Biodiesel Production Technology

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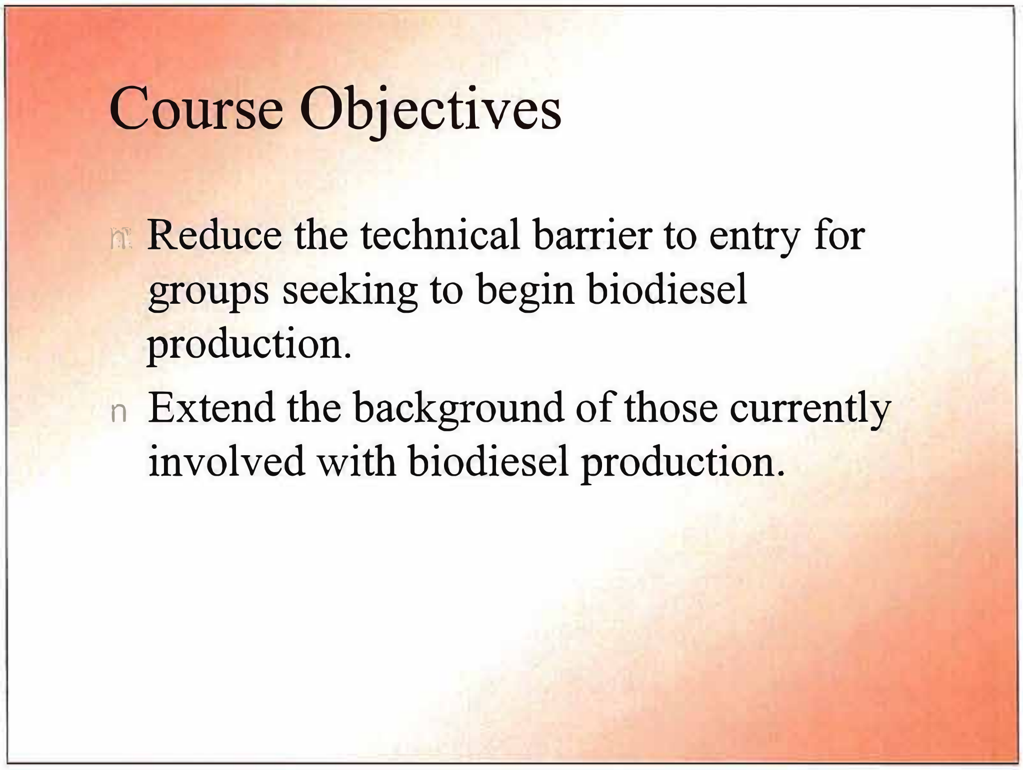


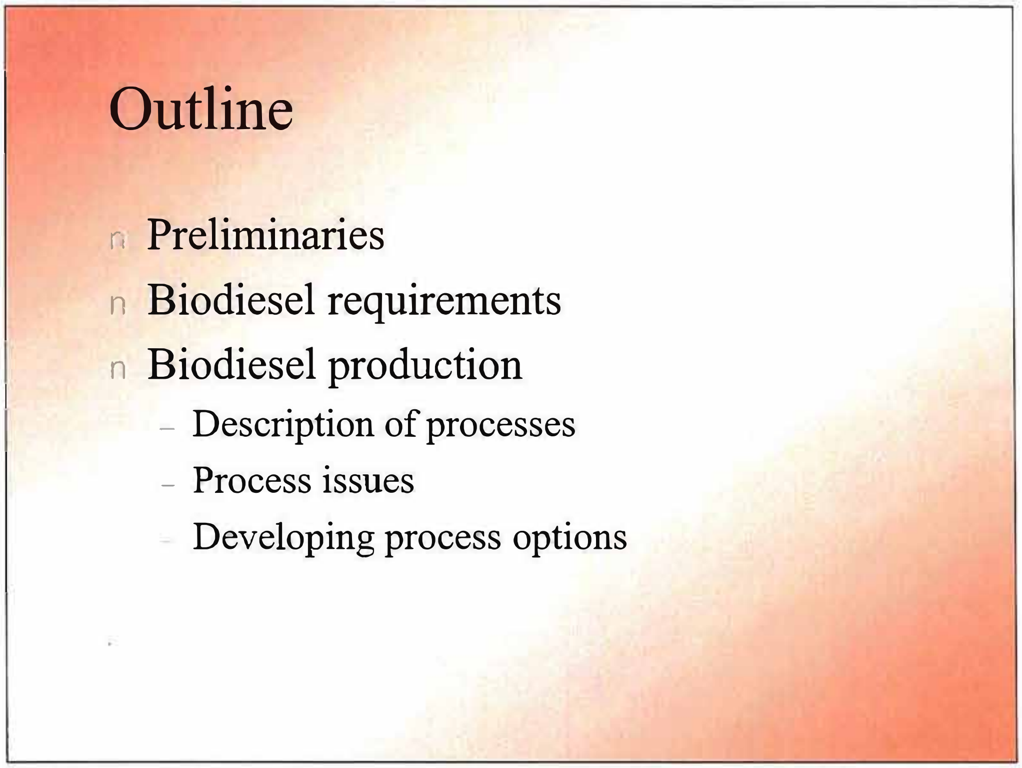
Course Objectives

- Reduce the technical barrier to entry for groups seeking to begin biodiesel production.
- Extend the background of those currently involved with biodiesel production.

Those who are thinking of getting in to biodiesel production should achieve a level where they can evaluate technology options and understand which questions they need to ask of the technology providers. They will also understand the connection between feedstocks and processing.

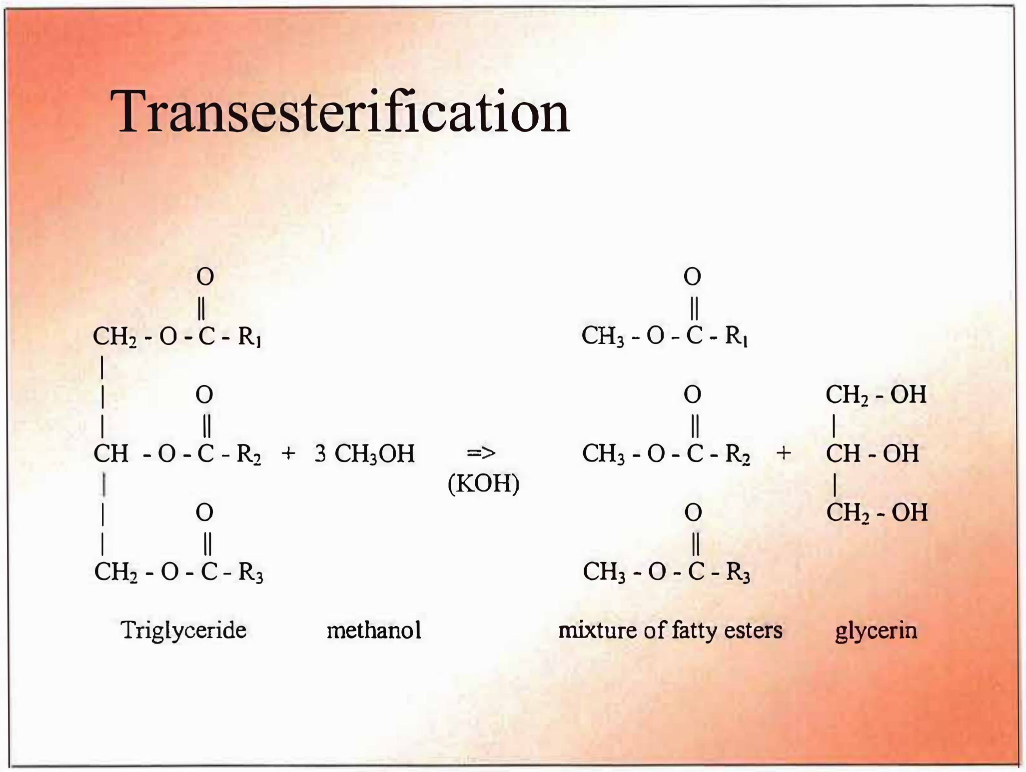
Those who are already in production should gain an improved background of the processes involved in conventional practices as well as some new ideas to consider. Hopefully, they will be able to look at their existing processes and think of new and better ways to do things.

This workshop is not intended to create an engineer. All plant designs should be reviewed by a qualified engineer, particularly to ensure compliance with safety and environmental requirements.



