Biodiesel Fuel at UConn

Certification of Biofuels to ASTM Standards

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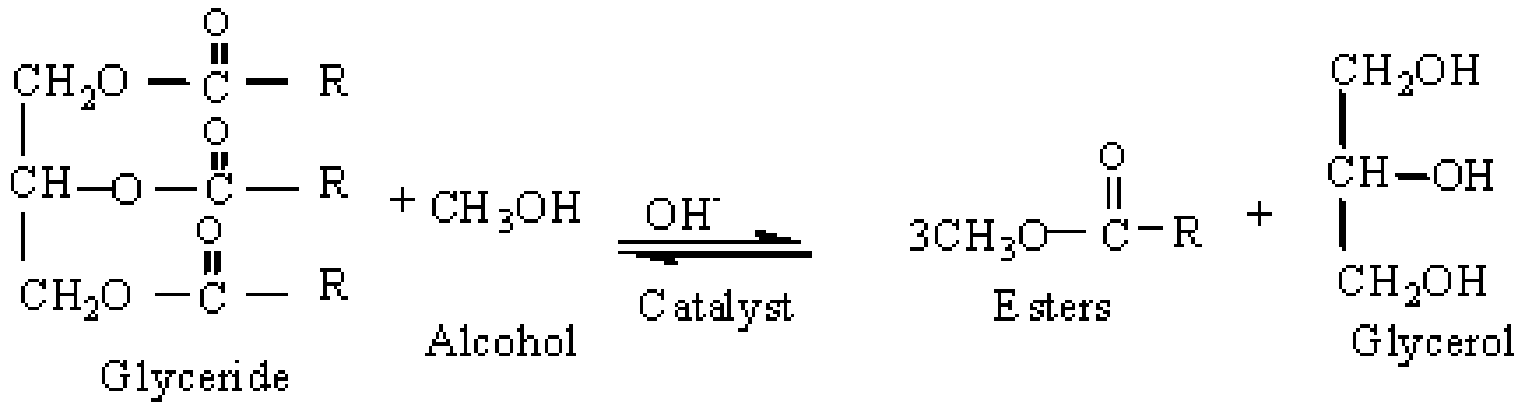
How is Biodiesel Made?

Waste Cooking Oil **Biodiesel** **Byproduct**



Glyceride = Component of Vegetable Oil

Alcohol = Methanol or Ethanol

Catalyst = Potassium Hydroxide

Esters = Biodiesel (light)

Glycerol = Byproduct (dark)

http://www.esru.strath.ac.uk/EandE/Web_sites/02-03/biofuels/what_biodiesel.htm

Waste Vegetable Oil

Reaction Mixture

Top Layer= Product Biodiesel

That needs water washing and further clarification Product

Bottom Layer- Glycerine

Which slowly phase separates

There are 14 different Required tests According to ASTM D 6751-03a

"Standard Specifications for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels"

These standard specifications cover biodiesel (B100) for use as a blend component with diesel fuel oils.

Requirements: The biodiesel specified shall be mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats.

Disclaimers: 1. To meet special operating conditions, modifications of individual limiting requirements may be agreed upon between purchaser, seller, and manufacturer.

2. Nothing in this specification shall preclude observance of federal, state, or local regulations which may be more restrictive.

Table 1 of D 6751. “Detailed Requirements for Biodiesel (B100)- Physical Tests- 1 of 6.

- **Flash Point (ASTM D 93).** Requirement of 130 ^{o}C minimum. It is the lowest temperature corrected to barometric pressure at which application of an ignition source causes the vapors of a sample to ignite. Requires a Pensky-Martens closed cup apparatus (manual or automated).
- This tests limits the amount of unreacted methanol in B100 sample. The flash point is important for legal requirement and safety precautions involved with fuel handling and storage.

Table 1 of D 6751. "Detailed Requirements for Biodiesel (B100)- Physical Tests- 2 of 6.

- **Kinematic Viscosity (ASTM D 445)** Limits between 1.9- 6.0 mm^2/sec at 40 ^oC. This test involves measuring the time it takes for a volume of liquid to flow under gravity at a specified temperature through a calibrated glass capillary viscometer.
- It is important for the required operational conditions, handling and optimum storage that various petroleum fuels have the proper viscosity.
- Note cooking oil has a viscosity up to 10 X greater than B100!

