

Biodiesel Quality

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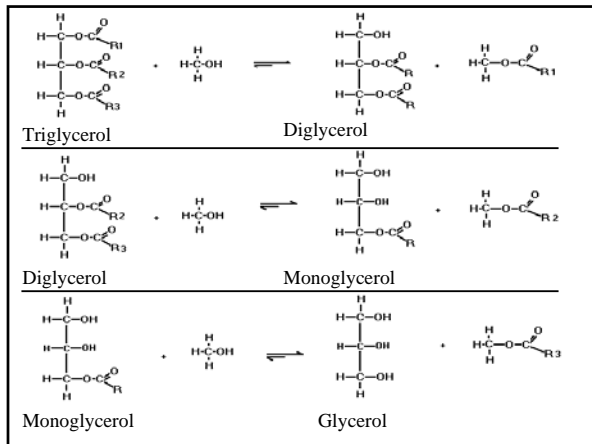
Product Quality

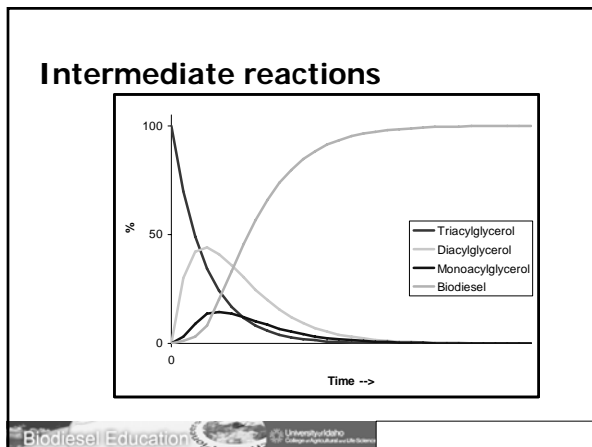
- Product quality is important – modern diesel engines are very sensitive to fuel.
- It is not biodiesel until it meets ASTM D6751.
- Critical properties are total glycerol (completeness of reaction) and acid value (fuel deterioration). Reaction must be >98% complete.

D6751 Specs

Biodiesel must meet the specifications of ASTM D 6751.

Property	Limits	Units
Total Glycerin	0.240 max.	% mass
Free Glycerin	0.020 max.	% mass
Flash Point	130 min.	°C
Sulfated Ash	0.020 max.	% mass
Acid Number	0.80 max.	mg KOH/g
Water & Sediment	0.050 max.	% vol.
Cloud Point	Report	°C
Carbon Residue	0.050 max.	% mass
Phosphorus Content	0.001 max.	% mass





Production issues

- Sum of tri, di, and mono acyl glycerols is called bound glycerol.
- Bound glycerol + free glycerol makes total glycerol.

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What are the implications?

- If biodiesel doesn't meet the total glycerol specification, nothing else matters.
- High total glycerol can cause high viscosity.
- Tends to form white flakes or sediments at the bottom of tank. The main problem is saturated monoglycerides.
- May cause filter plugging.
- May contribute to deposit formation.

Causes of high total glycerol

- Incomplete reaction. Getting a total glycerin below 0.24% requires 98% or better conversion of vegetable oil.
- Hydrolysis of mono di and tri glycerides during storage

Causes of incomplete reaction

- Not enough reaction time
- High FFA prevented complete reaction
- High water content
- Too much soap produced

How is it measured?

- Total glycerin is measured using a gas chromatograph (GC) (ASTM D6584).
- Outside laboratory testing costs \$200/test.
- A GC costs about \$40,000 and requires a trained operator. Realistically, all commercial producers need this capability on-site.
- AOCS method Ca 14-56 can be used as an alternative but can not be used to certify ASTM standard compliance.
- New methods are available for quick testing.

How to prevent?

- Make sure the FFA < 2% for base catalyzed reaction
- Make sure water content < 0.5%
- Processing at higher temperature
- Give enough time to complete the reaction
- Wash the biodiesel

Free glycerin

- Free glycerin is also a part of total glycerin and can be removed with a water wash.
- Warm water (~60°C) is more effective for water washing.
- Free glycerol also reduces the shelf life of biodiesel by absorbing atmospheric water and increasing water activity for microorganisms to grow.

Residual Alcohol

- European standards contain limits on alcohol (methanol) but the ASTM standard formally does not. It will soon.
- Flashpoint $> 130^{\circ}\text{C}$ will limit residual alcohol to less than 0.1%.
- Small amounts of alcohol will not affect engine.

