Quality Considerations and Control Factors for Homebrewing Biodiesel

John Bush

John@boulderbiodiesel.com

www.boulderbiodiesel.com

Quality?

- Modern Diesel Engines are very sensitive to fuel quality issues.
- Commercial “Biodiesel” defined by international quality standards - ASTM, DIN, EN . . .
- As a homebrewer, it’s up to you to determine your own quality standards

ASTM D6751 - Biodiesel Specification for United States

Property	Method	Limits	Units
Flash point, closed cup	D 93	130 min	°C
Water and sediment	D 2709	0.050 max	% volume
Kinematic viscosity, 40 ° C	D 445	1.9 – 6.0	mm^2/s
Sulfated ash	D 874	0.020 max	% mass
Total Sulfur	D 5453	0.0015 max*	% mass
Copper strip corrosion	D 130	No. 3 max	
Cetane number	D 613	47 min	
Cloud point	D 2500	Report to customer	°C
Carbon residue	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
Phosphorus	D 4951	0.0010 max	% mass
Vacuum distillation end point	D 1160	360 max, at T-90	°C

*for on-road fuel, beginning in 2006

(from the National Biodiesel Board www.biodiesel.org)

Most Important Specifications

Free and Total Glycerol

- Glycerol exists in two primary forms:
  - Free Glycerol - individual glycerol $C_3H_8O_3$ molecules
  - Bound Glycerol - the glycerol component found in triglyceride (TG), diglyceride (DG), and monoglyceride (MG) compounds

Most Important Specifications

Free Glycerol - 0.020% mass max.

- Most free glycerol settles out of the ester fraction after mixing and is removed, however some can remain suspended in the esters, particularly if there are soaps or other emulsifiers present.
- Glycerol is a polar compound, and is more soluble in water than fats/oils, so water washing helps remove leftover free glycerol from the esters.
- Excessive free glycerol indicates insufficient washing.

Most Important Specifications

Total Glycerol - 0.240% mass max.

- Total Glycerol = Bound Glycerol + Free Glycerol
- Bound Glycerol found in tri-, di-, or mono-glyceride compounds, which are reaction intermediaries.
  - Triglycerides - unreacted vegetable oil
  - Diglycerides, Monoglycerides - partially reacted oil
- Excessive bound glycerol indicates incomplete reaction.

Most Important Specifications

Total Glycerol - 0.240% mass max.

- Washed fuel that still does not meet spec usually due to incomplete reaction, and may need reprocessing.
- However, “Total Glycerol” includes both free and bound glycerol, so unwashed fuel may not meet this spec due to excessive free glycerol even if reaction is complete.

Most Important Specifications

Free and Total Glycerol - other comments

- Triglycerides are strongly polar and cannot be removed by water washing.
- Diglycerides and Monoglycerides express some polar and nonpolar properties, so are somewhat soluble in *both* fats/oils and water.
- This property makes it possible for fuel with *slight* excess of MGs and TGs prior to washing to “wash into spec” as the wash process can remove these to a some extent, however they also can contribute to emulsion formation.

Most Important Specifications

Water and Sediment - 0.050% vol. max.

- Excessive water indicates incomplete drying.
- The presence of emulsifiers (soaps, MGs, DGs) can hinder the drying process, making it difficult to dry insufficiently washed fuel.
- Properly filtered fuel should be free of sediments.

Most Important Specifications

Water and Sediment - 0.050% vol. max.

- Pure methyl esters allow some solubility of water, which can remain leftover from the wash process, or absorbed out of the atmosphere.
- Even thoroughly washed fuel (free of emulsifiers) may require active drying in addition to gravity settling, but this does not seem to always be the case.

Most Important Specifications

Sulfur 0.0015% mass max.????

- Questionable - this spec became more stringent in 2006 due to new ULSD standards, which limit sulfur content to 15 ppm max for on-road diesel fuels.
- Vegetable oils typically contain no sulfur, however WVO containing animal fats may contain small amounts due to sulfur-containing preservatives used in meats.
- This was previously a non-issue since the old sulfur limit (0.050% mass max.) was fairly generous, however it may become more of an issue with the new spec.

Other specs?

Flash Point - 130° C min.

- Caused by excess methanol leftover from reaction, biodiesel itself is non-flammable with a flash point of ~150° C.
- Washing removes methanol.

Sulfated Ash - 0.020% mass max.

- A test for residual metals leftover from catalysts - Na or K dependent on catalyst used.
- Washing removes residual soap and catalyst.