Table 1 of D 6751. “Detailed Requirements for Biodiesel (B100)- Physical Tests- 3 of 6.

- **Cloud Point (ASTM D 2500)** reported in degrees ^{o}C, The cloud point is defined as the temperature of a liquid sample when the smallest observable cluster of wax crystals first appears upon cooling under prescribed test conditions. B-100 generally has a higher cloud point than petroleum based diesel fuel. The cloud point is especially important as it limits the cold flow properties of the resulting blend.
- The intent of the cloud point measurement is to obtain the temperature at which the liquid fuel begins to change from a single liquid phase to a two phase system. This test can be in an automated instrument. The sample is cooled in a 1.5 +/- 0.1 ^{o}C/min device over the range from +70 tp -40 to ^{o}C, while being continuously illuminated by a light source.

Table 1 of D 6751. “Detailed Requirements for Biodiesel (B100)- Physical Tests- 4 of 6.

- **Water and Sediment (ASTM D 2709) 0.50 % volume, maximun.** This method describes the manual measurement of the actual volume of the lower phase. A special, 100-mL cone-shaped centrifuge tube is used and the full contents are centrifuged for 10 minutes at a minimum speed of 600 relative centrifugal force (rcf), with the sample held at 60 +/- 3 ^{o}C. The lower phase volume is readable to 0.005-0.10 mL. (UCONN has found that buying such a thermally controlled centrifuge may cost $ 15,000 and is available from only a few vendors. We are trying to improvise using a cheaper $ 1,500 centrifuge and a lot of hot air or heated nitrogen!- Consult Prof. Parnas for details about the “hot air”).

Table 1 of D 6751. “Detailed Requirements for Biodiesel (B100)- Physical Tests- 5 of 6.

- **Centane Number (ASTM D613)** >47 Centane No.

This ASTM method measures combustion characteristics of diesel fuels run in on a standard, test engine (single cylinder, four-stroke cycle, various compression, indirect injected), when standardized with n-centane having a CN =100 and alpha-methyl-naphthalane having a CN= 0.

- Requires a specially designed engine and mixing various fuel blends.
- Usually **t**his measurement is contracted to a an independent laboratory which is participating in the ASTM Subcommittee D02-01 Diesel National Exchange Group.

Table 1 of D 6751. “Detailed Requirements for Biodiesel (B100)- Physical Tests- 6 of 6.