Outline

- Preliminaries
- Biodiesel requirements
- Biodiesel production
  - Description of processes
  - Process issues
  - Developing process options



Transesterification

$$\begin{array}{l} CH_2 - O - \overset{\overset{O}{||}}{C} - R_1 \\ | \\ CH - O - \overset{\overset{O}{||}}{C} - R_2 \\ | \\ CH_2 - O - \overset{\overset{O}{||}}{C} - R_3 \end{array} + 3\,CH_3OH \underset{(KOH)}{\Rightarrow} \begin{array}{l} CH_3 - O - \overset{\overset{O}{||}}{C} - R_1 \\ CH_3 - O - \overset{\overset{O}{||}}{C} - R_2 \\ CH_3 - O - \overset{\overset{O}{||}}{C} - R_3 \end{array} + \begin{array}{l} CH_2 - OH \\ | \\ CH - OH \\ | \\ CH_2 - OH \end{array}$$

Triglyceride methanol mixture of fatty esters glycerin

Terminology:

Triglycerides: The primary constituent of vegetable oils and animal fats.

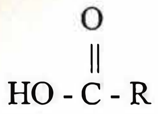
Esters: Organic compounds with the $R - O - \overset{\overset{O}{||}}{C} - R$ group. Note that triglycerides are also esters (triesters). Biodiesel consists of mono-esters.

Alcohol: Has an OH group attached to a hydrocarbon group.

Glycerin: Byproduct of biodiesel production. Has three OHs (tri-alcohol)

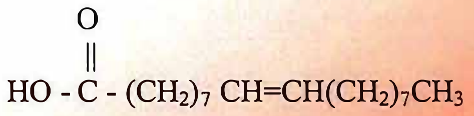
Other terminology

- Free fatty acids are a potential contaminant of oils and fats.



$$\mathrm{HO - \overset{\overset{O}{\|}}{C} - R}$$

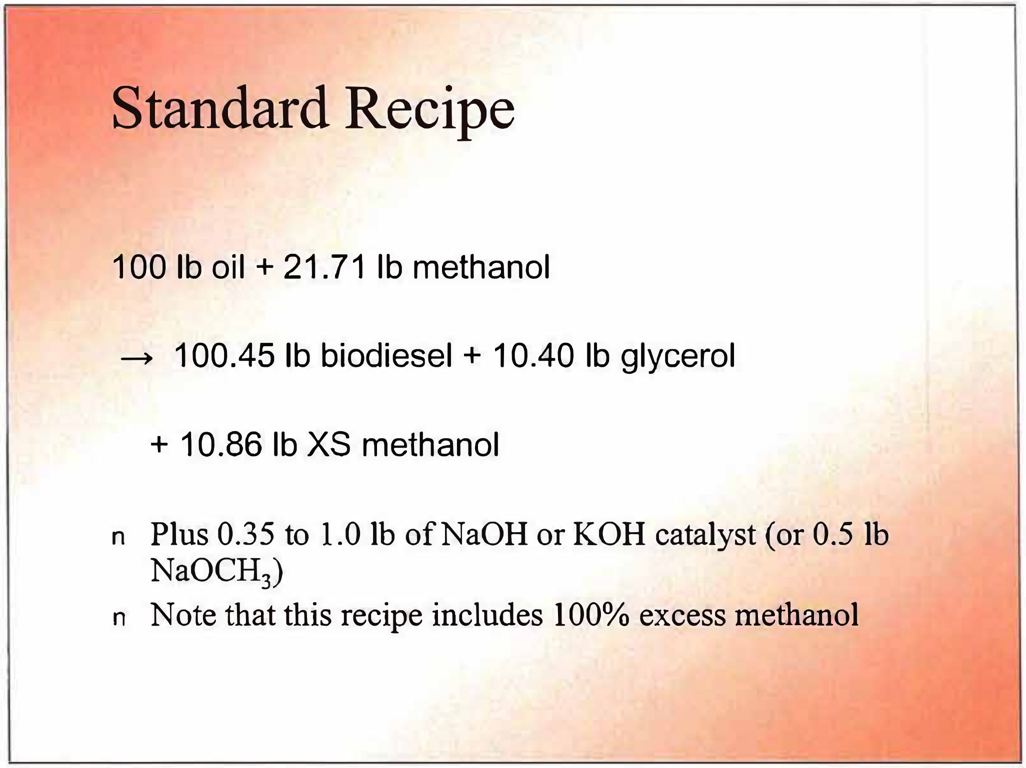
Carboxylic Acid (R is a carbon chain)



$$\mathrm{HO - \overset{\overset{O}{\|}}{C} - (CH_2)_7\ CH{=}CH(CH_2)_7CH_3}$$

Oleic Acid

Fatty acids will be split from triglycerides as an oil is abused (exposed to high temperature, water, enzymes, etc.)



Standard Recipe

100 lb oil + 21.71 lb methanol

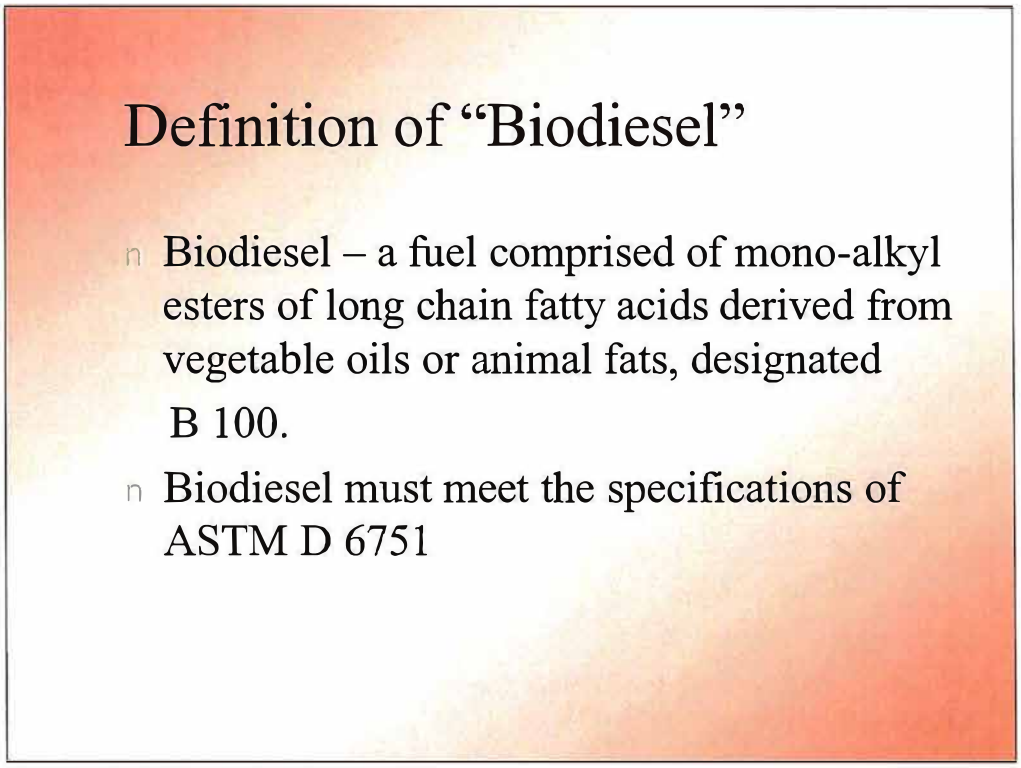
→ 100.45 lb biodiesel + 10.40 lb glycerol

+ 10.86 lb XS methanol

- Plus 0.35 to 1.0 lb of NaOH or KOH catalyst (or 0.5 lb $NaOCH_3$)
- Note that this recipe includes 100% excess methanol

Multi-step reactions can reduce the excess alcohol required. This involves adding a portion of the alcohol and catalyst, allowing the reaction to go to equilibrium, removing the glycerin that has formed, then adding additional methanol and catalyst and continuing the reaction.

Ethanol, and other alcohols, can be used instead of methanol. Larger amounts of these alcohols are required to reflect their higher molecular weights, but the operating temperatures can also increase and the yield of biodiesel will increase, also (lb of biodiesel/lb of oil).



