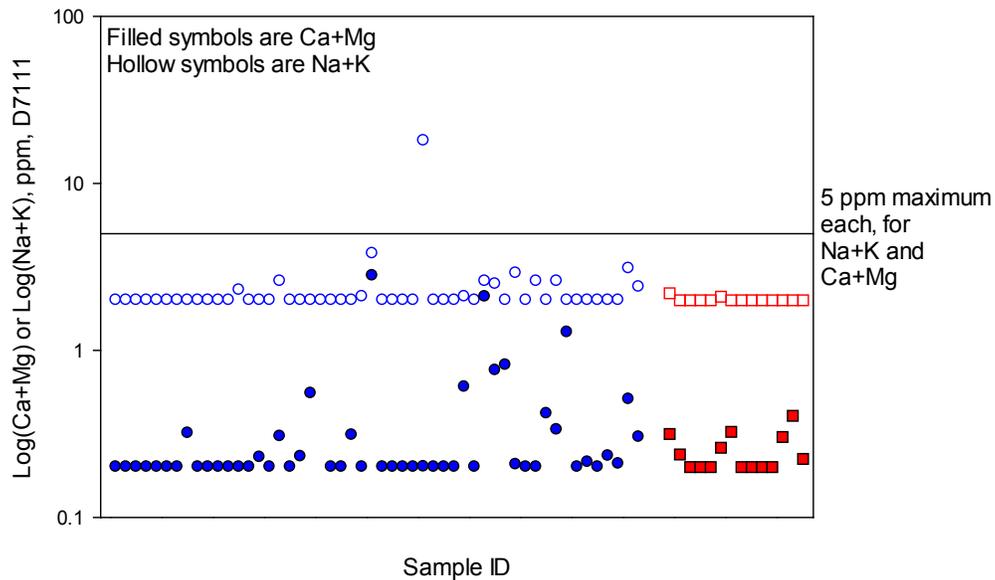


Figure 4. Oxidation stability results from B100 survey

### 3.7 Group I and II Metals

Metals in B100 are typically contaminants from the production and cleanup process and are limited to very low levels in D6751. Even at specification levels, the impact of metals on the emission control systems in new diesel engines may be significant [20]. A majority of the samples were at or below the method detection limit, <1 ppm for sodium (Na) and potassium (K) and <0.1 ppm for calcium (Ca) and magnesium (Mg). One sample had sodium content of 17 ppm of K, nearly three times the specification for Na+K combined. This sample also failed the CSFT and oxidation stability.

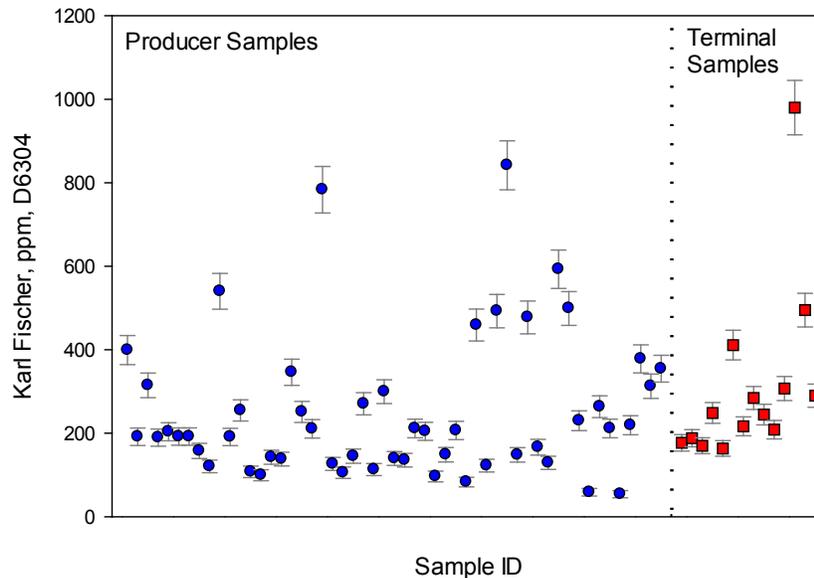
Metals can be present in biodiesel through residual catalyst (Na, K) and/or through cleanup of the finished product (Ca, Mg). In this study, 25 samples had metals above the detection limits but below the specification limit (in Figure 5, note the y-axis is logarithmic to better illustrate data variability). Ca was found in 21 of these samples, likely from hard water washing. The presence of Mg in biodiesel may be from dry wash adsorbents or, when found with Ca, from hard water washing. Mg was found above the detection limits in five samples in this study. Na and K were found in 14 samples in this study (one sample was grossly over the specification limit for Na).



**Figure 5. Plot of Na+K and Ca+Mg for B100 samples.**  
The y-axis is logarithmic to better illustrate the data variability.