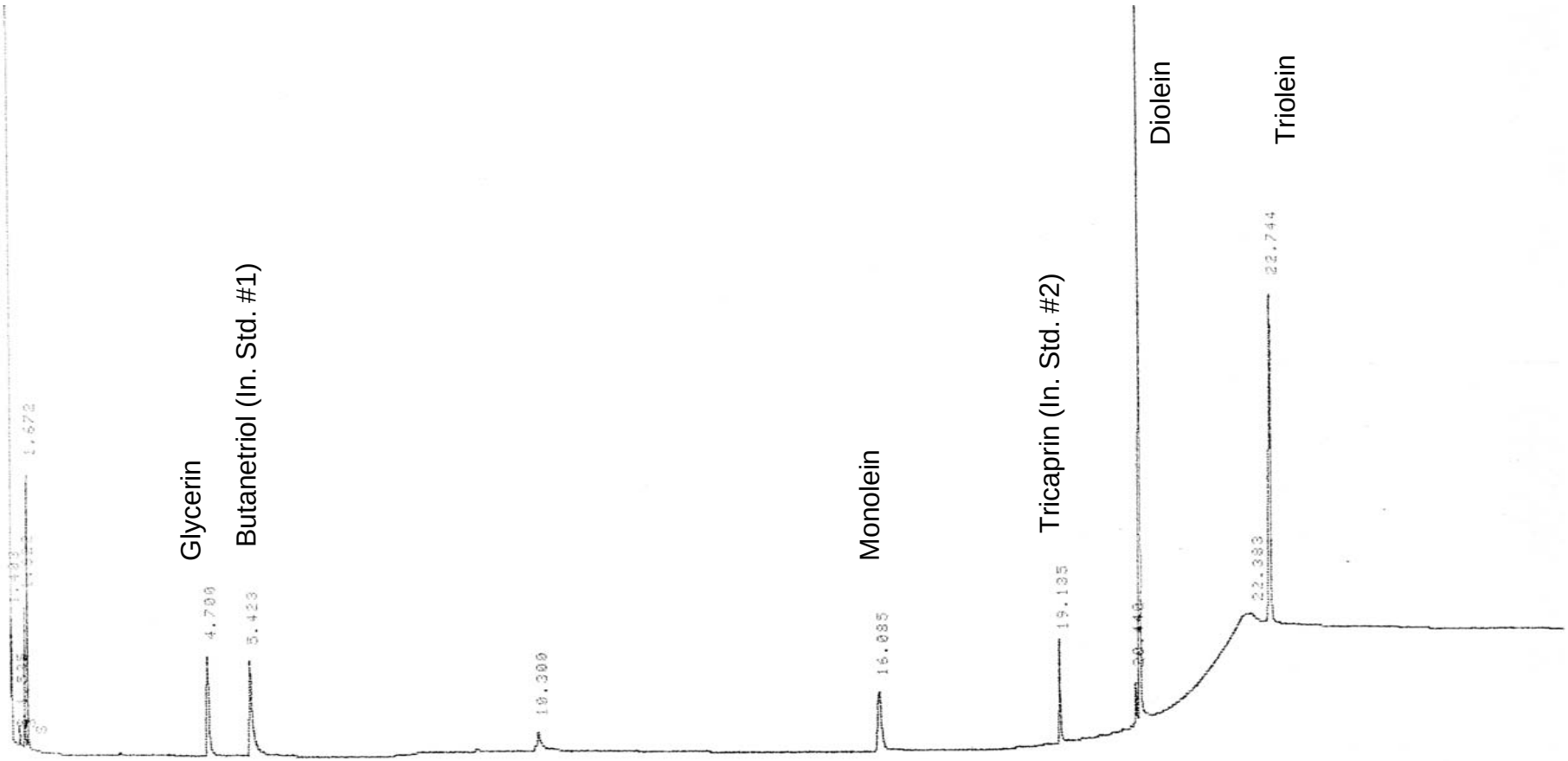
- **Distillation Temperature (ASTM 1160) requirement 360 ºC.** This test measures at what maximum temperature would the B-100 product completely be vaporized under a reduced pressure (ranging from 1 to 50 mm of mercury pressure). Data is collected of the initial and final boiling temperature point as well as the boiling curve (the volume per cent distilled over different temperature increments).
- Requires considerable amount of specified glassware, heating equipment and patience!

Table 1 of D 6751. “Detailed Requirements for Biodiesel (B100)- Chemical Tests 1 of 7.

- **Free and Total Glycerin (ASTM D 6584).** Requirement free glycerin < 0.020 % mass and total glycerin < 0.240 % mass. High levels of free and total glycerin can cause build-up and deposits in the fueling system. This test involves doing a 30 min. Gas Chromatographic (GC) analysis with a flame ionization detector (FID) and a special high temperature capillary GC column. Only 0.100 g. (about 7 drops) of the B-100 is weighted, two internal standards are added, any free acids are derivatized, diluted to 10 mL with heptane, and a 1.0 microL is injected on-column. This method gives a complete profile of the B100 product! Example chromatograms follow:

ASTM Method D6584 for Free and Total Glycerin

Showing the GC-FID of the six standards



ASTM Method D6584
Free and Total Glycerin

Sample 18.3 :

Bubble-Washed Biodiesel made by UCONN's Chem. Eng. Dept.