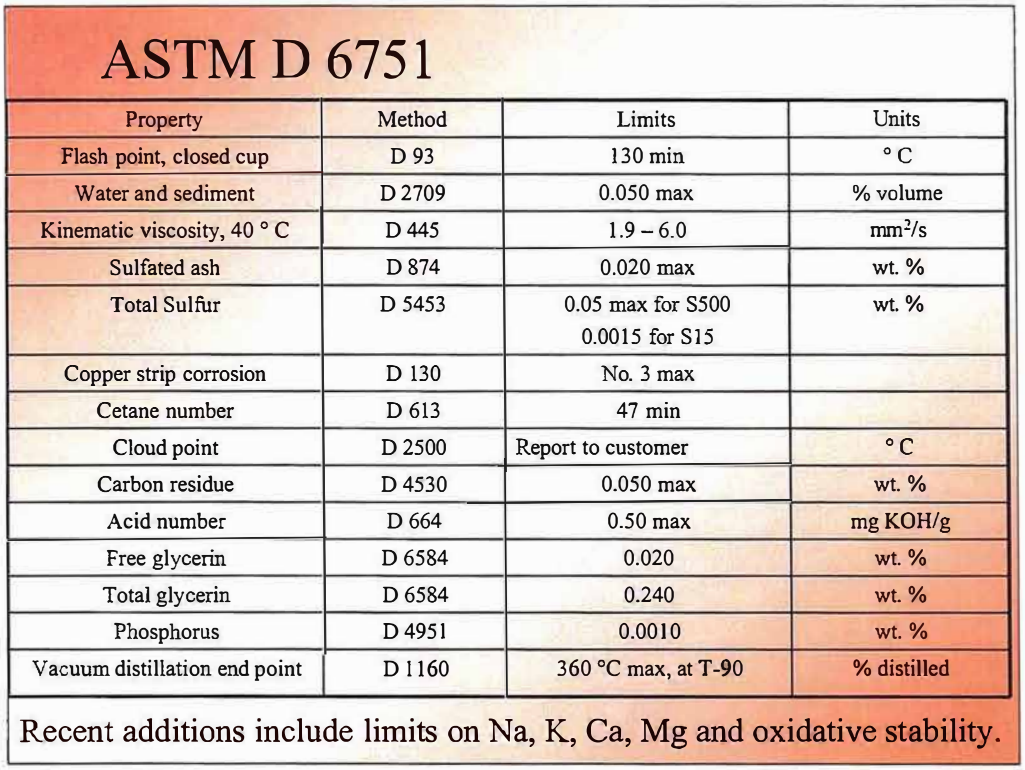
Definition of “Biodiesel”

- Biodiesel – a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, designated B 100.
- Biodiesel must meet the specifications of ASTM D 6751

Biodiesel is not …….

1. Straight vegetable oil (SVO): Use of straight vegetable oil in engines is not recommended. The basic problem seems to be that, due to the oil’s high viscosity, the spray pattern of the fuel is disrupted as it enters the engine. This allows some of the fuel to deposit on the cylinder wall rather than remain suspended in the air where it can be burned. The fuel on the wall is scraped down into the gap between the piston and cylinder wall. Some of the fuel is decomposed in the vicinity of the piston rings and can cause the rings to seize, which shortly after will result in cylinder wall scoring. This effect is probably aggravated by the glycerin portion of the oil molecule. Some of the oil will also be swept down into the lubricating oil where it can dilute the oil and since it is prone to oxidation, cause thickening of the oil, premature aging of the oil (consumption of additives) and a loss of lubrication. Some people have had a degree of success in using straight vegetable oil when the oil is heated to engine coolant temperatures before injecting it. This lowers the viscosity of the oil and lessens the effect on the injector spray pattern. However, long-term durability data for this case is limited and the small amount of reliable emissions data that are available indicate the emissions become worse.

2. Ethanol blends with diesel fuel: Adding 10 to 30% ethanol to diesel fuel has been proposed as a way to extend supplies of fossil fuels. Usually, it is necessary to add a co-solvent to keep the ethanol in solution, a cetane enhancer to compensate for the cetane-lowering effect of the ethanol, and a lubricity enhancer. With these additives, the ethanol blends, called “E-diesel,” appear to provide acceptable performance and engine durability. One remaining problem is the high flash point of the fuel. This makes the fuel less safe and it must be treated with the same safety standards as gasoline.



ASTM D 6751

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	wt. %
Total Sulfur	D 5453	0.05 max for S500 0.0015 for S15	wt. %
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	wt. %
Acid number	D 664	0.50 max	mg KOH/g
Free glycerin	D 6584	0.020	wt. %
Total glycerin	D 6584	0.240	wt. %
Phosphorus	D 4951	0.0010	wt. %
Vacuum distillation end point	D 1160	360 °C max, at T-90	% distilled

Recent additions include limits on Na, K, Ca, Mg and oxidative stability.

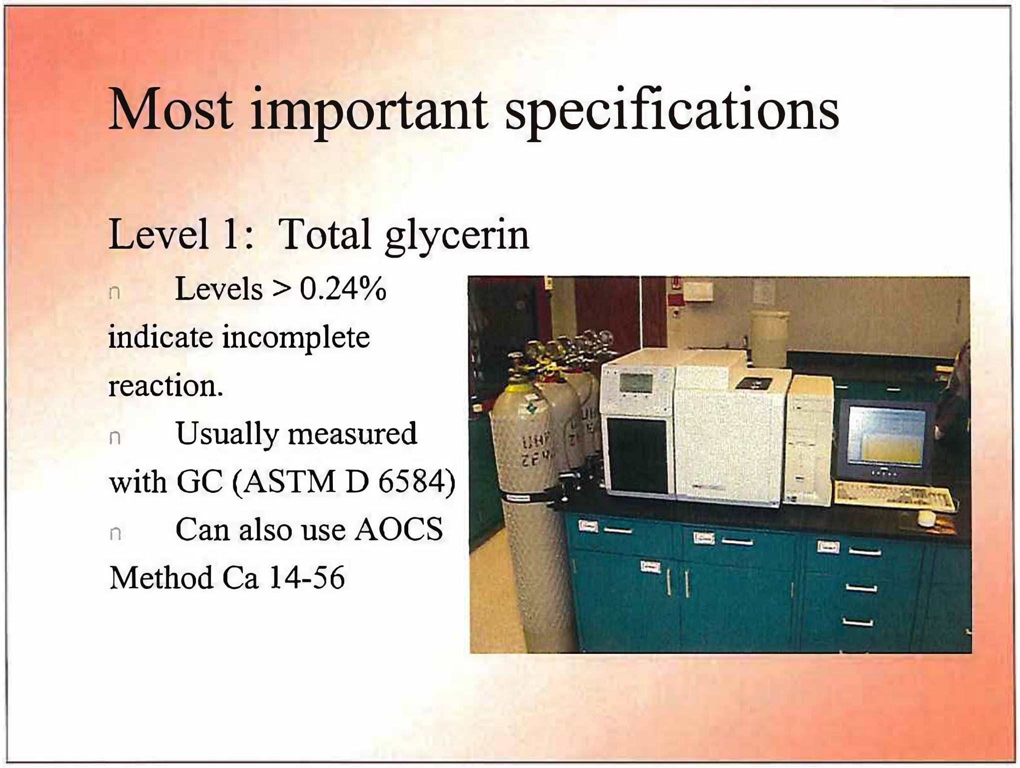
This is where it has to start. If the fuel does not meet ASTM D 6751, then it should not be called biodiesel.

Future changes *might* include tighter limit on viscosity, cold filtering, alternatives to vacuum distillation and other changes to more closely align the ASTM and European specifications.

ASTM D 6751 includes a narrative description of biodiesel as "mono-alkyl esters of long chain fatty acids derived from vegetable oils and animal fats."

Note that there are actually two specifications: S500, which is allowed up to 500 ppm of sulfur for off-highway applications, and S15, which is limited to 15 ppm sulfur for on-highway use (after ULSD regulations are implemented).

The European standard (EN 14214) is similar but has limits on Iodine value, which is a rough indicator of oxidative stability, and the maximum amounts of monoglycerides, diglycerides, and triglycerides that are present. It also mandates that the biodiesel must contain at least 96.5% esters.



