An Overview of ASTM D6751: Biodiesel Standards and Testing Methods

Alternative Fuels Consortium
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Summary

• Biodiesel production review
• Key elements in ASTM Specifications and Standard Test Methods
• ASTM Specification D 6751 – 07b, the specification of B 100 (biodiesel) fuel is described in detail.
• Key properties of B 100 are discussed in terms of their tests and specifications.
• Alternative testing procedures
• Other issues affecting fuel quality
Review of the Production Process

- Biodiesel is produced by a chemical reaction between methanol (or ethanol) and an oil or fat, in the presence of a catalyst.
- Requires a strong basic catalyst (NaOH or KOH)
- The reaction is called “Transesterification”
  - Changing one ester (vegetable oil) into another ester (biodiesel)
- Oil + Alcohol yields Biodiesel + Glycerol
Transesterification (i.e. the biodiesel reaction)

One triglyceride molecule is converted into three mono-alkyl-ester (biodiesel) molecules.
Producing Quality Fuel

Determined by:

– Feedstock quality
– Production process
– Post-production
– Analytical Capability
– Handling and Storage
ASTM D 6751 – 07b: Standard Specification for Biodiesel Fuel (B 100) Blend Stock for Distillate Fuels

- ASTM D 6751 has two grades
  - S500
  - S15 (Almost all biodiesel is already S15)
Potential Impurities: in Biodiesel

- Methanol – Degrades some plastics and elastomers, corrosive; Can lower flashpoint to unsafe levels (fire safety)
- Unconverted/partly converted oils (bound glycerin) – Results in very poor cold flow properties, injector and in-cylinder deposits, potential engine failure
- Free Glycerin – Results in injector deposits, clogged fuel filters, deposit at bottom of fuel storage tank
- Catalyst (caustic, NaOH) – Excessive injector, fuel pump, piston, and ring wear, filter plugging, issues with lubricant
  
  *All are limited by ASTM D6751 specification*
<table>
<thead>
<tr>
<th>Property</th>
<th>Test method</th>
<th>Limits</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium &amp; Magnesium</td>
<td>EN 14538</td>
<td>5 max ppm</td>
<td>(ug/g)</td>
</tr>
<tr>
<td>Flash point (closed cup)</td>
<td>D 93</td>
<td>93.0 min</td>
<td>°C</td>
</tr>
<tr>
<td>Water and sediment</td>
<td>D 2709</td>
<td>0.050 max</td>
<td>% volume</td>
</tr>
<tr>
<td>Kinematic viscosity, 40 °C</td>
<td>D 445</td>
<td>1.9-6.0</td>
<td>mm² / s</td>
</tr>
<tr>
<td>Sulfated ash</td>
<td>D 874</td>
<td>0.020 max</td>
<td>% mass</td>
</tr>
<tr>
<td>Sulfur</td>
<td>D 5453</td>
<td>0.05 or 0.0015 max a %</td>
<td>mass</td>
</tr>
<tr>
<td>Copper strip corrosion</td>
<td>D 130</td>
<td>No. 3 max</td>
<td></td>
</tr>
<tr>
<td>Cetane number</td>
<td>D 613</td>
<td>47 min</td>
<td></td>
</tr>
<tr>
<td>Cloud point</td>
<td>D 2500</td>
<td>Report</td>
<td>°C</td>
</tr>
<tr>
<td>Carbon residue</td>
<td>D 4530</td>
<td>0.050 max</td>
<td>% mass</td>
</tr>
<tr>
<td>Acid number</td>
<td>D 664</td>
<td>0.50 max</td>
<td>mg KOH / g</td>
</tr>
<tr>
<td>Free glycerin</td>
<td>D 6584</td>
<td>0.020</td>
<td>% mass</td>
</tr>
<tr>
<td>Total glycerin</td>
<td>D 6584</td>
<td>0.240</td>
<td>% mass</td>
</tr>
<tr>
<td>Phosphorus content</td>
<td>D 4951</td>
<td>0.001 max</td>
<td>% mass</td>
</tr>
<tr>
<td>Distillation temperature, T90 AET</td>
<td>D 1160</td>
<td>360 max</td>
<td>°C</td>
</tr>
<tr>
<td>Sodium/Potassium, combined</td>
<td>EN 14538</td>
<td>5 max, combined</td>
<td>ppm</td>
</tr>
<tr>
<td>Oxidation Stability</td>
<td>EN 14112</td>
<td>3 min</td>
<td>hours</td>
</tr>
<tr>
<td>Workmanship</td>
<td>Free of undissolved water, sediment, &amp; suspended matter</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Analytical Capabilities
Critical Parameters