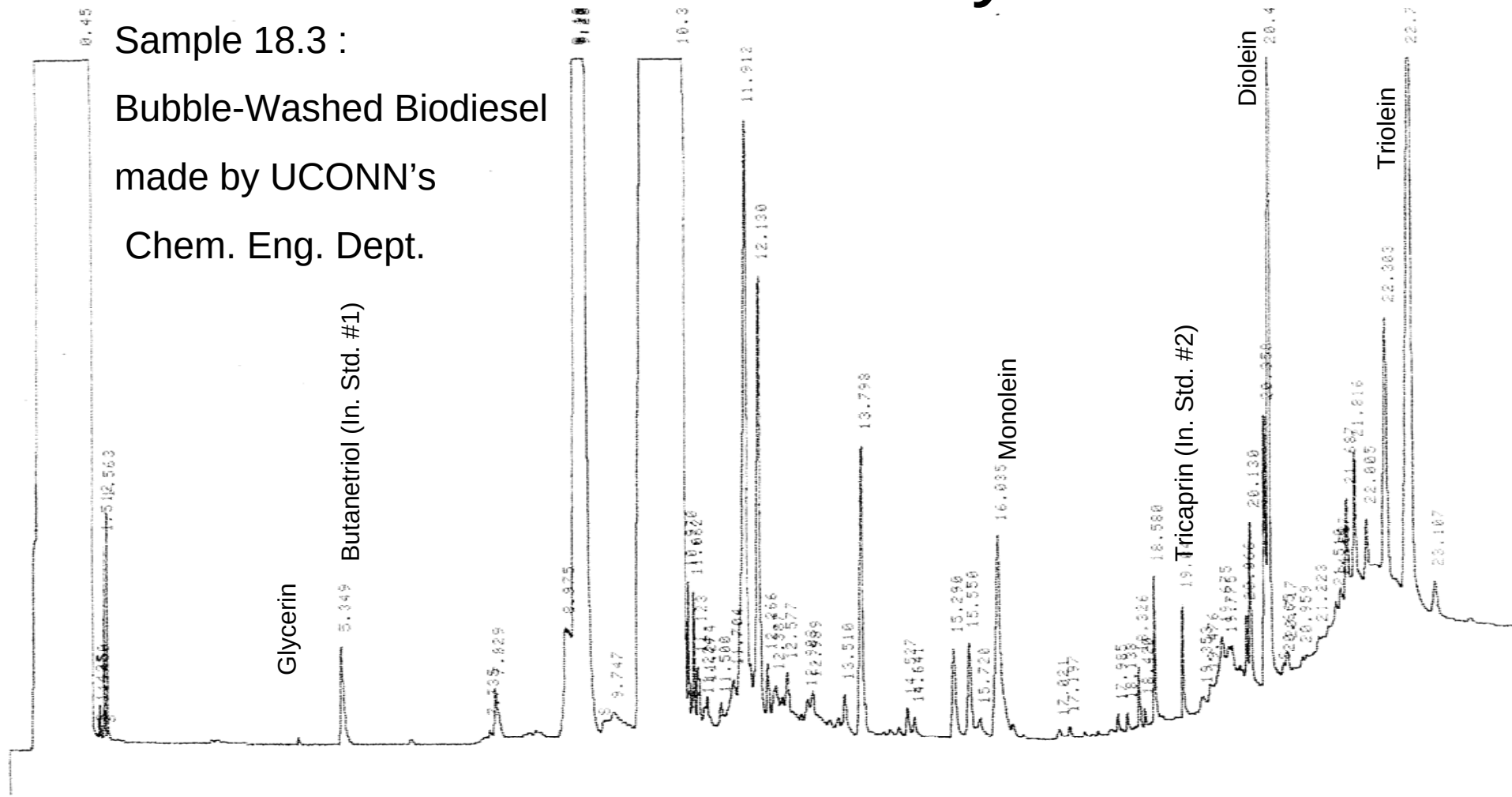


Table 1 of D 6751. “Detailed Requirements for Biodiesel (B100)- Chemical Tests 2 of 7.