### 3.8 Karl Fischer Water

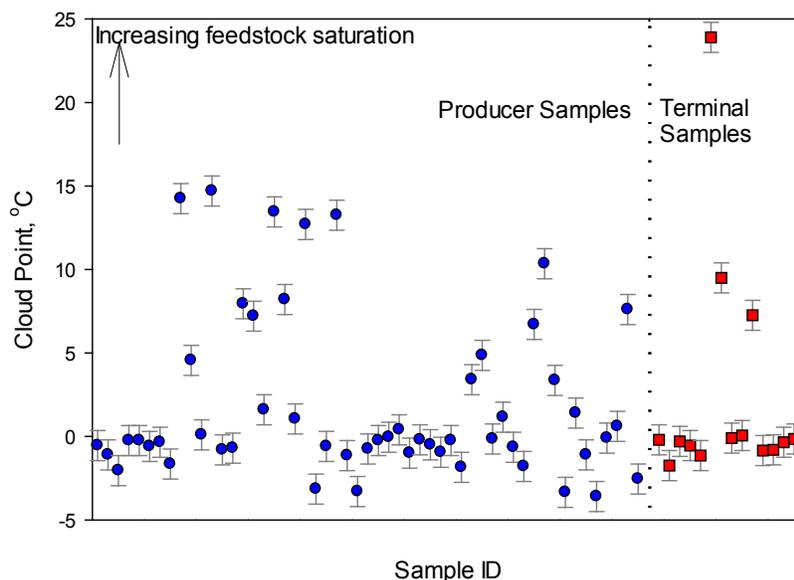
Although Karl Fischer water is not part of the D6751 specification, this parameter is important to measure, potentially providing data for future specification improvements. The water content of biodiesel has been shown to have a significant impact on filterability of biodiesel [21, 22]. These samples had an average water content of 264 ppm, well below the saturation limit of B100 (around 1,500 ppm), as illustrated in Figure 6.

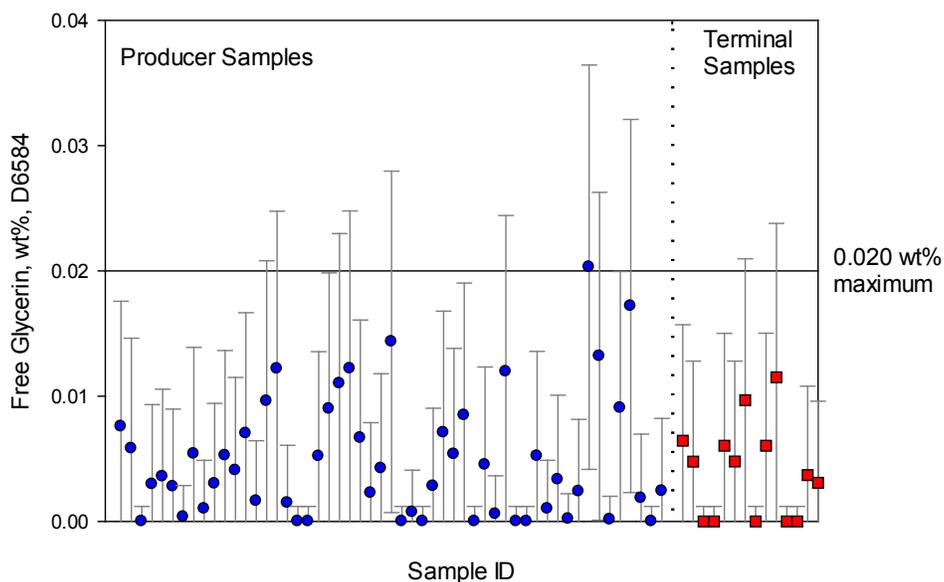


**Figure 6. Karl Fischer water results from B100 survey**

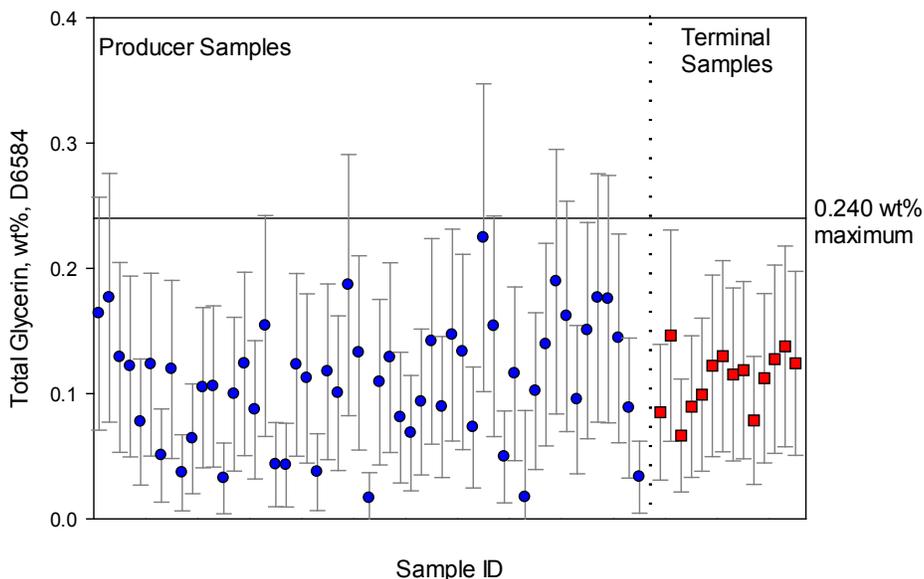
### 3.9 Cloud Point

CP is not limited in D6751 but is an important operability parameter that must be reported. The CP is the temperature where the fuel first begins to form crystals and is used to predict cold weather operability. For biodiesel, the CP is particularly important because biodiesel is almost always blended with petroleum diesel, and the CP of the biodiesel will have a significant impact on the final blend properties. CP is determined by the FAME profile and SMG content of the biodiesel, with higher levels of saturated FAME and SMG increasing CP [22, 23]. The average CP was around 2°C, although several samples had higher CPs (Figure 7).



