



TENNESSEE DEPARTMENT OF AGRICULTURE
Regulatory Services Division



Fuel Quality & ASTM D6751-09

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Tennessee Department of Agriculture

2009 Virginia & Tennessee Soy Biodiesel Workshops

Biodiesel 301: Soy Biodiesel and Our Changing Alt Fuels Landscape

August 25-26, 2009

Richmond, VA

Knoxville, TN



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Presentation Outline

- **History of ASTM D6751**
 - **The first ASTM Specification vs. Today's Specification**
 - **Important Changes to the Specification**
 - **Influence on Other Specifications**
 - **ASTM D975**
 - **ASTM D7467**
 - **ASTM D396**
- **What to expect next for D6751**
- **Questions**



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History of ASTM D6751

- **June 1994 – ASTM Committee D02 - Sub. E Formed the Biodiesel Task Force – Objective #1 – Development of Standard Specification for Biodiesel Fuel Blend Stock**
- **June 1999 – PS 121-99 was approved by D02**
- **December 2001 – ASTM Standard Specification Passes Committee D02 and is issued as ASTM D6751-02**
 - **Note: D6751 NOT designed for blends > B20**





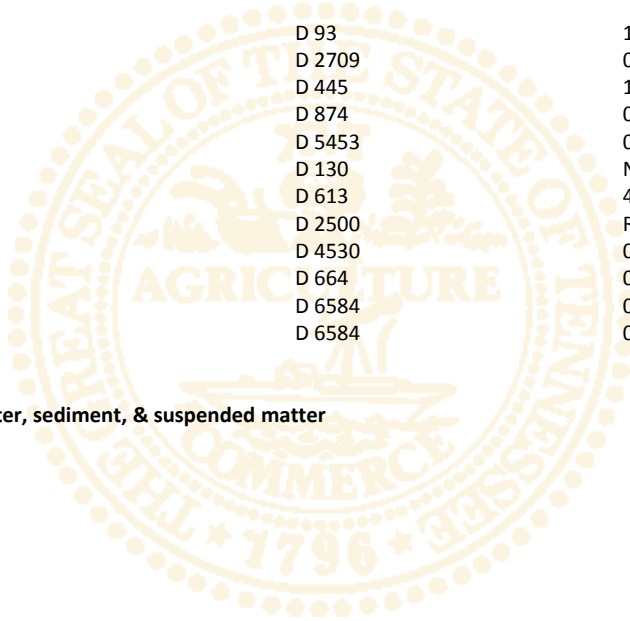
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ASTM PS 121-99

<u>Property</u>	<u>ASTM Method</u>	<u>Limits</u>	<u>Units</u>
Flash Point (closed cup)	D 93	100 min.	Degrees C
Water & Sediment	D 2709	0.050 max	Vol %
Kinematic Viscosity, 40 C	D 445	1.9 - 6.0	mm2/sec.
Sulfated Ash	D 874	0.020 max	mass %
Sulfur	D 5453	0.050 max (500)	% mass (ppm)
Copper Strip Corrosion	D 130	No. 3 max	
Cetane number	D 613	40 min	
Cloud Point	D 2500	Report	Degrees C
Carbon Residue on 100% sample	D 4530	0.050 max	% mass
Acid Number	D 664	0.80 max	mg KOH/g
Free Glycerin	D 6584	0.020 max	% mass
Total Glycerin	D 6584	0.240 max	% mass

Workmanship Free of undissolved water, sediment, & suspended matter





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ASTM D6751-09

<u>Property</u>	<u>ASTM Method</u>	<u>Limits</u>	<u>Units</u>
Calcium & Magnesium, combined	EN 14538	5 max	ppm
Flash Point (closed cup)	D 93	93 min.	Degrees C
Alcohol Control (One of the following must be met)			
1. Methanol Content	EN14110	0.2 max	mass %
2. Flash Point	D93	130 min	Degrees C
Water & Sediment	D 2709	0.050 max	Vol %
Kinematic Viscosity, 40 C	D 445	1.9 - 6.0	mm2/sec.
Sulfated Ash	D 874	0.020 max	mass %
Sulfur			
S 15 Grade	D 5453	0.0015 max (15)	% mass (ppm)
S 500 Grade	D 5453	0.050 max (500)	% mass (ppm)
Copper Strip Corrosion	D 130	No. 3 max	
Cetane number	D 613	47 min	
Cloud Point	D 2500	Report	Degrees C
Carbon Residue on 100% sample	D 4530	0.050 max	% mass
Acid Number	D 664	0.50 max	mg KOH/g
Cold soak filterability	Annex A1	360 max*	seconds
Free Glycerin	D 6584	0.020 max	% mass
Total Glycerin	D 6584	0.240 max	% mass
Phosphorus Content	D 4951	0.001 max	% mass
Distillation, T90 Atmospheric Equiv. Temp.	D 1160	360 max	Degrees C
Sodium/Potassium, combined	EN 14538	5 max	ppm
Oxidation Stability	EN 14112	3 min	hours