Residual Catalyst

- Like alcohol, there is no residual catalyst level included in ASTM standard. However, limits on potassium and sodium are coming.
- Most catalyst is removed with glycerol.
- Residual catalyst will show up in sulfated ash, which is $< 0.020\%$ max.
- Abrasive solids and residual catalysts can contribute to injector, fuel pump, piston and ring wear, and also to engine deposits.

Acid value

- Acid value is an indicator of amount of free fatty acid in the fuel. $\text{AV} > 0.8 \text{ mg KOH/g}$ usually means fuel has gone rancid.
- AV is expressed as the amount of KOH (in milligrams) necessary to neutralize free fatty acids contained in 1 g of oil.
- Free fatty acid level may increase with age due to hydrolysis or oxidation.

Implications

- Biodiesel with high acid value has been shown to increase fueling system deposits and may increase the likelihood for corrosion.
- Increased recycle temperature in new fuel system designs may accelerate fuel degradation which could result in high acid values and increased filter plugging potential.

Water and sediment

- Increases water activity for biological growth.
- An appreciable amount of water and sediment in the fuel tends to cause fouling in the fuel system.
- An accumulation of sediment in the storage tank and on the filter screen can obstruct the flow from the tank to the engine.
- Water causes corrosion of the fuel tank and equipment and if combined with soap material which may be present in biodiesel, cause emulsion or a hazy appearance.
- Biodiesel can absorb 1500 ppm of water while diesel only 50 ppm.

Cloud point

- The temperature when wax crystal that is similar in appearance to a cloud is formed upon cooling at prescribed rate.
- Though there is no specification set by ASTM, it plays a major role in cold weather operability.
- Cloud Point and Pour Point have been routinely used to characterize the cold flow operability of diesel fuels.

Effect on biodiesel blend

- Each % of biodiesel increase the cloud point by about 0.2°C.
- Each % of Soy biodiesel increases the pour point by 0.25°C whereas each % increase of canola or mustard biodiesel increases pour point by 0.1°C.

Phosphorus

- Soybean contains about 1-3% of phospholipids or gums. Canola is about the same.
- Phosphorus is limited to allow for the future use of catalytic converters for exhaust treatment.
- Phosphorus is a powerful catalyst poison.

Sulfur

- Soy biodiesel does not have any sulfur on it.
- Canola oil has about 3-25 ppm of sulfur
- Sulfur content was lowered to 15 ppm from the original 500 ppm to conform to the scheduled EPA sulfur reduction requirements which are to be implemented over a period extending through 2006

Cetane number

- Cetane number is mostly feedstock dependent.
- Soy biodiesel has cetane number about 50.
- Saturated feedstocks such as animal fats have cetane numbers > 60.
- Regular diesel fuel as a cetane number of 42-45.

Storage Stability

- Chemical changes in fuel over time in presence of air.
- Catalyzed by higher temperature, some metals (container material!) and light.
- Unsaturated fatty acid chains form hydroperoxides, then aldehydes and short chain acids.
- If water is present, hydrolysis can occur and form long-chain fatty acids.

Storage Stability

- Acid value and viscosity increase with time and can be used as an indication that fuel has deteriorated.
- Currently no way to quantitatively determine the oxidation status of the biodiesel fuel that does not have significant disadvantages.
- Highly unsaturated fatty acids (C18:2, linoleic acid; C18:3 linolenic acid) oxidize more readily.

Storage Stability

- Additives such as BHT and TBHQ can enhance stability.
- Soybean and canola-based biodiesel has natural antioxidants (tocopherols, i.e., vitamin E).

BQ -9000 Quality Management Program

- Website: www.bq-9000.com
- Purpose: Ensure that quality fuel is marketed and used:

"The program is a unique combination of the ASTM standard for biodiesel, ASTM D 6751, and a quality systems program that includes storage, sampling, testing, blending, shipping, distribution, and fuel management practices."

Open to any biodiesel manufacturer, marketer or distributor of biodiesel and biodiesel blends in the United States and Canada.

Testing requirements

- A COA must be generated for each production lot of fuel.
- Initially, full specification testing must be conducted on seven consecutive production lots. If successful, reduced testing is allowed.
- The following reduced set of tests must be conducted on every production lot:
 - Flash pt., water and sediment, cloud pt., Acid value, free and total glycerin, visual appearance.
- Full specification testing is required at least every 6 months.

Further information

- www.BiodieselEducation.org
- www.me.iastate.edu/biodiesel
- www.biodiesel.org