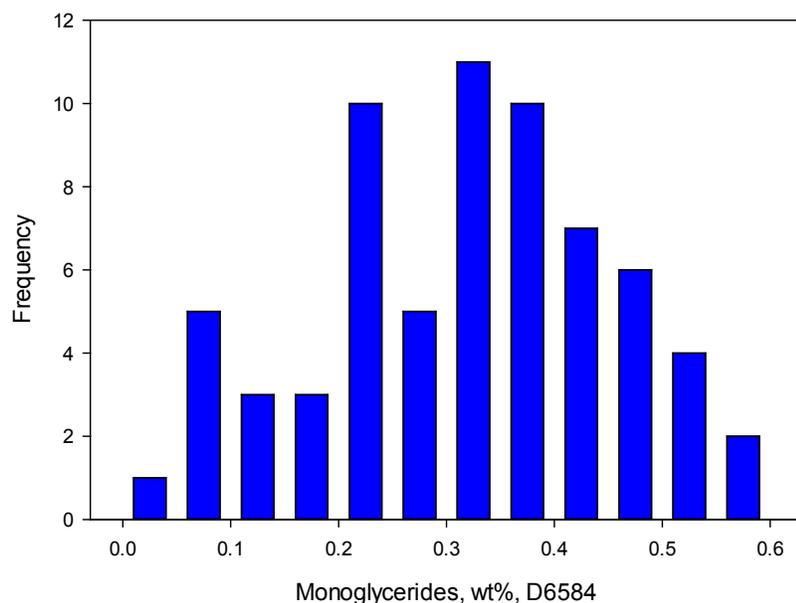


**Figure 8. Free glycerin for B100 survey samples**



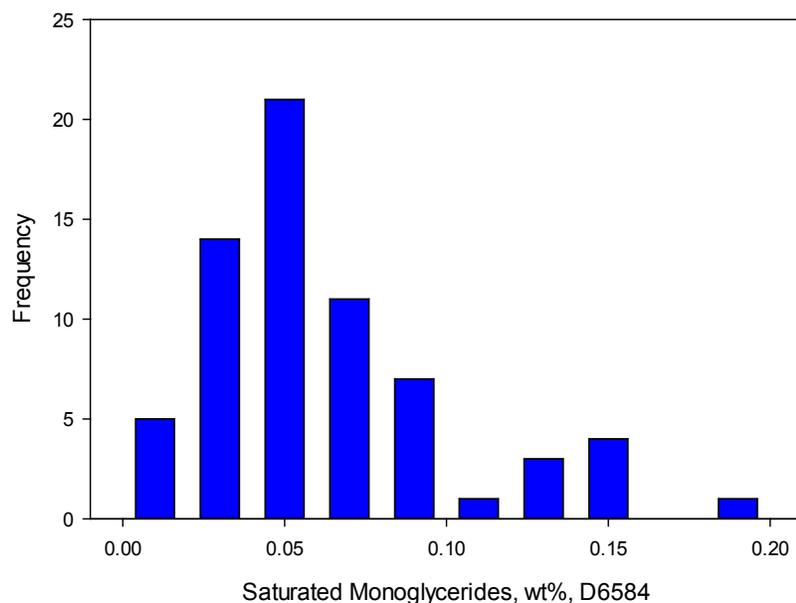
**Figure 9. Total glycerin for B100 survey samples**

The average MAGs in this study were 0.322 wt% (Figure 10). The MAG distribution was analyzed for normality using the Shapiro-Wilk Normality Test. The results show that the sample population in this study are normal ( $P = 0.417$ ). This result shows that the MAG content of biodiesel is not feedstock specific but rather a result of different production processes and technologies.



**Figure 10. Histogram of MAG content for B100 survey samples**

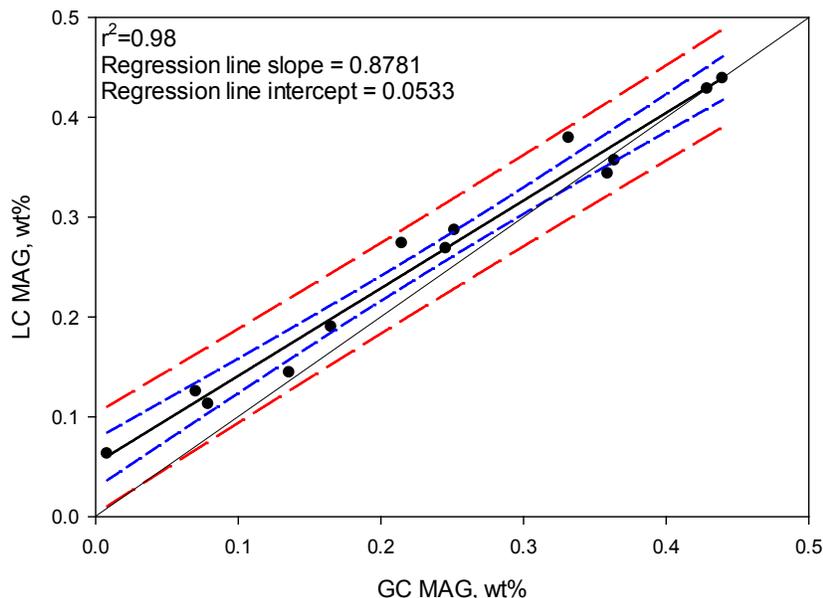
The average SMG content was 0.064 wt% (Figure 11). The Shapiro-Wilk test was applied to the SMG results; the sample distribution is not normally distributed ( $P < 0.001$ ). This result is not unexpected, as the SMG content is strongly related to the feedstock profile, as well as the total MAG content, and hence the production process.