* B100 intended for blending into diesel fuel that is expected to give satisfactory vehicle performance at fuel temperatures at or below -12 Deg. C shall comply with the cold soak filterability limit of 200 s, max. (VA & TN Lowest 10th Percentile = -11C)

Workmanship Free of undissolved water, sediment, & suspended matter

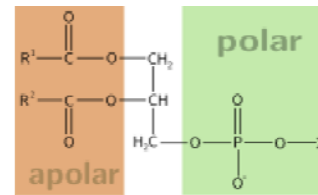
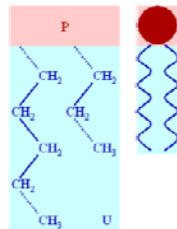


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D6751 Developmental Milestones Since Becoming a Full ASTM Standard

- 2002 Committee D02 Approved Phosphorous Content Value of .001 max % mass
 - o Rationale:
 - P can damage catalytic converters used in emissions control systems & converters are becoming more common on diesel equipment
 - B100 typically has less than 1 ppm, so 10 ppm not controversial
 - Potential Source – Mainly from phospholipids in feedstock – a lipid that is a major component of all cell membranes





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D6751 Developmental Milestones Since Becoming a Full ASTM Standard

- 2005 Committee D02 Approved :
 - o Revised Acid No. from 0.80 to 0.50 mg KOH/g max
 - o Addition of Total Na + K value of 5 ppm max to the Specification
 - o Rationale:
 - Data presented that the European value of 0.50 provided better control for Acid No. related issues (fuel system deposits, pump and filter operation).
 - Na & K important to injector, fuel pump, piston and ring wear, and engine deposits.

Introduced into fuel mainly during production process (catalyst residues)





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D6751 Developmental Milestones Since Becoming a Full ASTM Standard

- 2006 Committee D02 Approved :
 - o Addition of Ca + Mg value of 5 ppm max to the Specification
 - o Rationale: Ca and Mg, as abrasive solids, contribute to injector, fuel pump, piston and ring wear, as well as engine deposits. Metallic soaps contribute to filter plugging and engine deposits. Additionally, back pressure on exhaust particulate removal devices.

Introduced into fuel mainly during production process (water washing)

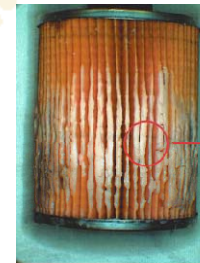
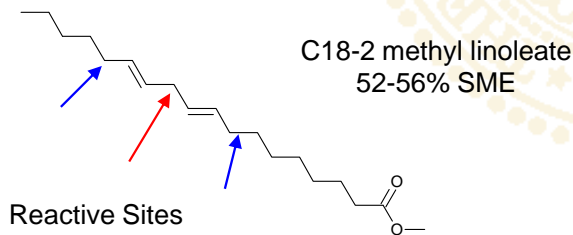


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D6751 Developmental Milestones Since Becoming a Full ASTM Standard

- 2006 Committee D02 Approved :
 - o Addition of Oxidation Stability Requirement value of 3 hr. min. to the Specification
 - o Rationale: Engine and FI Equipment Mfg. requested limit based on needs to prevent sediment formation in B20 blends made from D6751 material.