Flashpoint, °C
Acid Number, mg KOH/g
Total and Free Glycerin, % mass
Water and Sediment, volume %
Cloud point, °C
Oxidative Stability, hr
Sulfur, ppm
Visual appearance
Flash Point

Method ASTM D 93

- Recent Change- Limit: 93°C minimum
- Temperature
- A sample is heated in a close vessel and ignited. When the sample burns, the temperature is recorded.

Alcohol Control

- One of the following must be met:
  1. Methanol content EN 14110: 0.2 max % volume
  2. Flash point D 93 : 130 min °C
Flash Point Testing
Method D 2709
Limit of 500 ppm, examining the free water content
100 mL of sample are centrifuged at 800 rcf for 10 min at 21° to 32°C in calibrated tube.
Water and Sediment

- Biodiesel can absorb 1500 ppm of water while diesel only 50 ppm.
- Free water can cause corrosion of fuel injection parts.
- Housekeeping issue
Sterols or sterol glucosides?

Sterol glucosides are naturally occurring in vegetable oils

Can cause haze at 10-90ppm

Melting point is 240°C

ADM research: cold flow issues related to sterol glucosides.
Karl Fischer: Moisture Determination
Acid Number

- Test Method ASTM D 664
- Limits: 0.5 mg KOH/g maximum
- pH sensitive electrode
- May also be determined using indicators
Sulfated Ash

- Test Method ASTM D 874
- Limits: 0.020 % mass maximum
- Sample ignited and burned
- Ash + carbon (C removed by $H_2SO_4$)
- Indication of concentration of metal additives (Ba, Ca, Mg, Na, K, Sn, Zn)
- More than 0.020 % indicates residual soap & catalyst
Free and Total Glycerin

- Test Method ASTM D 6584
- Limits: 0.020 % mass free glycerin
- 0.240 % mass total glycerin
- Gas Chromatography with FID detection
- Quantifies glycerol, mono-, di- and triglycerides
Production Factors: Total Glycerol

- Measured with gas chromatograph (ASTM D6584) and requires a skilled operator.
- Saturated monoglycerides have very low solubility in biodiesel.
- If too high, there may be problems with fuel filter plugging and fuel stability.
Chromatograms – The Good

Free Glycerin = 0.0008
Total Glycerin = 0.1241
Chromatogram – The Bad

Free Glycerin = 0.4853  
Total Glycerin = 0.9237
Chromatogram – The Ugly

Free Glycerin = 0.0463
Total Glycerin = 2.3692
Sulfur

- Test Method ASTM D 5453
- Limits: 0.05 % mass maximum
- S oxidized to SO$_2$ at high temperatures
- UV fluorescence of emitted gases
  \[ \text{SO}_2 \rightarrow \text{SO}_2^* \rightarrow \text{SO}_2 \]
- S limits dictated by environmental considerations (S15 or S500)
- EPA regulations
- Feedstock variation
Cloud point

- Test Method ASTM D 2500
- Limits: No established limits
- Reported in °C
- Sample cooled and examined visually until first cloud appears.
- Indicates the lowest temperature at which fuel is usable.
- Generally higher than diesel.
Cold Flow

- Wax molecules in diesel fuel and biodiesel tend to crystallize at low temperatures.
- Crystals agglomerate to form large masses.
- This can cause filter plugging and eventually the fuel will become a solid mass.
- Soy biodiesel gels at 32°F
- #2 diesel fuel gels at 10 to 14 °F.
- Biodiesel from saturated feedstocks can gel as high as 50-55°F.
- In contrast, *petroleum* diesel fuel is a mixture of hundreds of different compounds that solidify at very different temperatures. So, even if some compounds crystallize at a relatively high temperature, many other compounds will stay liquid to a much lower temperature.
- Watch your soap & water content!
Cloud Point, CFPP, LTFT
Oxidative Stability