Most important specifications

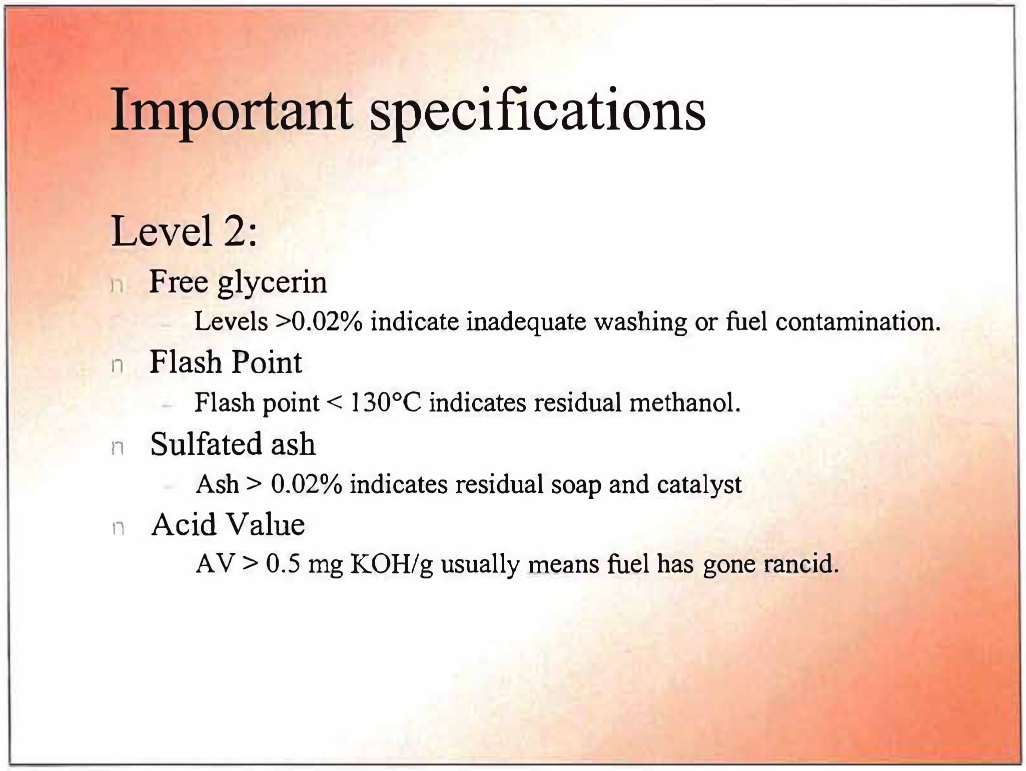
Level 1: Total glycerin

- Levels > 0.24% indicate incomplete reaction.
- Usually measured with GC (ASTM D 6584)
- Can also use AOCS Method Ca 14-56

Level 1: Total glycerin. If the fuel fails this specification, then nothing else matters. Fuel with a high total glycerin level will have tend to form white flakes or sediments at the bottom of the tank. These are mostly monoglycerides of saturated fatty acids. These compounds have very high melting points and have low solubility in methyl esters. Getting a total glycerin level below 0.24% requires 98% or better conversion of the oil to esters.

When they precipitate, monoglycerides of the saturated fatty acids can plug fuel filters. When the filter is opened, you will find a cold cream-like material, which is high in monoglycerides. If filter plugging is encountered at temperatures above 50°F, monoglycerides are the most likely cause.

AOCS method Ca 14-56 can be used to measure Free and Total Glycerin for process development work. It is not included in ASTM D 6751 so it cannot be used to certify compliance with that standard. Another alternative method uses enzyme-induced color changes and a spectrophotometer (Greenhill Method) although this method is less widely used. Saftest is another enzyme-based method. Infrared techniques are also available that can be used by unskilled operators after the appropriate calibrations have been developed.



Important specifications

Level 2:

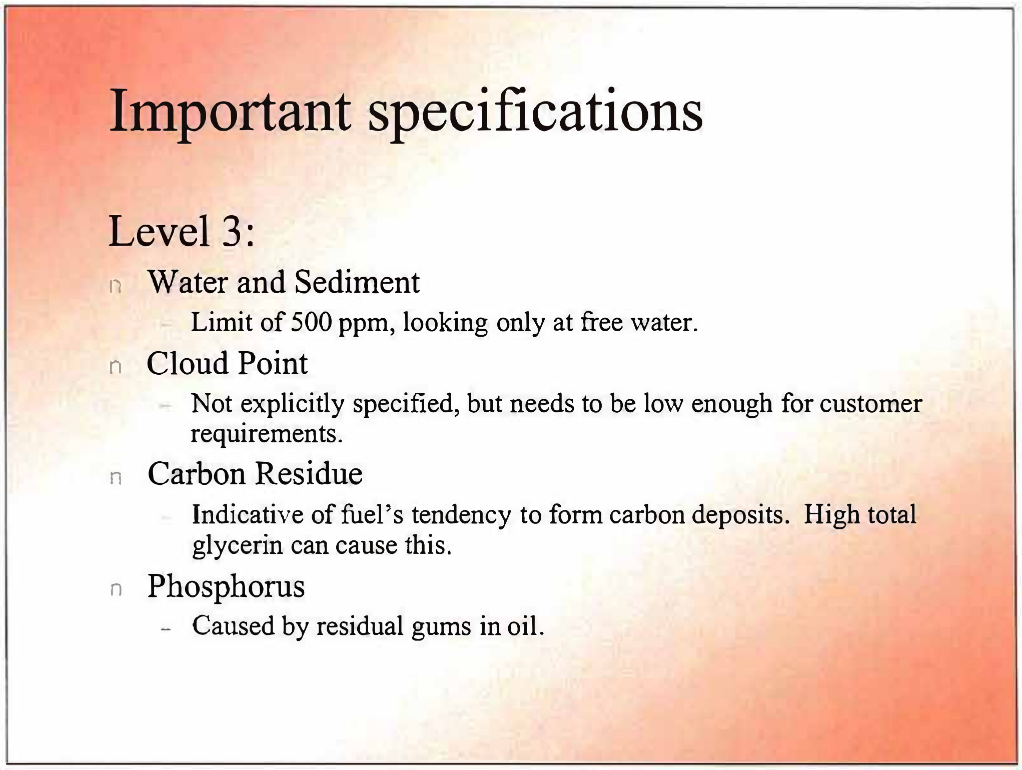
- Free glycerin
  - Levels >0.02% indicate inadequate washing or fuel contamination.
- Flash Point
  - Flash point < 130°C indicates residual methanol.
- Sulfated ash
  - Ash > 0.02% indicates residual soap and catalyst
- Acid Value
  - AV > 0.5 mg KOH/g usually means fuel has gone rancid.

Free glycerin: Water washing usually removes free glycerin and gets the level down to below 0.02%. Cold water is less effective than warm water (60°C). High levels of free glycerol will ultimately result in pools of free glycerol collecting at the bottom of storage tanks. The glycerol may attract water and provide an environment that will support algae growth in the fuel.

Flash Point: The flash point of methyl esters is greater than 150°C. If a flash point is measured that is substantially below this level, it is almost certainly due to methanol in the fuel. This is mostly a safety issue. If the flash point of the fuel is near room temperature, then the fuel is flammable and must be treated with the same safety precautions as gasoline. There have been some suggestions that this methanol may improve the cold flow properties of the biodiesel if left in the fuel. If the methanol is left in the fuel, the fuel cannot meet ASTM D 6751.

Sulfated Ash: The sulfated ash is determined by heating the fuel in the presence of air so that all organic materials are burned away and the only material that is left is inorganic. The ash is treated with sulfuric acid in a procedure that is intended to enhance the sensitivity to sodium and potassium compounds that may remain from the catalyst.

Acid Value: Even when working with a high free fatty acid feedstock, the acid value of the biodiesel after alkali-catalyzed transesterification should be low (about 0.2 mg KOH/g). However, if the biodiesel is old, there can be an increase in free fatty acids. These can come about due to hydrolysis, which will produce long-chain fatty acids from the original methyl esters. Or, they can be produced by oxidation reactions that will split the long chain esters in the vicinity of the double bonds and produce short chain acids. It is these short chain acids, and their close relatives, aldehydes and ketones, that give the rancid biodiesel its characteristic unpleasant smell.



Important specifications

Level 3:

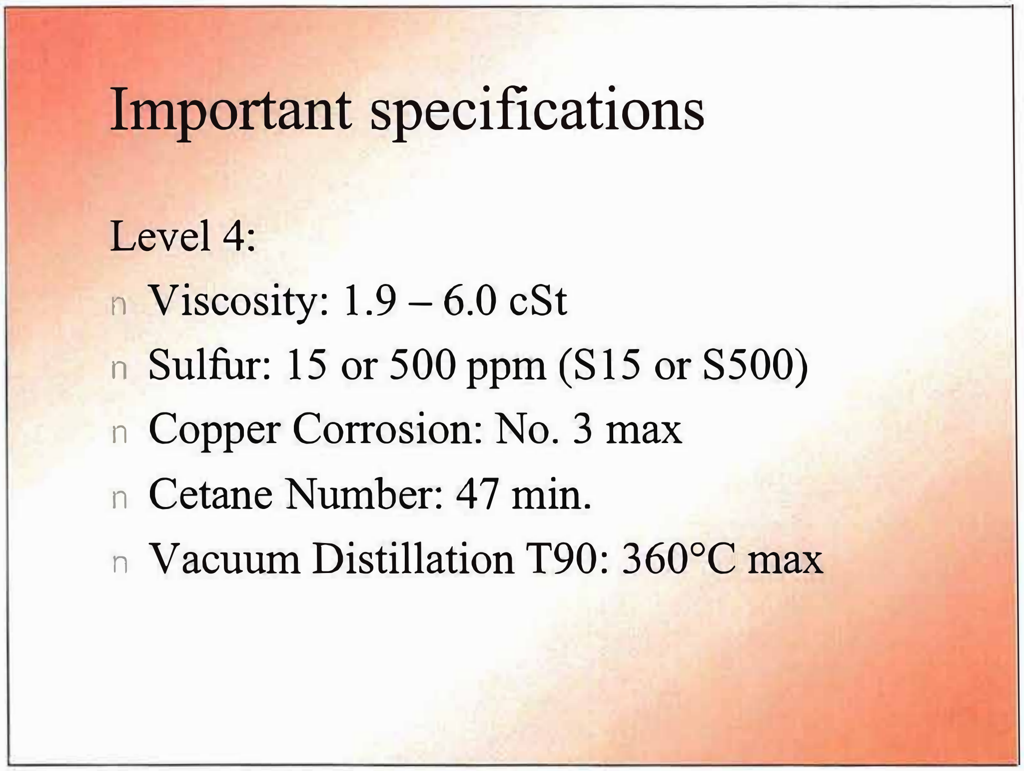
- Water and Sediment
  - Limit of 500 ppm, looking only at free water.
- Cloud Point
  - Not explicitly specified, but needs to be low enough for customer requirements.
- Carbon Residue
  - Indicative of fuel's tendency to form carbon deposits. High total glycerin can cause this.
- Phosphorus
  - Caused by residual gums in oil.