**Figure 11. Histogram of SMG content for B100 survey samples**

The newly developed LC method was validated by selecting a range of samples and comparing the MAGs from the GC to the results on the LC. The samples were selected from both the

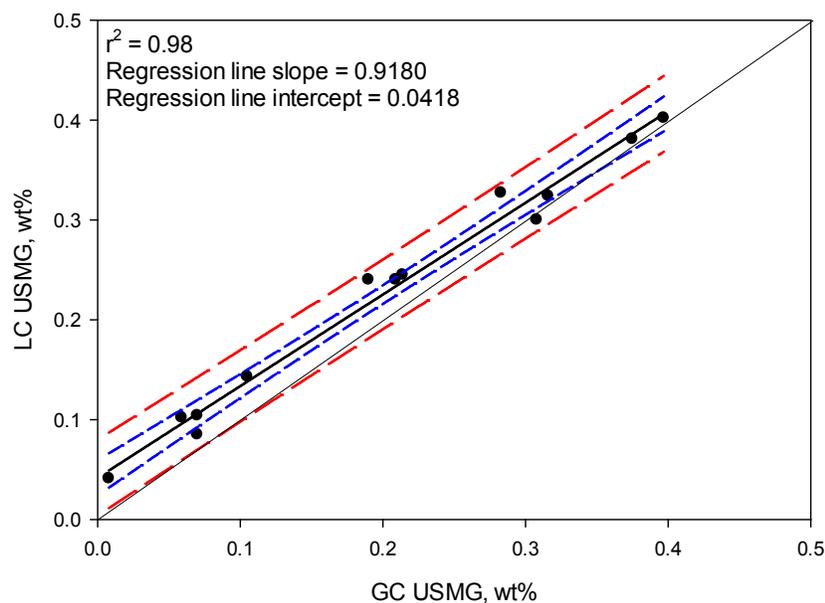
terminals and the producers, covering the range of total MAG and SMG content observed in the larger data set. Figure 12 shows the results from the two methods for total MAGs in the biodiesel samples. The data show a very good fit ( $r^2 = 0.98$ ) between the two methodologies. The regression line is slightly less than 1, where two samples have MAGs by LC greater than by GC.



**Figure 12. Correlation of MAGs by GC and LC.**

The thin line is a parity line, where MAG content is equal between the two methods. The heavy line is the regression line, the short dashed line is the 95% confidence intervals, and the long dashed line is the 95% prediction band.

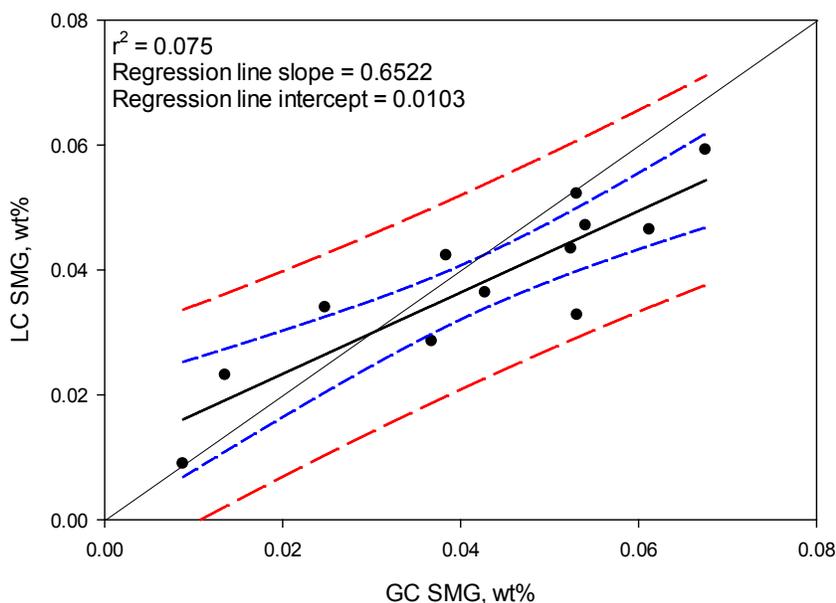
To investigate the source of the points where the LC MAG was greater than the GC MAG, the SMG and USMGs were analyzed individually. The USMGs are the main component of the MAGs for most traditional biodiesels. The USMGs by GC and LC are illustrated in Figure 13. As with the total MAGs, the same two samples have relatively higher USMGs by LC than by GC. The fit of the regression line is also very good, with  $r^2 = 0.98$ , a slope of 0.9180, and an intercept of 0.0418. While the GC method has been used for many years, a known drawback of the method is the lack of separation of the USMGs. The LC method separates the USMGs, and this analysis confirms that the USMGs are accurately measured by the GC method even though they are not separated.



**Figure 13. Correlation of USMGs by GC and LC.**

The thin line is a parity line, where USMG content is equal between the two methods. The heavy line is the regression line, the short dashed line is the 95% confidence intervals, and the long dashed line is the 95% prediction band.

The SMGs are slightly harder to correlate than the USMGs due to the much lower levels present in these samples. The lower concentrations of SMGs in biodiesel led to higher experimental error, especially by the GC, where the limit of quantitation was estimated at 0.020 wt%. The goodness of fit falls to 0.75 for the SMGs, and the slope drops to 0.6522, with an intercept at 0.0103. The data in Figure 14 is the SMG measured directly by each method, rather than the difference between the MAGs and USMGs. While a better correlation could be obtained by using the difference, the SMGs are important compounds that can be measured directly and should be reported this way.