- Equipment: Rancimat or OSI
- Method: EN 14112; 3 minimum hours
- Equipment cost: 10k- 17k
- Recent addition to ASTM 6751
- Products of oxidation in biodiesel are various acids or polymers, can cause fuel system deposits and lead to filter plugging & fuel system malfunctions.
- Additives can improve the oxidation stability performance of biodiesel.
Fuel oxidation

- Biodiesel will react with oxygen from the air to form polymers, acids, etc.
- Acids:
  - Presence indicated by increasing Acid Value
  - Cause corrosion of metal components
  - Corrosion can be aggravated by water
- Polymers:
  - Sediments that can plug fuel filters and coat metal surfaces
Visual Inspection
Class I & II metals: Ca/Mg/Na/K

Calcium & Magnesium & Sodium & Potassium can be in biodiesel as abrasive solids or soluble metallic soaps.

Solids contribute to injector, fuel pump, piston, and ring wear, & engine deposits.

Soluble metallic soaps have little effect on wear, but filter clogging & engine deposits.

These compounds may also be collected in exhaust particulate removal devices.
Less Critical Parameters

- Cetane
- Distillation Temperature
- Viscosity
- Carbon Residue
- Phosphorus
- Copper Strip Corrosion
Other Biodiesel Testing

- Saftest
- Completeness of Reaction (3/27 Methanol Test)
- Soap test: AOCS method
- Wilkes Infraspec
- Paradigm Sensors
- Fleet Biodiesel
- pH Lip Test
- Wika Water test
- Microbial growth, algae-x
Completion of Reaction

- Dissolve 3 ml of biodiesel in 27 ml of methanol.
- The biodiesel should be fully soluble in the methanol forming a clear bright phase.
- If you observe un-dissolved material at the bottom of the sample the reaction did not proceed to completion.
- Each ml of undissolved material corresponds to 4% by volume.
Samples Passing the 3/27 Test

0.0900 Bound Glycerin
Crystal clear, no cloudiness or precipitate.

0.2139 Bound Glycerin
Although cloudy, there were no droplets of precipitate.
Samples Failing the 3/27 Test

0.9256 Bound Glycerin
Note the falling droplets of unreacted oil.

1.8260 Bound Glycerin
Biodiesel Conversion Test
BioPro Go/No Go Oil Testing Kit

Acid Number Qualitative Tests

Pass

Fail
Soap- AOCS test method

- Gels at ambient temperature as little as 5%
- Cause problems with glycerol separation and washing
- Soap can be split by acidulating
- Soap is usually clear and very viscous
- Methanol will act as a cosolvent and keep soap in solution with the biodiesel
- High soap levels = high sulfated ash number
- High FFA and water content lead to soap formation in process
Soap Test

Titrating from blue/green to straw yellow….
Wilkes InfraSpec measures percent biodiesel in diesel fuel, ethanol in gasoline, water in ethanol as well as total glycerides during the biodiesel pass/fail determination in less than 5 minutes.
* Paradigm Sensors’ i-SPEC™ tests TOTAL GLYCERIN in blended fuels (B6-B20), which is in accordance with ASTM proposal that the biodiesel portion of the fuel must meet ASTM 6751 prior to blending.
Fleet Biodiesel
pHLip Test

Titration of “Near-Spec” Biodiesel into Reference Soy B100

Reference  20%  40%  60%  80%  100%
< 0.2% Total Glycerin  All had <0.005% Free Glycerin  0.31% Total Glycerin
Wika Water Test
Microbial growth

• Certain varieties of bacteria and fungi can grow in diesel fuel tanks.
• Growth occurs at the interface of the fuel and water at the bottom of the fuel tank.
• Water must be drained from tank bottoms on a regular basis.
• ULSD
• Biocides are available to control microbial growth.
  • Dead microbes can still plug filters.
  • Water elimination is preferred over treatment.
Bacteria Growth