Water and sediment: The test method specified here uses a centrifuge to separate water and sediment. It will only pick up free water, if any exists. Biodiesel can contain up to 1500 ppm of dissolved water, which will show up with a Karl-Fisher titration measurement – but this water will not be included in the water and sediment test.

Cloud Point: The cloud point is mostly a function of the feedstock. If the feedstock contains large amounts of saturated fats (beef tallow, pork lard, hydrogenated vegetable oils, etc.) then the cloud point might be as high as 50-60°F.

Carbon Residue: This is generally a low priority test as it has little credibility in the engine business as a predictor of the fuel's carbon deposit formation tendency. It is included as Level 3 only because it does seem to increase if the total glycerin is too high. Most likely the partially reacted monoglycerides contribute to the carbon residue.

Phosphorus: Soybean oil, canola oil, and some other vegetable oils contain phosphorus compounds called phospholipids or gums. These are usually removed during processing as they can be sold as crude lecithin to the food industry. Tests have shown that even if these gums are not removed prior to processing, the gums do not pass through to the biodiesel. If there is phosphorus in the biodiesel, it is probably due to contamination. Phosphorus is limited in all diesel fuels to allow for the future use of catalysts for exhaust aftertreatment. Phosphorus is a powerful catalyst poison.



Important specifications

Level 4:

- Viscosity: 1.9 – 6.0 cSt
- Sulfur: 15 or 500 ppm (S15 or S500)
- Copper Corrosion: No. 3 max
- Cetane Number: 47 min.
- Vacuum Distillation T90: 360°C max

Viscosity: This is mostly a function of feedstock and, thus, cannot be controlled. It will increase with time as the fuel oxidizes and should be monitored for fuel in storage. If it is out-of-spec, then it is indicative of serious fuel degradation.

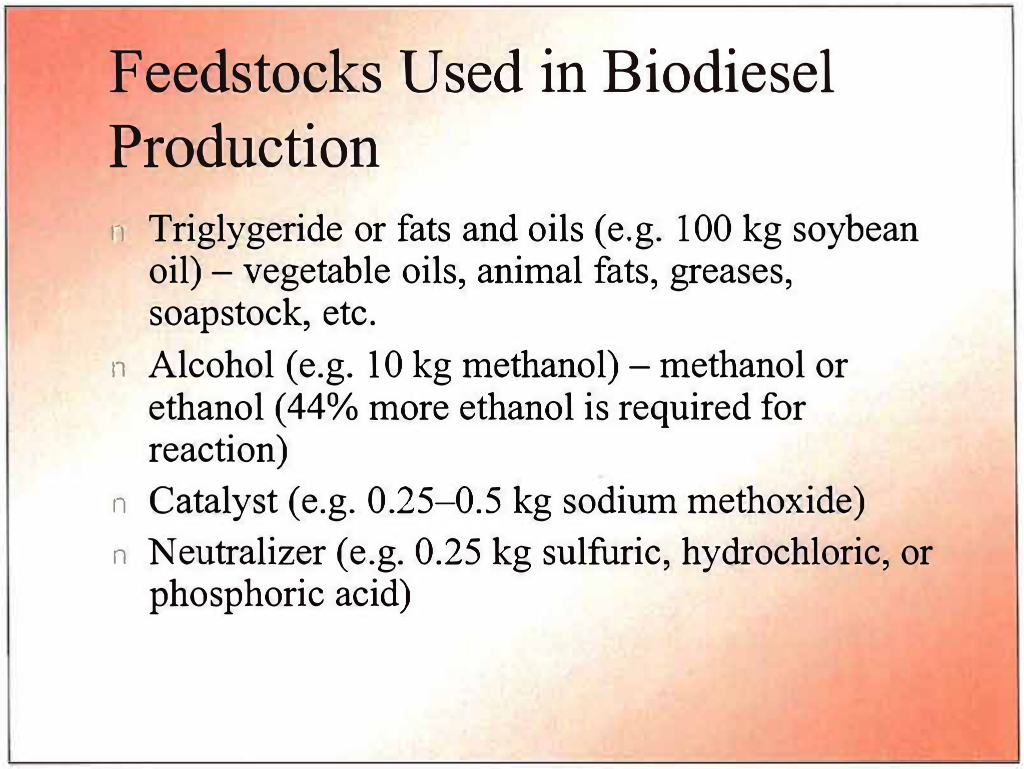
Sulfur: This is also mostly a function of feedstock. Some animal fats and recycled oils have high sulfur levels and may not meet the 2006 ultra low sulfur diesel fuel standards. This fuel can be sold to the off-highway market that will continue to offer 500 ppm sulfur fuels.

Copper Corrosion: This is a test that looks at the tendency of the fuel to cause corrosion of copper components. It is usually associated with acidic, sulfur-containing fuels. I have never seen a sample of biodiesel fail this test.

Cetane Number: This is mostly feedstock dependent. Soy-based biodiesels will have cetane numbers between 48 and 52, depending on the level of oxidation. Oxidized fuels tend to have higher cetane number due to the presence of peroxide compounds. More saturated biodiesels have higher cetane numbers. Beef tallow and yellow grease will be in the range of 60-65.

Vacuum Distillation T90: This is meaningless value for biodiesel. It may be an indicator of fuel contamination but only if the contaminant is a very high boiling point material such as lubricating oil.

Other quantities: Na, K, Ca, Mg are now limited. These are likely to be contaminants introduced during processing and probably do not need to be checked on each batch. Oxidative stability will be most strongly affected by feedstock. Oils with high levels of polyunsaturates will have the most difficulty with this test.



Feedstocks Used in Biodiesel Production

- Triglygeride or fats and oils (e.g. 100 kg soybean oil) – vegetable oils, animal fats, greases, soapstock, etc.
- Alcohol (e.g. 10 kg methanol) – methanol or ethanol (44% more ethanol is required for reaction)
- Catalyst (e.g. 0.25–0.5 kg sodium methoxide)
- Neutralizer (e.g. 0.25 kg sulfuric, hydrochloric, or phosphoric acid)

After the transesterification reaction, the catalyst and soaps will preferentially separate into the glycerin although some will remain with the biodiesel. Within a few hours, most of the residual catalyst in the biodiesel will convert to soap.

Although the soap can be washed directly from the biodiesel with water, less water is required if the soap is split prior to washing.

The soap is usually split be adding a strong acid:

$$\text{Na-Soap} + \text{HCl} \rightarrow \text{FFA} + \text{NaCl}$$

(See also p. 49)

Triglyceride Sources

- Vegetable oils: soybean, canola, palm, algae, etc.
- Inedible oils: jatropha, crambe
- Rendered animal fats: beef tallow, lard, chicken fat
- Rendered greases: yellow grease, brown grease
- Recovered materials: trap grease, float grease, soapstock, (low triglyceride, high FFA)

Suitable feedstocks for a base-catalyzed process require FFA < 1 % and preferably < 0.5 %. The oil must be dry, preferably < 0.1 % moisture.

Yellow grease is a standard commodity product. Its primary specifications are Free fatty acids < 15%, MIU (moisture, insolubles, and unsaponifiables) < 2%. Many suppliers use restaurant waste oils as the primary component of yellow grease.