- **Acid Number (ASTM D 664) < 0.80 mg KOH/g of oil.**
  This method measures the acid number or the amount of base that is needed to neutralize either the starting cooking oil or the final B100 product.
- **This measurement is important because used cooking oil often is acidic, due to oxidized fatty acids and that acidity must be neutralized for the full and proper transesterification reaction to occur. This method specifies the use of a potentiometric titration with a special dual-junction pH electrode as it involves a mostly non-aqueous titration.**
- **Alternate D 974 (by color indicator titration) or D 3242 methods may be used.**

Acid Number UCONN's waste cooking oil, 5.2 mg KOH/g of oil

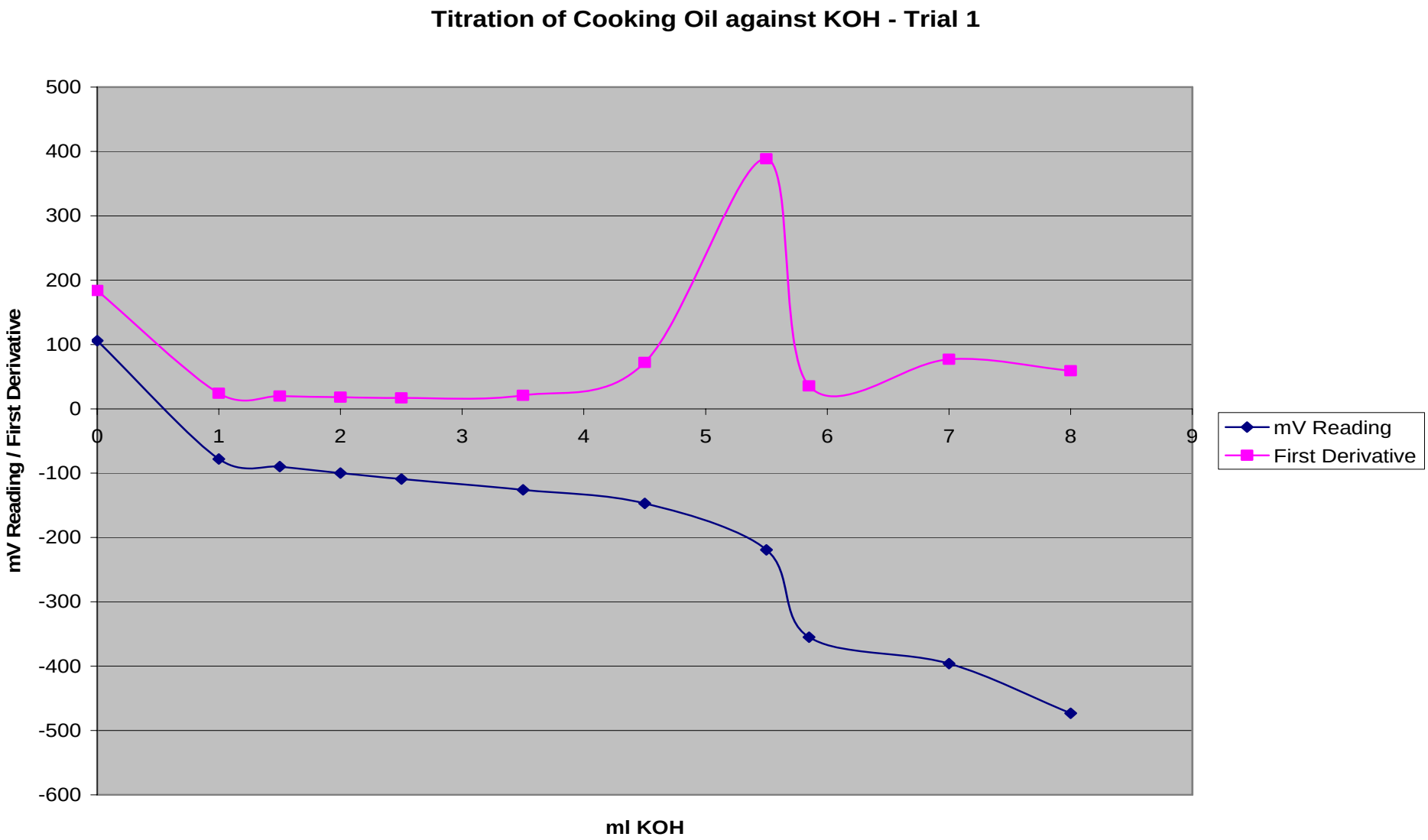


Table 1 of D 6751. "Detailed Requirements for Biodiesel (B100)- Chemical Tests 3 of 7.