Even more specs

Acid Number - 0.80 mg KOH/g max.

- Can indicate fuel has gone rancid.
- Normally associated with fuel stored improperly for long periods of time.

Carbon Residue - 0.050 % mass max.

- Tests for solid carbon compounds leftover from incomplete combustion.
- MGs, DGs, or TGs present in fuel usually the cause, so fuel that meets spec for total glycerol should be fine.

Still more specs

Phosphorus - 0.001% mass max.

- Caused by residual gums in feedstock, which are naturally present in most raw vegetable oils.
- Not much of an issue with WVO since it has already been refined, bleached, and deodorized.

Kinematic Viscosity - 1.9 - 6.0 mm^2/s

- Affected by level of reaction completion, so fuel that meets total glycerol spec should be fine.

Specs, specs, specs . . .

- Copper corrosion - No. 3 max
  - Affected by residual soaps and catalyst.
- Cetane Number - 47 min.
  - Easily passed with most WVO.
- Vacuum Distillation End Point - 360° C
  - This is something that is important in the petroleum industry but has practically no relevance for biodiesel and doesn't indicate much about the actual quality of the fuel.

So, about those important specs . . .

1. Free and Total glycerol
   - Usually measured by gas chromatograph (GC).
2. Water and sediment
   - Fairly simple to test for water, sediment typically filtered out.
3. Cloud Point
   - Easy to test.

If only we all had GCs . . .

But since we don't . . .

- There are other tests used to look at bound glycerol, but regardless, its important to know what is required to actually meet spec . . .
  - Understanding the chemistry of *transesterification of vegetable oils* is key.
  - Fortunately, this has been extensively studied and tested for decades - the process has been known for a long time.
  - Results of many university studies are readily available and open-source! You just need to know where to look and what to look for.

Reactions Contributing to Methyl Ester Production

1. Transesterification of Fats (Triglycerides) to form Fatty Acid Methyl Esters and Glycerol

1 Triglyceride + 3 Methanol ↔ 3 Methyl Ester + 1 Glycerol

- The fatty acid *R* groups remain unchanged, and types vary depending on feedstock used.
- This reaction is facilitated with a strong base catalyst.

Reactions Contributing to Methyl Ester Production

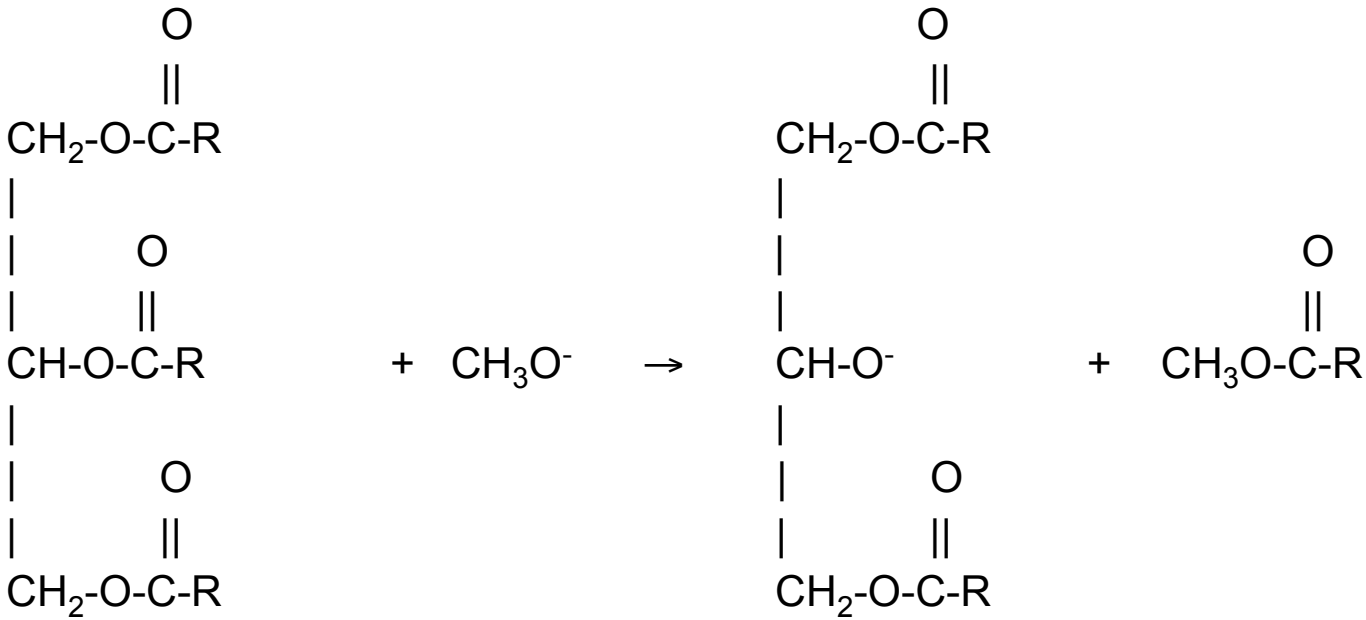
2. Reaction of Catalyst (NaOH) with Methanol