During summer months, rendered fats from dead stock will have FFA levels exceeding 25%. This material may be blended with lower FFA streams to produce yellow grease, or sold directly at a discount as brown grease.

If you are looking at algae as an oil source you should read a case study written by Krassen Dimitrov at http://www.nanostring.net/Algae/CaseStudy.pdf

You may not agree with all of his conclusions but you should understand the issues that he raises. See also

http://i-r-squared.blogspot.com/2007/05/algal-biodiesel-fact-or-fiction.html

Alcohols

- Methanol: Used for all production in Europe and U.S.
- Ethanol: Currently in use in Brazil.
- Note that production of ethyl esters requires 44% more lbs of ethanol than production of methyl esters. However, the lbs of extra ethanol shows up as more biodiesel yield.
- Use of ethanol provides an "all-biobased" product.
- Ethanol recovery can be problematic.

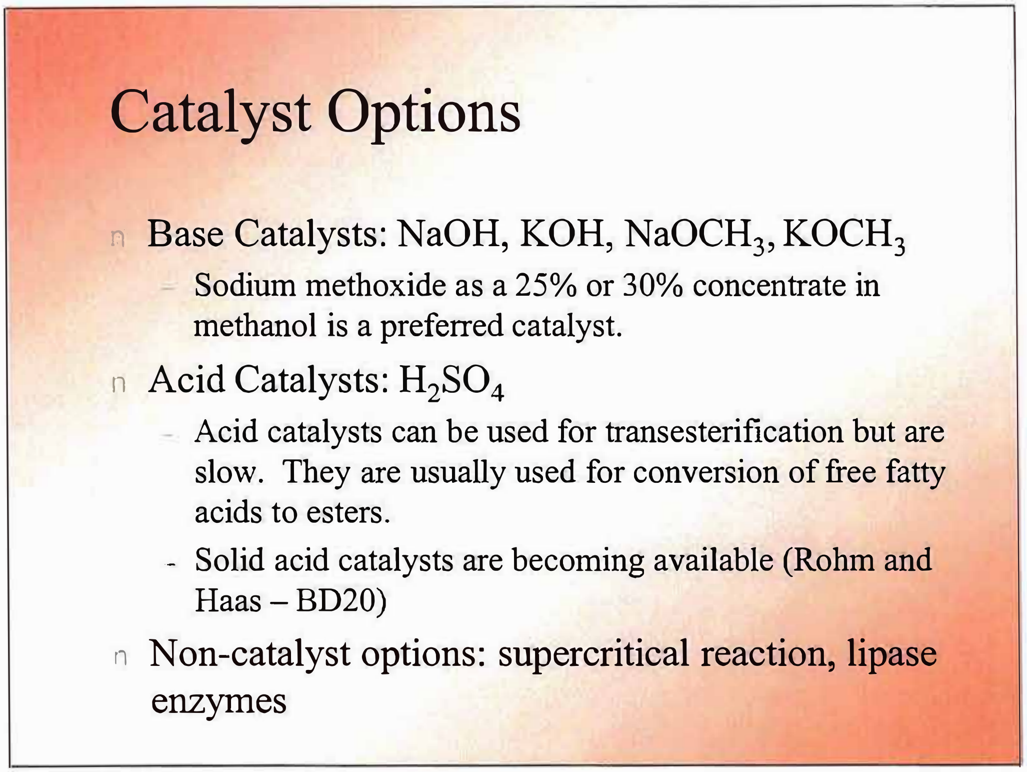
Ethanol can operate at higher temperatures at atmospheric pressure (due to higher boiling point). More ethanol is required for the reaction due to its higher molecular weight (44% more, MWet = 46.07 compared with MWme=32.04). However, ethyl esters will return about 104% yield based on the weight of oil supplied compared with only 100% for methyl esters. The increased number of pounds of alcohol corresponds to an increase in pounds of biodiesel. Depending on the cost of ethanol compared with methanol, ethyl esters may make economic sense.

Most ethanol that is available in this country is from corn and it is considered to be "bio-based." While methanol can also be made from biological sources (i.e. Smithfield plant in Utah: pig manure to methane to syn gas to methanol), most methanol comes from fossil sources (natural gas).

Ethanol and water form an azeotrope. This means that when the concentration of the mixture is about 95% ethanol/5% water, it is not possible to separate the mixture through simple distillation. In most cases, a device called a molecular sieve is used to separate them. This adds considerable cost to the biodiesel plant. This may provide an argument for co-locating a biodiesel plant and an ethanol plant. The ethanol plant would already have the ethanol purification equipment.

Isopropyl esters can be used to make biodiesel. These isopropyl esters provide superior cold flow properties but the reaction is slower and has greater sensitivity to water and soap formation. Isopropyl alcohol and water also form an azeotrope which complicates alcohol recovery in a similar manner to ethanol.

Wang, P.S., M.E. Tat, and J. Van Gerpen, "The Production of Fatty Acid Isopropyl Esters and Their Use as Diesel Engine Fuel," Journal of the American Oil Chemists Society, 82(11):845-849 (2005).



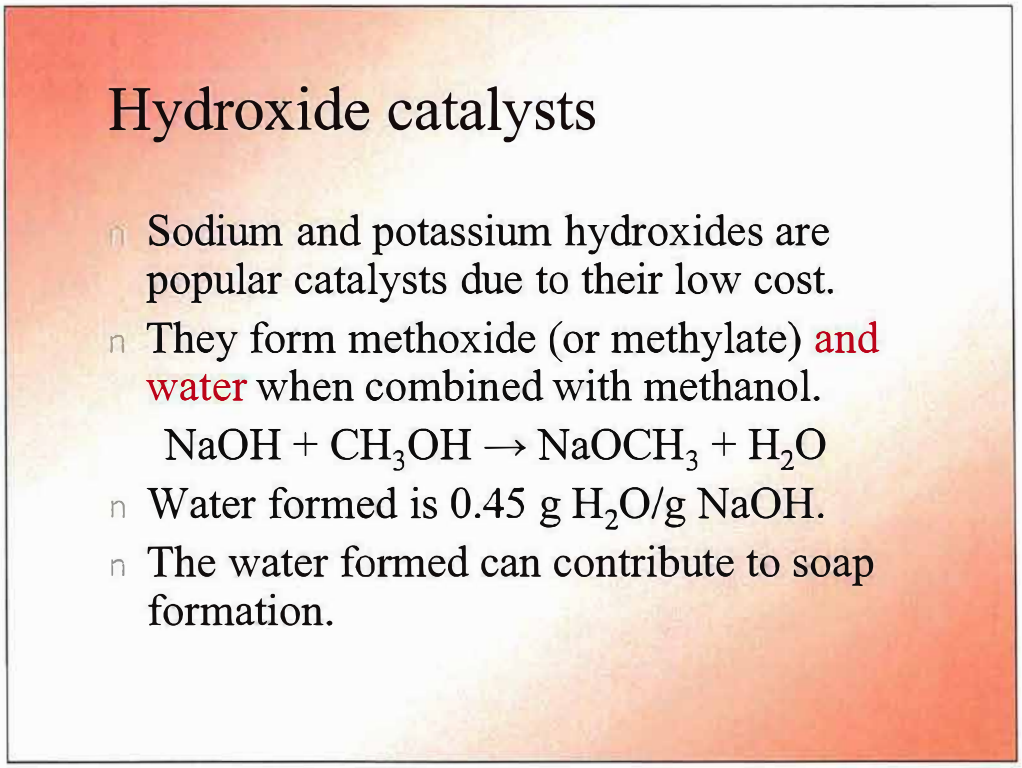
Catalyst Options

- Base Catalysts: NaOH, KOH, $NaOCH_3$, $KOCH_3$
  - Sodium methoxide as a 25% or 30% concentrate in methanol is a preferred catalyst.
- Acid Catalysts: H_2SO_4
  - Acid catalysts can be used for transesterification but are slow. They are usually used for conversion of free fatty acids to esters.
  - Solid acid catalysts are becoming available (Rohm and Haas – BD20)
- Non-catalyst options: supercritical reaction, lipase enzymes

Sodium methoxide and sodium methylate are the same thing.

Supercritical processing is discussed more later (p. 78).

Solid catalysts will be discussed later.



Hydroxide catalysts

- Sodium and potassium hydroxides are popular catalysts due to their low cost.
- They form methoxide (or methylate) and water when combined with methanol.

  $NaOH + CH_3OH \rightarrow NaOCH_3 + H_2O$
- Water formed is 0.45 g H_2O/g NaOH.
- The water formed can contribute to soap formation.