Deposits from oxidation in a B20 field test



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D6751 Developmental Milestones Since Becoming a Full ASTM Standard

- 2006 Committee D02 Approved :
 - o Revised Flash Point Limit and Procedure to control MeOH Content
 - Lowered FP requirement from 130 to 93 Deg. C
 - Placed control on ROH limit by requiring that either:
 - FP 130 min or
 - MeOH Content 0.2 % vol max
 - o Rationale: Limits the level of unreacted ROH remaining in finished fuel – influences FP and premature injector failure



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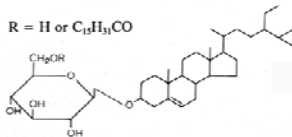


D6751 Developmental Milestones Since Becoming a Full ASTM Standard

- 2008 Committee D02 Approved :
 - o Cold Soak Filtration Test Method & Specified a Cold Soak Filtration Limit of 360 seconds, max (200 s max if ambient temperatures expected to be -12 Deg. C or lower)
 - 300 mL B100 chilled to 40°F, 16 h, warmed to room temp, vacuum filtered through a 0.7µm glass fiber filter. Sample must pass through filter in 360 s
 - This test is NOT specifically a Low Temperature Operability Test:
 - Developed to control precipitates above the Cloud Point, i.e. Minor Compounds including; Monoglycerides, Sterol Glucosides, Soaps, Water

β-sitosterol glucosides

R = H or C₁₂H₂₅CO





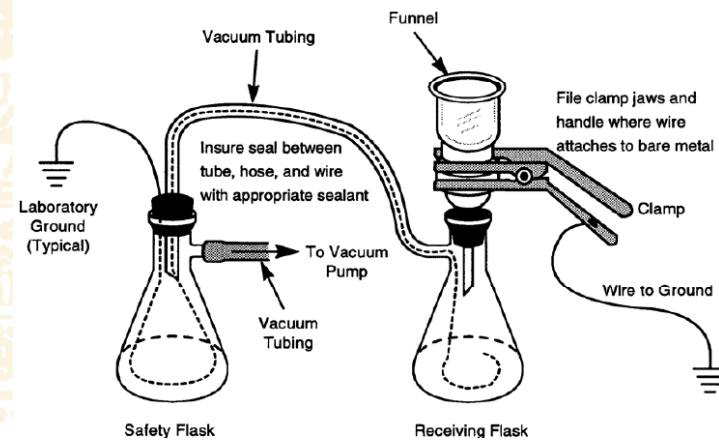
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D6751 Developmental Milestones Since Becoming a Full ASTM Standard

ADM Study on Minor Compounds Effect on Cold Soak Filtration:

Components added, ppm				Responses	
MG	SG	Soap	Water	CP, °C	Filter time, s
0	40	0	500	1.4	1022
10000	0	40	500	3.6	107
10000	40	20	0	2.1	904
0	0	0	500	0.6	83
10000	20	40	0	2.4	868
0	40	40	0	0.3	1412
0	0	40	0	1.6	488
10000	40	40	500	3.9	3562
5000	40	0	0	0.3	440
10000	0	0	0	1.8	97
10000	20	0	500	2.3	2139
0	20	0	0	0.4	87
10000	40	0	250	2.2	895
5000	0	20	250	1.4	201
0	20	40	500	0.4	1531
5000	20	20	250	0.5	446
5000	20	20	250	0.6	362
5000	20	20	250	0.5	394
7500	10	10	125	1.4	103
2500	30	10	250	0.7	320
7500	30	30	375	2.3	1207
5000	40	40	500	1.3	2431
0	40	0	250	0.8	982
0	0	0	500	1.4	85
10000	20	40	0	2.3	609
0	40	40	0	0.4	1265
0	0	40	0	0.6	558
0	20	40	500	0.5	1497
10000	0	40	500	3.6	105
10000	40	20	0	2.3	889





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Example of Field Problem Related to Minor Compounds

- **Late 2007 Contacted by a Biodiesel Marketer Regarding Filter Plugging in Customer Fleet**
- **Contacted Fleet Operator For Description of Problem**
 - Verified Fuel Systems in Problem Vehicles
 - Verified when Problem Began
 - Collected Plugged Filters and Samples of the Biodiesel Blends
- **Contacted Biodiesel Marketer**
 - Collected Sample of B100 Currently In Stock



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Example of Field Problem Related to Minor Compounds

- **The Fleet Operator Confirmed That:**
 - All Vehicles Affected Had 2002 and 2003 High Pressure Fuel Systems
Older Models Without High Pressure Systems Had No Issues
 - Fleet had been operating on ~B10 since May 2007 w/o Issue
 - Within 2-3 Week period, 15 Vehicle Failures
 - No Change in Filter Brands, No Additional Additives Being Used