$$CH_3OH + NaOH \rightarrow CH_3O\text{-}Na + H_2O$$

- CH_3O-Na exists as the anion CH_3O^- (methoxide) and the cation Na^+.
- Note that water is produced by this reaction.

Reactions Contributing to Methyl Ester Production

3. The reaction of Methoxide with Triglyceride

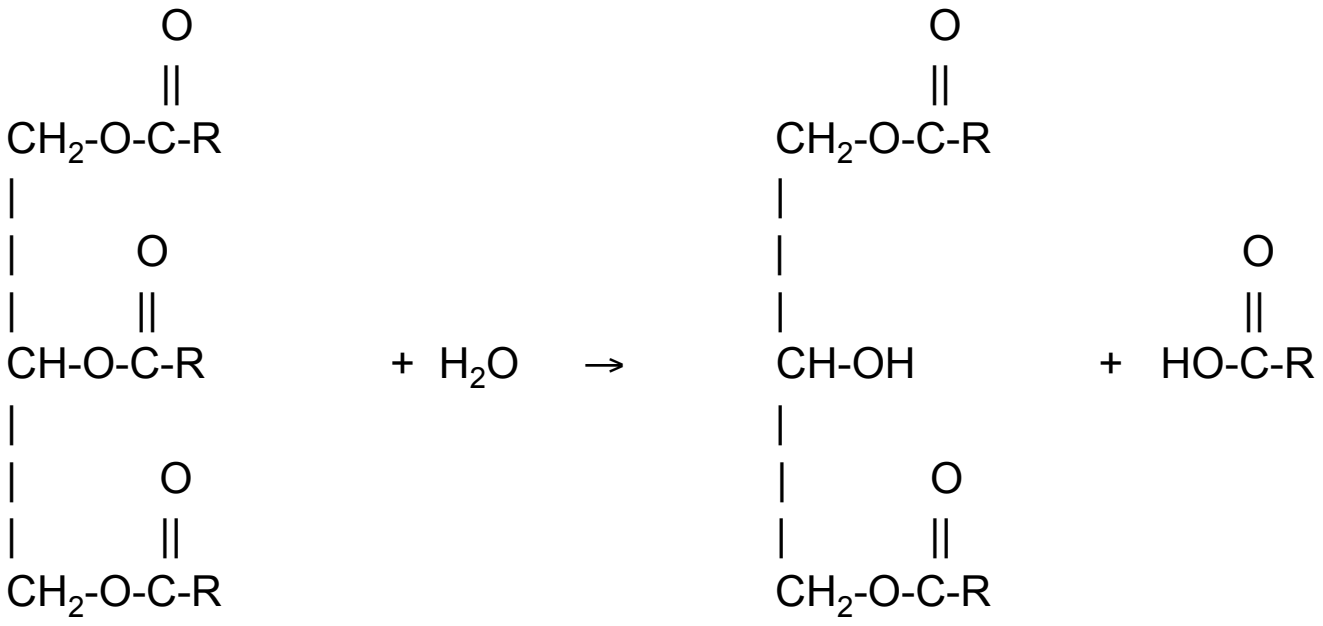


Triglyceride Methoxide Triglyceride Anion Methyl Ester

- The triglyceride anion then needs a proton to form a diglyceride.
- If the triglyceride anion takes a proton from methanol, then another methoxide anion is formed, regenerating the catalyst.