If the common amount of sodium hydroxide (1% based on the weight of oil) is used, almost ½% of water will be formed. The target for water in the oil is < 0.1%. When sodium hydroxide is used, this goal is defeated by the creation of 4.5 times more water in the reactant mixture.

The primary concern with water is soap formation during the alkali-catalyzed transesterification reaction. Water will also inhibit the acid-catalyzed esterification reaction

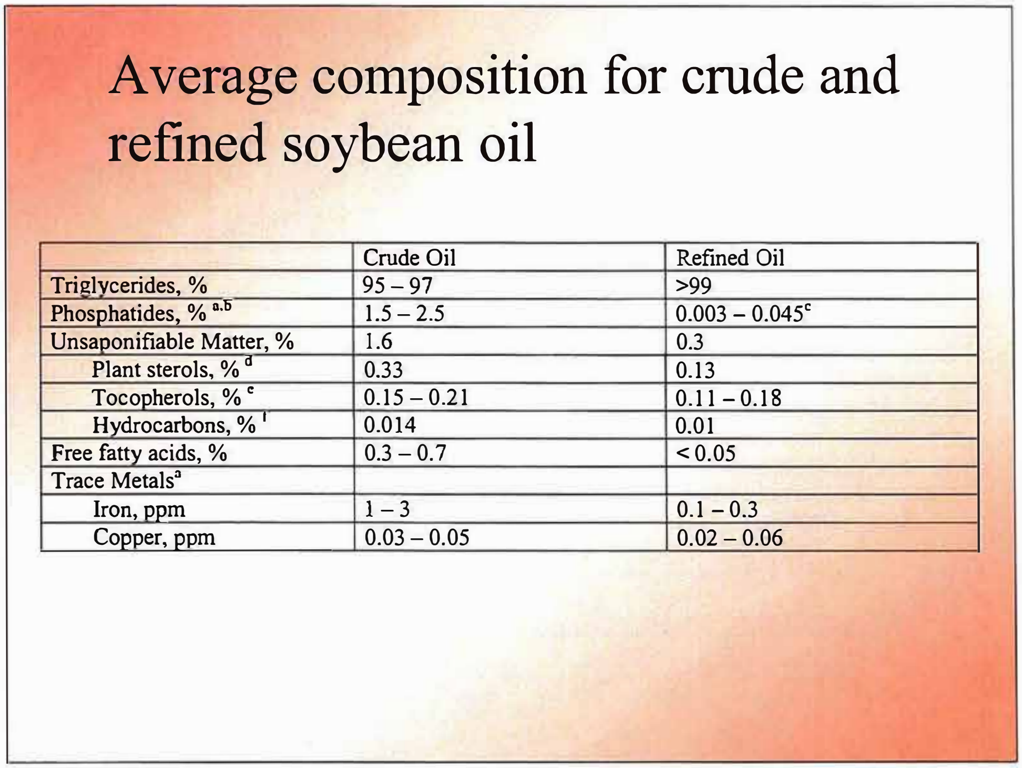
Processing: Lets start at the beginning:

Oil production

- Two choices: solvent extraction and mechanical extraction (expeller-extraction)
- Solvent extraction recovers virtually all of the oil from the seed.
  - High infrastructure cost.
  - Process favored by large plants.
- Mechanical extraction leaves 5-7% oil in the meal.
  - Lower infrastructure cost.
  - Favored by small plants.

Mechanical extraction leaves 5-7% of the oil in the meal. This is about 1/3 of the total oil for soybeans. Many sources claim that this meal has desirable properties for animal feed and should command a premium price from feeders. However, if the producer cannot get a premium price, the economics of mechanical extraction become difficult to justify.

For soybeans 80-82% of the soybean weight is meal. Although this portion sells for less per pound than the oil, it has a higher overall value.



Average composition for crude and refined soybean oil

	Crude Oil	Refined Oil
Triglycerides, %	95 – 97	>99
Phosphatides, % [a,b]	1.5 – 2.5	0.003 – 0.045[c]
Unsaponifiable Matter, %	1.6	0.3
Plant sterols, % [d]	0.33	0.13
Tocopherols, % [e]	0.15 – 0.21	0.11 – 0.18
Hydrocarbons, % [f]	0.014	0.01
Free fatty acids, %	0.3 – 0.7	< 0.05
Trace Metals[a]		
Iron, ppm	1 – 3	0.1 – 0.3
Copper, ppm	0.03 – 0.05	0.02 – 0.06

a Evans, C.D., G.R. List, R.E. Beal, L.T. Black. 1974. JAOCS. 51:444-448.

b List, G.R., A.J. Heakin, C.D. Evans, L.T. Black, T.L. Mounts. 1978. JAOCS. 55:521-522.

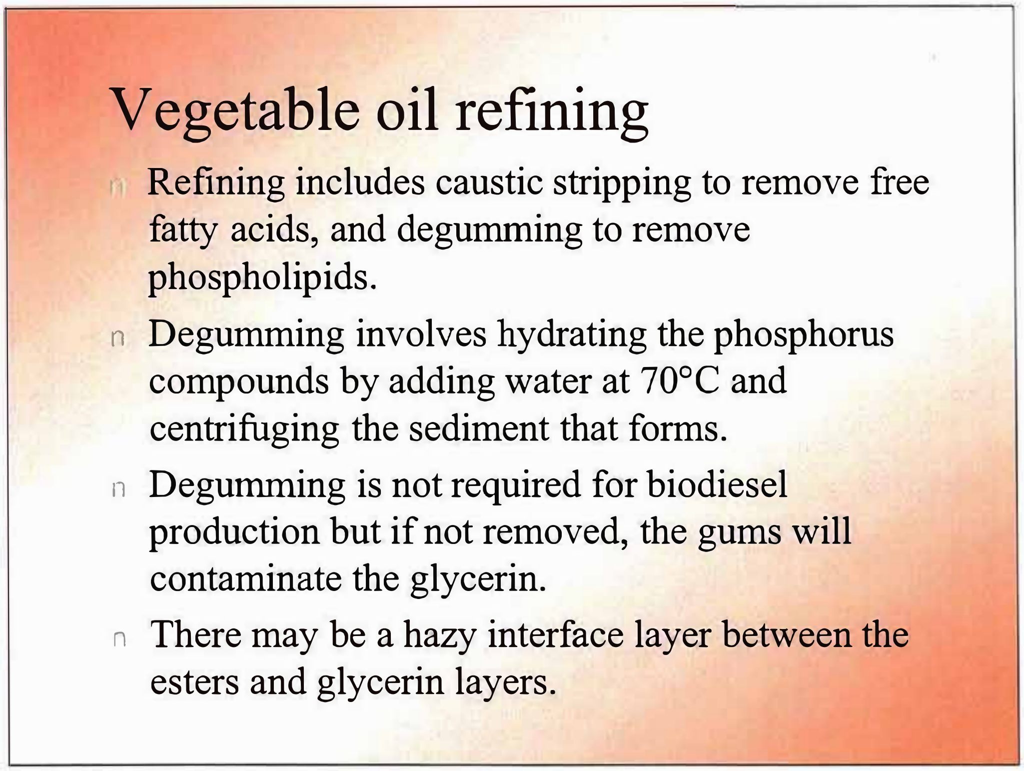
c Corresponding to 1-15 ppm of phosphorus

d Weihrauch, J.L., J.M. Gardiner. 1978. J. Am. Diet. Assoc. 73:39-47.

e Bauernfeind, J.C. 1977. Crit. Rev. Food Sci. 8:337-382.

f Gutfinger, T., A. Letan. 1974. J. Sci. Food Agric. 25:1143-1147.

Erickson, D.R., E. H. Pryde, O.L. Brekke, T.L. Mounts, and R.A. Falb, Editors, “Handbook of Soy Oil Processing and Utilization,” Published jointly by the American Soybean Association, St. Louis, MO, and the American Oil Chemists” Society, Champaign, IL, 1980.