Fungal Growth
Operational issues

- Microbial growth – ULSD & moisture
  Treat your storage tanks for moisture/biocide
- Incomplete reaction
- Aged fuel
- Cold Flow
- Low energy content (not harmful)

Fuel filter plugging is the most common operational issue
Certificate of Analysis

Piedmont Biofuels

Certificate of Analysis

Shipment Manifest Number: 2007107
Customer’s P.O. Number: verbal

CARRIER NAME

CUSTOMER NAME

<table>
<thead>
<tr>
<th>Product Code</th>
<th>Description</th>
<th>Gallons</th>
</tr>
</thead>
<tbody>
<tr>
<td>B99</td>
<td>B99 99% Dyed Biodiesel Mixture (99.99% B100/0.01% MV)</td>
<td></td>
</tr>
<tr>
<td>B80</td>
<td>Ultralow Sulfur Diesel (For B80 mixture)</td>
<td></td>
</tr>
</tbody>
</table>

This fuel is ultra low sulfur diesel blended with methyl ester biodiesel and contains dye. This fuel has a min cetane of 40, a max cloud of 15 and max sulfate of 15 ppm with lubeity. Customer and carrier certify and warrant their compliance with all security requirements under USDOT Regulations including 49 CFR 172.

Piedmont Biofuels Industrial LLC is responsible for collecting and remitting the state motor fuel taxes for any products subject to such tax under North Carolina Regulations.

Driver’s Signature: 

Date: 

Received by: 

Date: 

CERTIFICATE OF ANALYSIS OF B100

Report Date: 

Lot Number: 

Product Identification: Fatty Acid Methyl Ester

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>Typical value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flashpoint</td>
<td>ºC</td>
<td>above 148 ºC / 300 ºF</td>
</tr>
<tr>
<td>Total and Free Glycerin</td>
<td>% Mass</td>
<td>0.12%</td>
</tr>
<tr>
<td>Water and Sediment</td>
<td>% volume</td>
<td>ND</td>
</tr>
<tr>
<td>Moisture</td>
<td>PPM</td>
<td>1000 ppm</td>
</tr>
<tr>
<td>Acid Number</td>
<td>mg KOH/g</td>
<td>0.1 - 0.2</td>
</tr>
<tr>
<td>Soap</td>
<td>PPM</td>
<td>less than 20 ppm</td>
</tr>
</tbody>
</table>

* Property values are expressed as follows:

- ND = None Detected
- " = Latest Value

The preceding data is provided at the request of and for the convenience of the customer. It is the responsibility of the customer to verify data contained on the report and to perform any other analysis necessary to prove or disprove the intended use by the customer.
Biodiesel Quality Standard

ASTM D 6751 Standards

- Fuel quality is critical for proper functioning
- Standards ensure satisfactory operation in diesel engines

BQ 9000 Certification

- Certifies biodiesel producers and markers
- Feeling of confidence for:
  - Biodiesel Producers
  - Engine and Vehicle Manufacturers
  - Distributors
  - Consumers
B5 & B20 ASTM Specifications

- December ASTM Meeting: 4 ballots passed subcommittee
- New cold soak filtration method (sterol glucosides saturated monoglycerides, soap, water) 360 sec minimum
- Up to B5 in ASTM D975
- Up to B5 in ASTM D396
- Stand alone B6-B20 specification passed subcommittee level
To Recap

- Small and large scale production can produce quality biodiesel
- On-site and in-process analysis is essential
- Watch for residual contamination
- Correct product handling and storage procedures is essential
- Final product must meet ASTM D 6751
Contact

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rachel@biofuels.coop
919-321-8260
www.biofuels.coop
The Role of Sterol Glucosides on Filter Plugging
By Inmok Lee, Lisa M. Pfalzgraf, George B. Poppe, Erica Powers and Troy Haines

Resources

• http://biofuels.coop/
• www.biodiesel.org
• http://www.bq-9000.org/
• www.me.iastate.edu/biodiesel
• http://www.uidaho.edu/bioenergy/index.html
• http://www.cytoculture.com/
• http://www.biodieselmagazine.com
• http://www.algae-x.net/