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Sample Results

Lab 1	Result	Spec , Max	R of Method	r of Method
Total Glycerin, Mass %	0.167	0.24	0.095	0.037
Free Glycerin, Mass %	0.031	0.02	0.020	0.004
Lab 2.	Result	Spec , Max	R of Method	r of Method
Total Glycerin, Mass %	0.135	0.24	0.079	0.035
Free Glycerin, Mass %	0.025	0.02	0.018	0.004
Acid No., mg KOH/g	0.33	0.5	0.188	0.059
Cold Soak Filtration, s	>1200	N/A	N/A	N/A
Water Content, ppm	70	500	216	19.42
Phosphorous, ppm	3	10	N/A	N/A
Ca + Mg, ppm	7	5	2.229	0.4334
Na + K, ppm	1	5	1.13	.213
Lab 3	Result	Spec , Max	R of Method	r of Method
Total Glycerin, Mass %	0.140	0.24	0.081	0.035
Free Glycerin, Mass %	0.027	0.02	0.019	0.004
Cold Soak Filtration, s	>900	N/A	N/A	N/A
Phosphorous, ppm	<10	10	N/A	N/A
Ca + Mg, ppm	6	5	2.08	0.4102
Na + K, ppm	<2	5	N/A	N/A

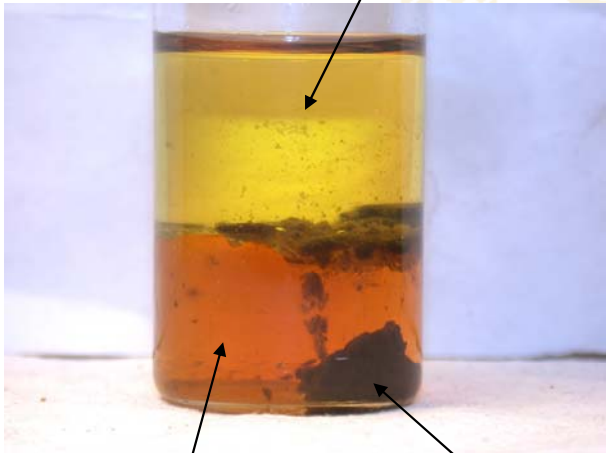


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Filter Analysis

Diesel/Biodiesel



MeOH/Water/Glycerin

Reformed Solids – Mainly Sitosterol Compounds



CC(C)[C@H]1CC[C@@H]2[C@@]1(CC[C@H]3[C@H]2CC=C4[C@@]3(CC[C@@H](C4)O)C)C



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Passage of the Cold Soak Filtration Test Method and Limits in Table 1 of D6751 Generated:

- 1. Revision of ASTM D975 Standard Specification for Diesel Fuel to allow up to 5% by volume Biodiesel**
- 2. Passage of a new ASTM D7467 Standard Specification for Biodiesel Blend (B6 to B20)**
 - a) D975 limits plus: Acid No., Oxidation Stability, and Biodiesel Content**
- 3. Revision of ASTM D396 Standard Specification for Fuel Oils to allow up to 5% Biodiesel**

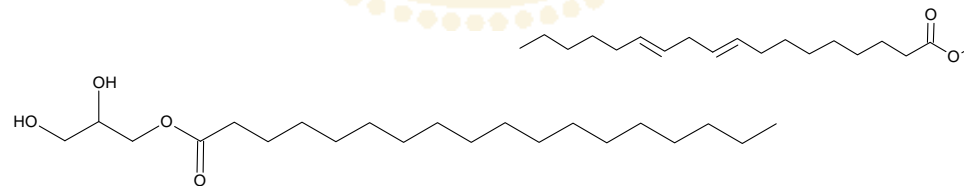


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What is Next For Biodiesel?

- **Restriction on monoglyceride content being discussed – (saturated)**
- **New definition of biodiesel- feedstock not derived from oils/fats**
 - **Biomass / Cane Carbohydrate + ROH → biodiesel**
 - **Catalysts are designer microbes**
 - **Structures of output molecules can be controlled**
 - **Process can also make HC's, ROH, others**
- **New Test Methods**
 - **Water & Sediment**
 - **Acid No.**





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Questions ?

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