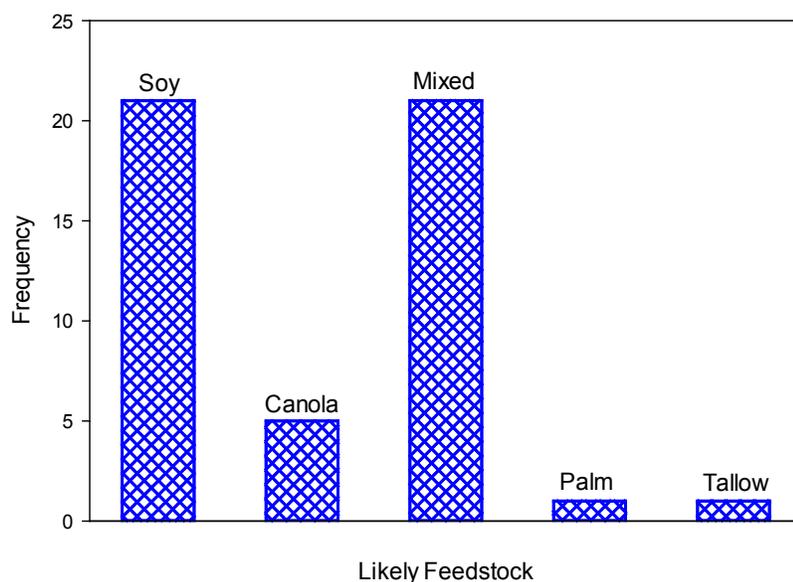


**Figure 14. Correlation of SMGs by GC and LC.**

The thin line is a parity line, where SMG content is equal between the two methods. The heavy line is the regression line, the short dashed line is the 95% confidence intervals, and the long dashed line is the 95% prediction band.

### 3.11 FAME Profile

The FAME profile of the samples was measured to determine the likely feedstock used to produce the sample. The FAME profile is complementary to the CP and SMG measurements. A histogram of the likely feedstock for each B100 sample is shown in Figure 15. The samples were roughly split between soy and mixed feedstocks. It should be noted that mixed feedstock includes mixtures of vegetable oils, mixtures of animal fats, or a combination of animal and vegetable feedstocks. The CP and FAME profile showed that, while almost half of the samples were produced from mixed feedstocks, the low average CP of the samples indicates a significant percent of vegetable oil in these feedstocks.



**Figure 15. Histogram of likely feedstock for B100 survey samples**

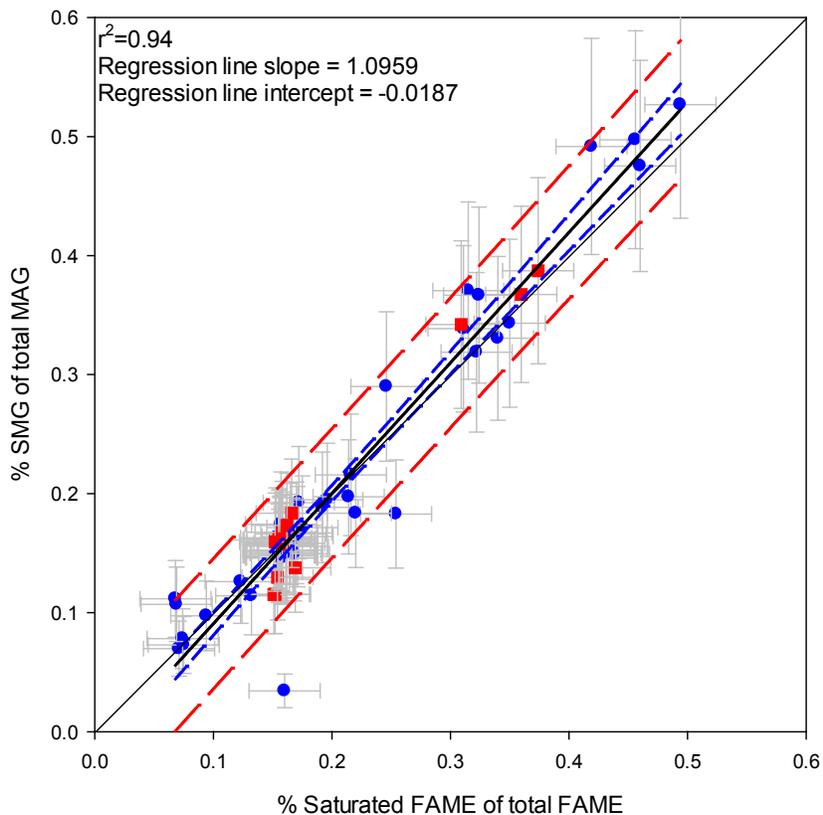
The FAME profile of the biodiesel should correlate to the types of MAGs in the sample. The amount of saturated FAME can be expressed as a percent of total FAME. The amount of SMG can also be expressed as a percent of total MAG. The percent saturated FAME should roughly equal the percent SMG in a sample.

Figure 16 shows the correlation of saturated FAME to SMG for the samples in this study. As shown, the correlation is very good, with  $r^2 = 0.94$ , an intercept of  $-0.0187$ , and a slope of  $1.0959$ . One sample falls outside the prediction band, a distilled soy biodiesel. While the methodology was clearly able to resolve other very low SMG samples, this sample fell outside the statistically expected bands, either due to an error in the SMG analysis or the saturated FAME analysis. After reviewing the data, the source of this error is unclear.

Although they are within the 95% prediction bands, a few samples are nearly outside this statistically defined interval when applying the error bars of the methods. For example, there is one sample with a 25% saturated FAME and only 18% SMG. This sample has a CP of  $4.8^{\circ}\text{C}$  and is produced from mixed feedstocks. In contrast, there is a sample with 25% saturated FAME but SMG content of nearly 30%. This sample has a CP of  $4.5^{\circ}\text{C}$ . Although both samples meet the D6751 specification, analysis of the FAME and SMG illustrates some differences in the production processes between the companies that performed the analyses.

Another sample worth highlighting contained 41% saturated FAME and nearly 50% SMG. This sample was known to have a field issue, though it met the D6751 specification. One speculation for the higher than expected SMGs in these samples is that the production process was operating at nonoptimum temperatures. McNeill and coworkers found that, at less than optimum temperatures, saturated monoglycerides are a favored product [21]. Thus, a B100 may have more SMG than expected by its FAME profile.