- **Total Sulfur by Ultraviolet fluorescence (ASTM D 5453) <**0.0015 % mass or 15 ppm). This is the preferred (referee) test although other less sensitive methods can be used. The oil sample is inserted into a high temperature combustion tube, heated to 1200 ^{o}C, where the sulfur in an oxygen rich atmosphere is oxidized to SO_2. The SO_2 molecule is exposed to UV light which converts the molecule to excited SO_2*. This excited molecule emits fluorescent light which is detected by a sensitive photomultiplier.
- Requires a combustion tube, heater, sample insersion drive and a special sulfur analyzer.

Table 1 of D 6751. “Detailed Requirements for Biodiesel (B100)- Chemical Tests 4 of 7.

- **Carbon Residue (ASTM D 4530)** <0.050 % mass

  This method involves the measurement of the carbon residue formed after evaporation and heating to 500 ^{o}C in an inert (nitrogen) atmosphere. Can be done in an automated process starting with 15-mL capacity cups. The volatiles are swept away by the nitrogen gas stream and the carbon residue weighted.
- The carbon residue provides indication of the relative coke formation tendency of the fuel. However, the non-carbon ash residues present in the fuel sample will add to the carbon residue value.
- While ASTM D4530 is the referee method, ASTM D 189 or D524 may also be used.

Table 1 of D 6751. “Detailed Requirements for Biodiesel (B100)- Chemical Tests 5 of 7.

- **Sulfated Ash (ASTM D 874)** <0.020 % mass

  This method involves evaporating 50 – 100 mL of the B100 product until only ash and carbon remains. After cooling the residue is treated with concentrated sulfuric acid and heated to 775 ^{o}C in a muffle furnace until all of the carbon is oxidized to CO_2. The residual ash is cooled, re-treated with sulfuric acid, and heated again to 775 ^{o}C until a constant weight is obtained.
- The sulfated ash content is a measure of the concentration of metal containing compounds in the unused fuel.

Table 1 of D 6751. “Detailed Requirements for Biodiesel (B100)- Chemical Tests 6 of 7.

- **Phosphorus Content and the presence of other additive elements** by Inductively Coupled Plasma Atomic Emission Spectrometry (ASTM D 4951) This test covers the quantitative determination of Ba, B, Ca, Cu, Mg, P, S and Zn in unused fuels, lubricating oils and additives. < 0.001 % mass for Phosphorus.
- P can damage the catalytic converters used in emission controls that are becoming more common on diesel-powered vehicles.
- A very small, ca. 100 mg, sample is weighed, diluted in appropriate solvents, internal standards added and aspirated into the ICP instrument. The elemental emission is measured. (UCONN cost ca. $ 6/sample).

Table 1 of D 6751. “Detailed Requirements for Biodiesel (B100)- Chemical Tests 7 of 7.

Copper strip corrosion (ASTM D 130)dark tarnish max

•A polished copper metal strip is completely immersed for 3.0 hours in 30 mL of the fuel, which is contained in a glass test tube, but sealed in stainless steel holder immersed in a 100 ^{o}C bath. At the end of the heating period, the copper strip is removed, washed and the color and tarnish level assessed against a series of ASTM Copper Strip Corrosion Standards.

•This test serves to measure the relative corrosivity of the fuel to copper, brass and bronze parts in the fuel system. But seems to very subjective!

ASTM (American Society for Testing and Materials) Testing for Uconn Produced Biodiesel

Various Parametes **ASTM tests:**

Test	Acceptable range	UConn biodiesel result
Free Glycerin	0.02 mass % max.	0.000 mass %
Total Glycerin	0.24 mass % max.	0.214 mass %
Water & Sediment	0.05 vol. % max.	0.005 vol. %
Kinematic Viscosity	1.9-6.0 cSt @ 40° C	4.632 cSt @ 40° C
Cloud Point	(formerly 3° C max.)	-2.0° C
Acid Number	0.80 mg KOH/g max.	0.24 mg KOH/g

- **Nov. 2004 UCONN Biodiesel meets all of the above ASTM tests!**