Reactions Inhibiting Methyl Ester Production

1. Hydrolysis of Triglyceride to form Diglyceride and Free Fatty Acid



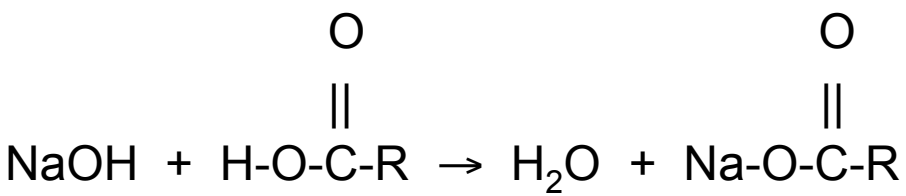
Triglyceride Water Diglyceride Free Fatty Acid

Reactions Inhibiting Methyl Ester Production

1. Hydrolysis of Triglyceride to form Diglyceride and Free Fatty Acid
   - High heat increases the rate of this reaction.
   - It is particularly prevalent in deep fryers, and is the primary reason used cooking oil contains free fatty acids.
   - It can also happen during biodiesel processing. The presence of a base catalyst facilitates this reaction in a similar way as it facilitates transesterification.
     - For example, water dissolves NaOH into Na^+ and OH^- ions.
     - OH^- (hydroxide) ions can attack the ester bounds just as methoxide ions can, producing free fatty acids.
     - The remaining diglyceride anion can then take a proton from water, regenerating the hydroxide ion.
   - Excessive catalyst or water (greater than ~1%) can create conditions where this reaction occurs more readily than the transesterification reaction and inhibits reaction completion.

Reactions Inhibiting Methyl Ester Production

2. Reaction of Alkali Catalyst with Free Fatty Acid to form Soap



Lye FFA Water Soap

- Note that water is also a product.
- This reaction does not lead to regeneration of catalyst.
- Excessive soap production can slow down or stop the transesterification reaction by neutralizing the catalyst.
- Initial FFA levels of greater than ~1% (Equaling an acid value of about 2 using KOH) are difficult or impossible to react with single stage base-catalyzed transesterification and meet spec for total glycerol

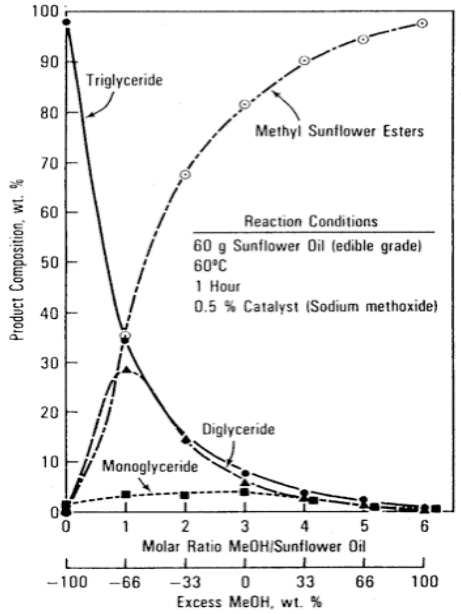
Optimizing Reaction Conditions

Reactants vs. Products

- In order to maximize conversion of triglycerides + methanol into methyl esters + glycerol, the relative concentrations of reactants and products must be considered.
- An excess of one of the reactants can “drive the reaction further to the right,” increasing extent of conversion into products.
- Twice the stoichiometric quantity of methanol has been found to be effective at maximizing methyl ester production.
  - This equals about 25% the volume of the oil for most WVO

Optimizing Reaction Conditions

Effect of alcohol to oil ratio on reaction completion[1]



[1] B. Freedman, E.H. Pryde, and T.L. Mounts, "Variables Affecting the Yields of Fatty Esters from Transesterified Vegetable Oils," JAOCS, 61 (1984) 1638-1643.

- The chart at left shows percent composition of reactants and products at different molar ratios of methanol to sunflower oil.
- A 3:1 MeOH to Oil ratio is the stoichiometric quantity.

Optimizing Reaction Conditions

Reactants vs. Products

- Sometimes, simply using excess reactants alone will not be sufficient due to excessive products and byproducts from side reactions.
- Another strategy is to remove reaction products and inhibitors - glycerol, soap, water, etc. - then continuing with additional reactant (methanol/methoxide).
- This “multiple stage” approach is useful when processing oils with high FFA content, due to inevitable soap and water production from the FFAs.

Optimizing Reaction Conditions

Mixing

- Triglycerides are strongly nonpolar, whereas methanol is strongly polar.
- “Oil and water don’t mix.”
- Initial reaction rate is limited by the rate at which methanol and oil can transfer across the interface between them.
- Intense mixing is helpful initially to maximize surface area of interface between oil and methanol.