It is difficult to speculate the exact cause of data falling near the edge of the prediction band and the impact on operability of blends made with these fuels. Only one case is known to the authors where an operability problem occurred, and no attempt is made to further predict operability based on this data.



**Figure 16. Correlation of saturated FAME to SMG.**

The thin line is a parity line, where % saturated FAME would equal % SMG. The heavy line is the regression line, the short dashed line is the 95% confidence intervals, and the long dashed line is the 95% prediction band.

### 3.12 No. 1-B Grade Biodiesel

Although D6751 did not include the No. 1-B grade of biodiesel when this study was conducted, 70% of the samples in this project would have met the requirements had they been in place. Two samples would not have met the 200-sec CSFT requirement, and 19 samples had MAGs over the 0.40 wt% limit. Of the 19 samples with MAGs above 0.40 wt%, one was from a terminal and the other 18 were directly from the producers.

## 4 Conclusions

Samples of biodiesel were collected from terminals and producers throughout the United States. The samples collected in this study were typically high quality and met the D6751 specification limits, with a few notable exceptions. In particular, one sample failed multiple properties and was clearly an outlier compared to other samples in this survey. The failure rates on CSFT and oxidation stability were less than 5%, with one failure on flash point and no failures on the other critical properties tested.

Most of the samples had metals at or near the detection limits, and well below the specification limits in D6751. A further analysis of the metals in the samples showed that Ca appeared most often above the detection limits, followed by K. Na was only found in the presence of other metals, and Mg was most rarely found in these samples.

The MAGs were normally distributed, as expected, with an average of 0.322 wt%. Feedstock analysis showed the samples split between soy and mixed feedstocks. SMGs were not normally distributed due to the wide variety of feedstocks encountered in this study. An analysis of SMG and saturated FAME content showed that a good correlation can be made between saturated FAME and SMG.

A novel method was developed to analyze biodiesel for MAGs, USMGs, and SMGs, and compared to the standard D6584 method. The novel method, based on UPLC, showed excellent correlation to the referee GC method. An advantage of the UPLC method is the separation of the USMGs, which are not resolved in the GC method; this may provide useful information in the future. Additional samples need to be run to further validate the method.

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## Appendix–Supplementary Information

Appendix Table – B100 Survey Data

Sample ID	Free Glycerin, wt%	Total Glycerin, wt%	MAG by GC, wt%	SMG by GC, wt%	SMG by LC, wt%	MAG by LC, wt%	Diglycerides, wt%	Triglycerides, wt%	% SMG by GC	% SMG by LC	% Saturated FAME	CP, °C	Karl Fischer, ppm	Acid value, mgKOH/g	Rancimat, hrs	CSFT, sec	Flash, °C	Na+K, ppm	Ca+Mg, ppm
1	0.008	0.164	0.478	0.078	0.094	0.625	0.165	0.074	16.4%	15.1%	17.1%	-0.6	399	0.320	11.0	80	149	<2	<0.2
2	0.006	0.177	0.344	0.056	0.058	0.522	0.326	0.316	16.3%	11.1%	15.3%	-1.1	192	0.219	15.0	76	134	<2	<0.2
3	0.000	0.129	0.447	0.031	-	-	0.069	0.027	7.0%	-	7.1%	-2.0	315	0.202	10.1	85	179	<2	<0.2
4	0.003	0.122	0.364	0.053	0.033	0.357	0.113	0.073	14.6%	9.2%	15.7%	-0.3	190	0.314	7.6	73	169	<2	<0.2
5	0.004	0.077	0.231	0.034	0.043	0.352	0.039	0.037	14.8%	12.2%	15.6%	-0.3	204	0.152	6.0	73	164	<2	<0.2
6	0.003	0.123	0.332	0.053	0.052	0.379	0.161	0.100	16.0%	13.8%	15.8%	-0.6	192	0.150	17.2	76	137	<2	<0.2
7	0.000	0.051	0.143	0.025	0.024	0.223	0.087	0.000	17.4%	10.8%	15.7%	-0.4	192	0.150	17.2	73	187	<2	<0.2
8	0.005	0.119	0.409	0.060	0.040	0.352	0.054	0.000	14.8%	11.2%	15.7%	-1.7	158	0.251	5.1	99	118	2	0.319
9	0.001	0.037	0.135	0.091	0.093	0.181	0.003	0.000	67.0%	51.5%	51.2%	14.3	121	0.160	12.3	110	174	<2	<0.2
10	0.003	0.064	0.229	0.066	0.049	0.298	0.009	0.000	29.0%	16.6%	24.6%	4.56	540	0.250	18.8	80	174	<2	<0.2
11	0.005	0.105	0.359	0.052	0.043	0.343	0.043	0.000	14.6%	12.6%	15.8%	0.1	191	0.244	9.6	80	134	<2	<0.2
12	0.004	0.106	0.345	0.182	0.161	0.410	0.068	0.021	52.7%	39.4%	49.4%	14.7	255	0.387	15.6	85	140	<2	<0.2
13	0.007	0.032	0.070	0.014	0.023	0.125	0.018	0.041	19.2%	18.5%	17.2%	-0.8	108	0.159	11.2	140	176	2.3	<0.2
14	0.002	0.100	0.349	0.052	0.056	0.483	0.051	0.000	14.8%	11.7%	15.5%	-0.7	100	0.150	14.1	153	127	<2	<0.2
15	0.010	0.124	0.376	0.124	0.119	0.493	0.076	0.052	33.0%	24.0%	34.0%	8.0	143	0.372	8.8	89	154	<2	0.229
16	0.012	0.087	0.212	0.068	0.071	0.284	0.100	0.049	31.9%	24.9%	32.2%	7.2	138	0.262	9.7	98	157	<2	<0.2
17	0.001	0.154	0.493	0.096	0.077	0.591	0.115	0.074	19.5%	13.0%	19.6%	1.6	346	0.382	9.4	102	168	2.6	0.305

Sample ID	Free Glycerin, wt%	Total Glycerin, wt%	MAG by GC, wt%	SMG by GC, wt%	SMG by LC, wt%	MAG by LC, wt%	Diglycerides, wt%	Triglycerides, wt%	% SMG by GC	% SMG by LC	% Saturated FAME	CP, °C	Karl Fischer, ppm	Acid value, mgKOH/g	Rancimat, hrs	CSFT, sec	Flash, °C	Na+K, ppm	Ca+Mg, ppm
18	0.000	0.043	0.136	0.068	0.059	0.144	0.053	0.000	49.7%	41.1%	45.6%	13.5	251	0.211	17.7	97	173	<2	<0.2
19	0.000	0.043	0.165	0.061	0.046	0.190	0.000	0.000	37.1%	24.5%	31.5%	8.2	211	0.406	9.5	86	179	<2	0.231
20	0.005	0.123	0.364	0.042	0.034	0.419	0.117	0.058	11.4%	8.2%	13.2%	1.1	784	0.390	5.7	84	159	<2	0.552
21	0.009	0.112	0.320	0.158	0.133	0.387	0.109	0.038	49.2%	34.4%	41.9%	12.7	127	0.228	22.0	83	148	<2	<0.219
22	0.011	0.037	0.079	0.009	0.009	0.113	0.020	0.029	11.2%	7.9%	6.8%	-3.2	106	0.270	7.7	78	132	<2	<0.2
23	0.012	0.117	0.375	0.056	0.055	0.504	0.054	0.000	14.9%	11.0%	16.8%	-0.6	145	0.155	7.0	83	121	<2	<0.2
24	0.007	0.100	0.263	0.125	0.120	0.352	0.129	0.061	47.5%	34.0%	46.0%	13.3	271	0.191	9.6	96	155	<2	0.311
25	0.002	0.187	0.598	0.100	0.086	0.654	0.146	0.074	16.7%	13.2%	17.0%	-1.2	113	0.242	9.5	93	137	2.1	<0.2
26	0.004	0.133	0.433	0.032	0.030	0.498	0.096	0.017	7.3%	6.0%	7.5%	-3.3	300	0.246	6.9	117	180	3.8	2.799
27	0.014	0.016	0.008	0.000	0.022	0.063	0.000	0.000	3.4%	34.9%	16.0%	-0.8	140	0.100	11.6	72	185	<2	<0.2
28	0.000	0.109	0.360	0.055	0.040	0.442	0.089	0.025	15.2%	9.0%	15.7%	-0.3	136	0.224	7.8	207	180	<2	<0.2
29	0.001	0.129	0.426	0.067	0.071	0.550	0.100	0.027	15.8%	13.0%	16.4%	-0.1	212	0.262	7.2	74	187	<2	<0.2
30	0.000	0.081	0.252	0.038	0.042	0.287	0.101	0.006	15.2%	14.7%	16.2%	0.4	205	0.066	7.4	141	182	<2	<0.2
31	0.003	0.068	0.076	0.031	0.032	0.141	0.135	0.246	40.7%	23.1%	16.7%	-1	97	0.087	2.7	720	179	18	0.201
32	0.007	0.093	0.246	0.037	0.029	0.269	0.132	0.027	15.0%	10.6%	15.7%	-0.2	149	0.257	6.9	94	160	<2	<0.2
33	0.005	0.142	0.477	0.076	0.076	0.605	0.085	0.000	15.8%	12.6%	15.8%	-0.5	207	0.388	6.1	80	131	<2	<0.2
34	0.008	0.089	0.230	0.036	0.030	0.313	0.121	0.030	15.6%	9.5%	15.5%	-1.0	83	0.292	2.6	80	116	<2	<0.2
35	0.000	0.147	0.299	0.051	0.082	0.419	0.162	0.432	17.1%	19.7%	17.5%	-0.3	459	0.162	5.0	121	177	2.1	0.603
36	0.005	0.133	0.429	0.054	0.047	0.428	0.079	0.056	12.6%	11.0%	12.3%	-1.9	123	0.315	6.8	94	143	<2	<0.2
37	0.001	0.073	0.237	0.051	0.044	0.273	0.074	0.000	21.6%	16.1%	21.6%	3.4	493	0.398	29.9	105	123	2.6	2.096
38	0.012	0.224	0.498	0.091	0.075	0.738	0.304	0.365	18.3%	10.2%	25.1%	4.9	842	0.263	2.0	106	101	2.5	0.759
39	0.000	0.154	0.536	0.080	0.080	0.691	0.100	0.000	15.0%	11.5%	15.8%	-0.2	148	0.106	4.7	97	150	<2	0.815
40	0.000	0.049	0.167	0.031	0.022	0.202	0.043	0.000	18.9%	11.0%	19.2%	1.2	478	0.159	14.0	106	169	2.9	0.207