Optimizing Reaction Conditions

Temperature

- As triglycerides are converted to diglycerides and monoglycerides, mixing intensity becomes less of a limiting factor for the rate of reaction, since DGs and MGs are slightly polar and more soluble in the methanol.
- Reaction rate increases with temperature, so maintaining a high temperature becomes more important in this stage of the reaction.
- ~55° C is a good temperature to work with because it is practical and avoids the boiling point of methanol.

Optimizing Reaction Conditions

A comparison of the effects of temperature and mixing intensity on reaction completion of the transesterification of soybean oil[1]

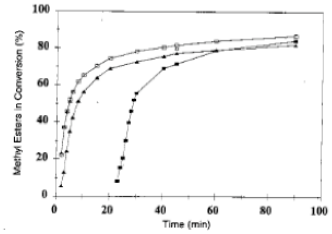


FIG. 2. The effect of mixing intensity and time on the overall conversion to methyl esters at 50°C. (■) N_{Re} = 3100; (▲) N_{Re} = 6200; (□) N_{Re} = 12400; (△) N_{Re} = 18600. See Figure 1 for abbreviation.

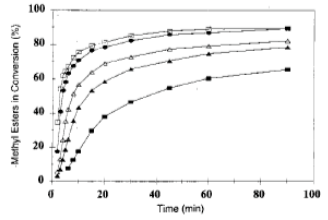


FIG. 4. The effect of temperature and time on the overall conversion to methyl esters at N_{Re} = 6200. (■) 30°C; (▲) 40°C; (△) 50°C; (●) 60°C; (□) 70°C. See Figure 1 for abbreviation.

[1] Noureddini, H. and D. Zhu, "Kinetics of Transesterification of Soybean Oil," JAOCS, V. 74, No. 11, 1997, pp. 1457-1463.

- The top chart compares percent reaction completion with different mixing intensities.
  - After about 45 minutes, they all are about the same, but the samples with higher mixing intensity get there much faster.

Optimizing Reaction Conditions

A comparison of the effects of temperature and mixing intensity on reaction completion of the transesterification of soybean oil[1]

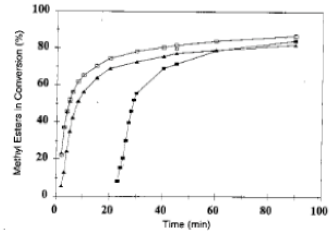


FIG. 2. The effect of mixing intensity and time on the overall conversion to methyl esters at 50°C. (■) N_{Re} = 3100; (▲) N_{Re} = 6200; (□) N_{Re} = 12400; (△) N_{Re} = 18600. See Figure 1 for abbreviation.

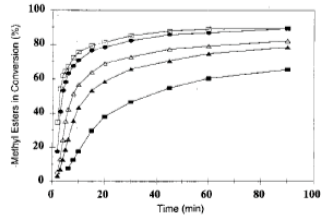


FIG. 4. The effect of temperature and time on the overall conversion to methyl esters at N_{Re} = 6200. (■) 30°C; (▲) 40°C; (△) 50°C; (●) 60°C; (□) 70°C. See Figure 1 for abbreviation.

[1] Noureddini, H. and D. Zhu, "Kinetics of Transesterification of Soybean Oil," JAOCS, V. 74, No. 11, 1997, pp. 1457-1463.

- The bottom chart compares percent reaction completion at different temperatures.
  - After 20 minutes or so, the rate of increase slows for all, but the samples at higher temps level off at a higher percent completion.
  - At the end of the test, all samples are still increasing, but higher temp samples are closer to completion.

Optimizing Reaction Conditions

Conclusion:

- Regardless of whether or not it is practical to analyze a fuel to determine if it is within spec or not, a thorough understanding of the chemistry behind the reaction and the factors controlling completion will help you establish a reliable process technique that will produce quality fuel, and you will be better at troubleshooting issues that arise and cause problems with the quality of the fuel.

Resources and References

- Noureddini, H. and D. Zhu, “Kinetics of Transesterification of Soybean Oil,” JAOCS, V. 74, No. 11, 1997, pp. 1457-1463.
- B. Freedman, E.H. Pryde, and T.L. Mounts, “Variables Affecting the Yields of Fatty Esters from Transesterified Vegetable Oils,” JAOCS, 61 (1984) 1638-1643.
- Canakci, M. and J. Van Gerpen, "Biodiesel Production from Oils and Fats with High Free Fatty Acids", Transactions of the American Society of Agricultural Engineers, V. 44, No. 6, 2001, pp. 1429-1436.