Sample ID	Free Glycerin, wt%	Total Glycerin, wt%	MAG by GC, wt%	SMG by GC, wt%	SMG by LC, wt%	MAG by LC, wt%	Diglycerides, wt%	Triglycerides, wt%	% SMG by GC	% SMG by LC	% Saturated FAME	CP, °C	Karl Fischer, ppm	Acid value, mgKOH/g	Rancimat, hrs	CSFT, sec	Flash, °C	Na+K, ppm	Ca+Mg, ppm
41	0.005	0.116	0.347	0.055	0.056	0.529	0.111	0.039	15.7%	10.5%	15.6%	-0.7	167	0.225	6.6	86	148	<2	<0.2
42	0.001	0.017	0.060	0.037	0.043	0.175	0.002	0.000	61.8%	24.8%	16.8%	-1.8	129	0.191	17.6	88	182	2.6	<0.2
43	0.003	0.102	0.366	0.134	0.327	0.389	0.025	0.000	36.7%	84.0%	33.6%	6.7	593	0.334	6.7	105	155	<2	0.418
44	0.000	0.139	0.448	0.152	0.182	0.697	0.148	0.009	33.9%	26.1%	31.1%	10.4	499	0.288	0.7	125	169	2.6	0.334
45	0.002	0.189	0.578	0.114	0.112	0.598	0.246	0.007	19.7%	18.7%	21.4%	3.4	230	0.273	6.7	181	171	<2	1.281
46	0.020	0.162	0.440	0.043	0.036	0.439	0.171	0.019	9.7%	8.3%	9.4%	-3.4	59	0.174	8.7	145	151	<2	<0.2
47	0.013	0.095	0.297	0.049	0.045	0.325	0.031	0.005	16.6%	13.7%	16.5%	1.4	264	0.379	7.4	87	115	<2	0.214
48	0.000	0.150	0.534	0.081	0.092	0.681	0.080	0.000	15.1%	13.5%	15.5%	-1.1	212	0.127	8.1	89	146	<2	<0.2
49	0.009	0.176	0.540	0.042	0.046	0.590	0.155	0.042	7.8%	7.8%	7.4%	-3.6	54	0.338	8.7	98	167	<2	0.233
50	0.017	0.175	0.512	0.080	0.069	0.534	0.144	0.042	15.6%	12.8%	15.6%	-0.1	219	0.179	3.7	130	127	<2	0.209
51	0.002	0.144	0.486	0.089	0.076	0.647	0.087	0.032	18.4%	11.8%	22.0%	0.6	378	0.486	3.8	100	179	3.1	0.509
52	0.000	0.088	0.224	0.077	0.070	0.262	0.169	0.050	34.3%	26.9%	35.0%	7.6	313	0.192	6.0	91	175	2.4	0.302
53	0.002	0.030	0.075	0.008	0.026	0.114	0.042	0.013	10.7%	22.8%	6.9%	-2.6	355	0.114	5.9	359	-	-	-
54	0.006	0.085	0.237	0.033	0.052	0.330	0.075	0.059	13.77%	15.9%	16.9%	-0.2	177	0.193	11.9	82	168	2.2	0.316
55	0.005	0.146	0.472	0.075	0.077	0.568	0.092	0.052	15.79%	13.6%	15.8%	-1.8	188	0.285	9.2	76	137	<2	0.238
56	0.000	0.067	0.215	0.025	0.034	0.274	0.054	0.027	11.54%	12.4%	15.2%	-0.3	170	0.142	12.6	76	171	<2	<0.2
57	0.000	0.090	0.250	0.029	0.032	0.365	0.107	0.085	11.52%	8.8%	15.4%	-0.6	249	0.177	11.9	75	168	<2	<0.2
58	0.006	0.099	0.297	0.039	-	-	0.063	0.065	12.96%	-	15.9%	-1.2	164	0.174	7.3	75	160	<2	<0.2
59	0.005	0.122	0.373	0.145	0.139	0.433	0.078	0.087	38.73%	32.0%	37.4%	23.9	411	0.275	8.0	95	160	2.2	0.261
60	0.010	0.130	0.388	0.142	0.130	0.450	0.095	0.055	36.74%	28.9%	35.8%	9.5	217	0.226	13.6	90	158	<2	0.325
61	0.000	0.115	0.344	0.058	0.060	0.464	0.111	0.091	16.75%	12.8%	15.8%	-0.1	285	0.226	8.2	73	171	<2	<0.2
62	0.006	0.119	0.308	0.050	0.049	0.379	0.169	0.074	16.12%	12.8%	15.5%	0.1	245	0.267	5.9	76	140	<2	<0.2
63	0.012	0.079	0.174	0.060	0.065	0.229	0.106	0.058	34.21%	28.3%	30.9%	7.3	209	0.347	12.9	107	157	<2	<0.2

Sample ID	Free Glycerin, wt%	Total Glycerin, wt%	MAG by GC, wt%	SMG by GC, wt%	SMG by LC, wt%	MAG by LC, wt%	Diglycerides, wt%	Triglycerides, wt%	% SMG by GC	% SMG by LC	% Saturated FAME	CP, °C	Karl Fischer, ppm	Acid value, mgKOH/g	Rancimat, hrs	CSFT, sec	Flash, °C	Na+K, ppm	Ca+Mg, ppm
64	0.000	0.112	0.346	0.056	0.042	0.415	0.103	0.071	16.22%	10.1%	15.6%	-0.9	307	0.177	14.3	75	168	<2	<0.2
65	0.000	0.128	0.319	0.051	0.048	0.383	0.193	0.155	15.93%	12.6%	15.2%	-0.8	979	0.305	6.7	86	166	<2	0.313
66	0.004	0.138	0.358	0.066	0.064	0.464	0.184	0.133	18.35%	13.9%	16.6%	-0.4	495	0.227	8.2	175	165	<2	0.406
67	0.003	0.124	0.310	0.054	0.051	0.397	0.169	0.150	17.33%	12.8%	16.2%	-0.2	290	0.215	8.4	85	162	<2	0.224