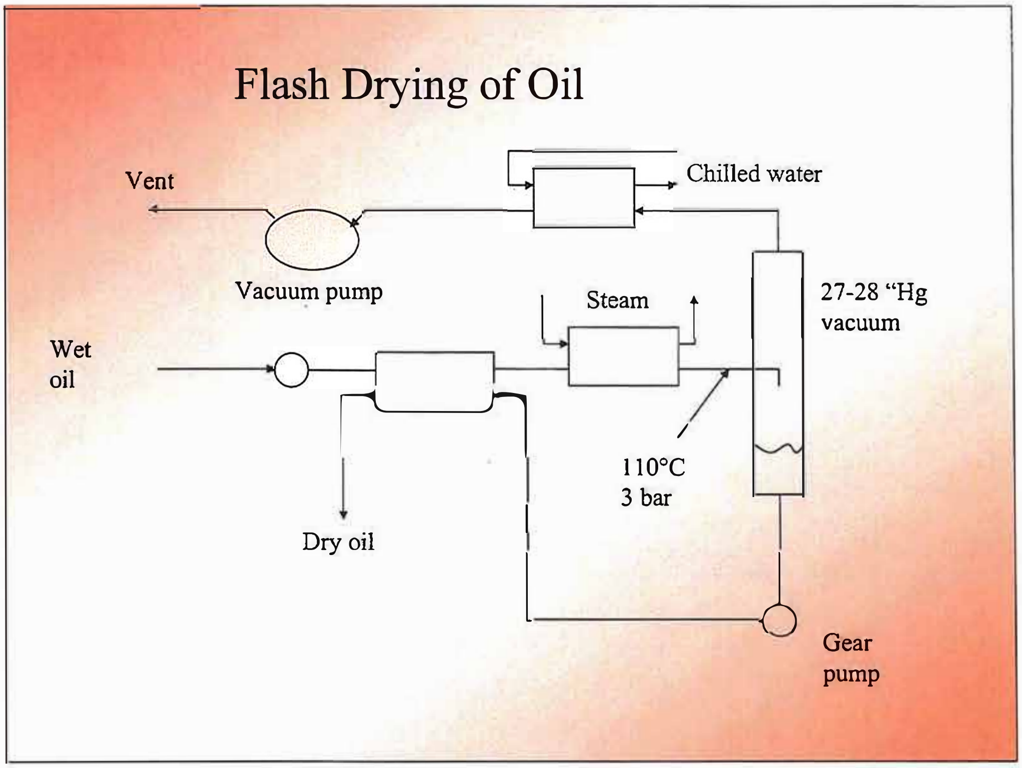


Vegetable oil refining

- Refining includes caustic stripping to remove free fatty acids, and degumming to remove phospholipids.
- Degumming involves hydrating the phosphorus compounds by adding water at 70°C and centrifuging the sediment that forms.
- Degumming is not required for biodiesel production but if not removed, the gums will contaminate the glycerin.
- There may be a hazy interface layer between the esters and glycerin layers.

Caustic stripping involves adding a water/sodium hydroxide solution to the oil to encourage the free fatty acids to form soap. Then, the soapy water is removed with a centrifuge. The resulting product is called *soapstock*. Because it carries some triglycerides and free fatty acids (if the soap is split by acidulation), it has been considered as a low cost feedstock for biodiesel. Currently, it is mostly used as an animal feed ingredient.

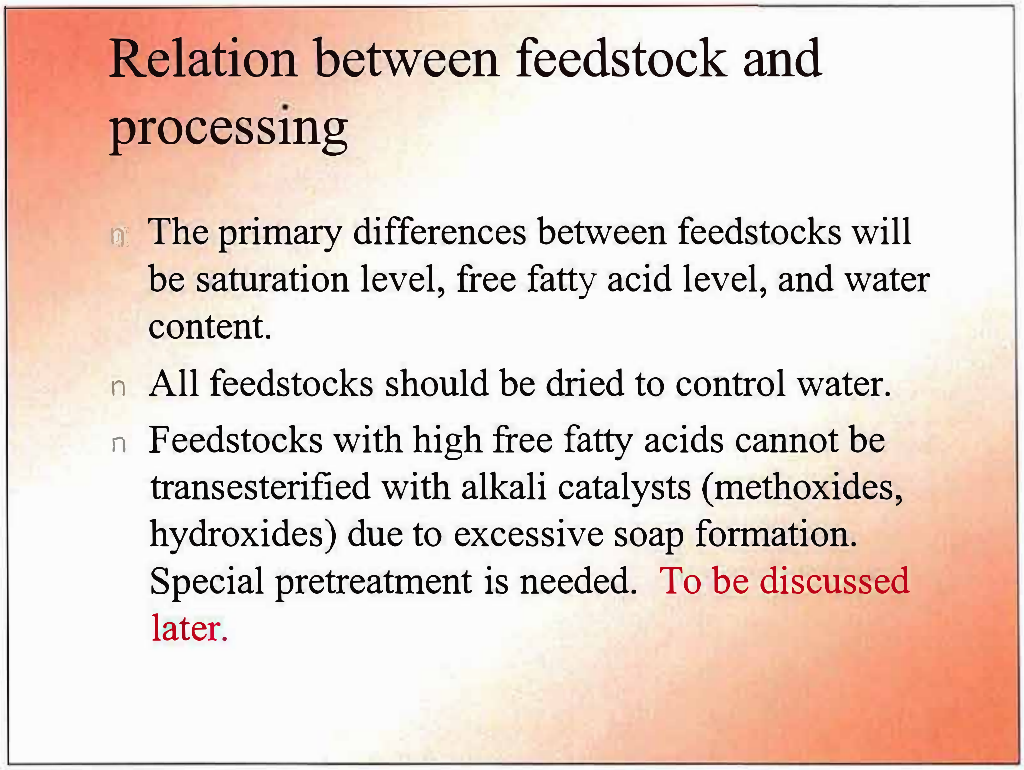
Van Gerpen, J.H. and B. Dvorak, “The Effect of Phosphorus Level on the Total Glycerol and Reaction Yield of Biodiesel,” presented at Bioenergy 2002, The 10th Biennieal Bioenergy Conference, Boise, ID, Sept. 22-26, 2002.



Flash Drying of Oil

Feedstocks should be dried before biodiesel production. Water content should be less than 0.1%, if possible.

Rendered products and "as-pressed" oils will generally have about 0.5% water content. Drying these oils before processing will yield substantial benefits from lower soap production.



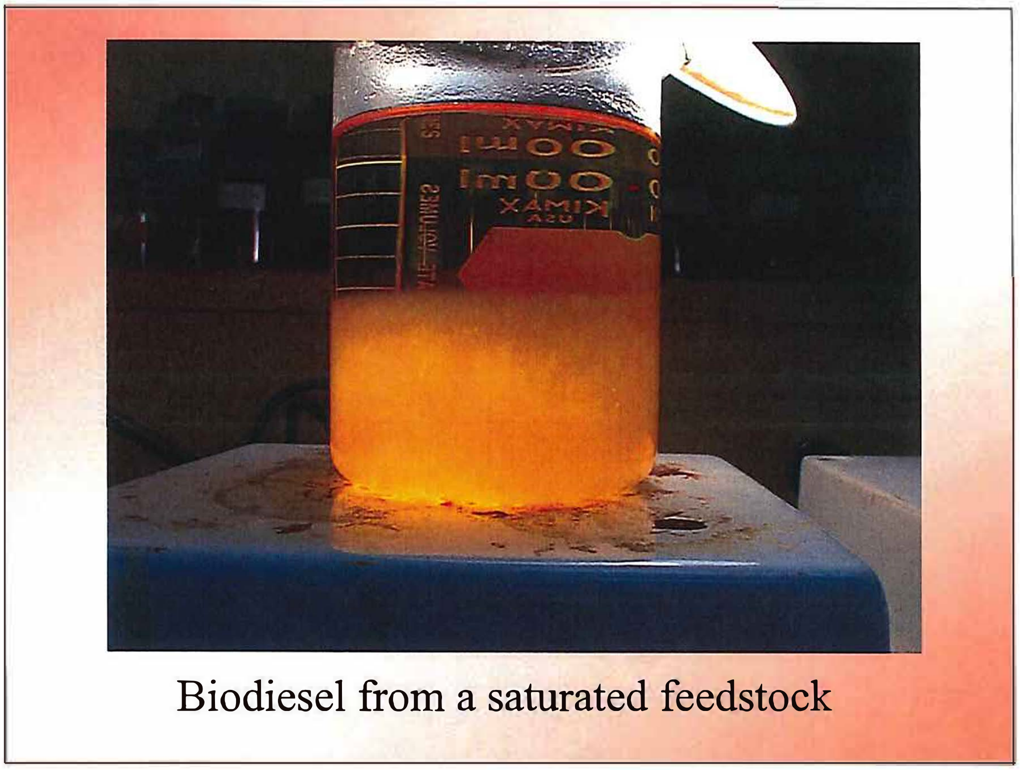
Relation between feedstock and processing

- The primary differences between feedstocks will be saturation level, free fatty acid level, and water content.
- All feedstocks should be dried to control water.
- Feedstocks with high free fatty acids cannot be transesterified with alkali catalysts (methoxides, hydroxides) due to excessive soap formation. Special pretreatment is needed. To be discussed later.

If you know three things about a feedstock, you can design a process to convert it to biodiesel:

- Water content
- Free fatty acid content
- % non-triglycerides (unsaponifiable matter)

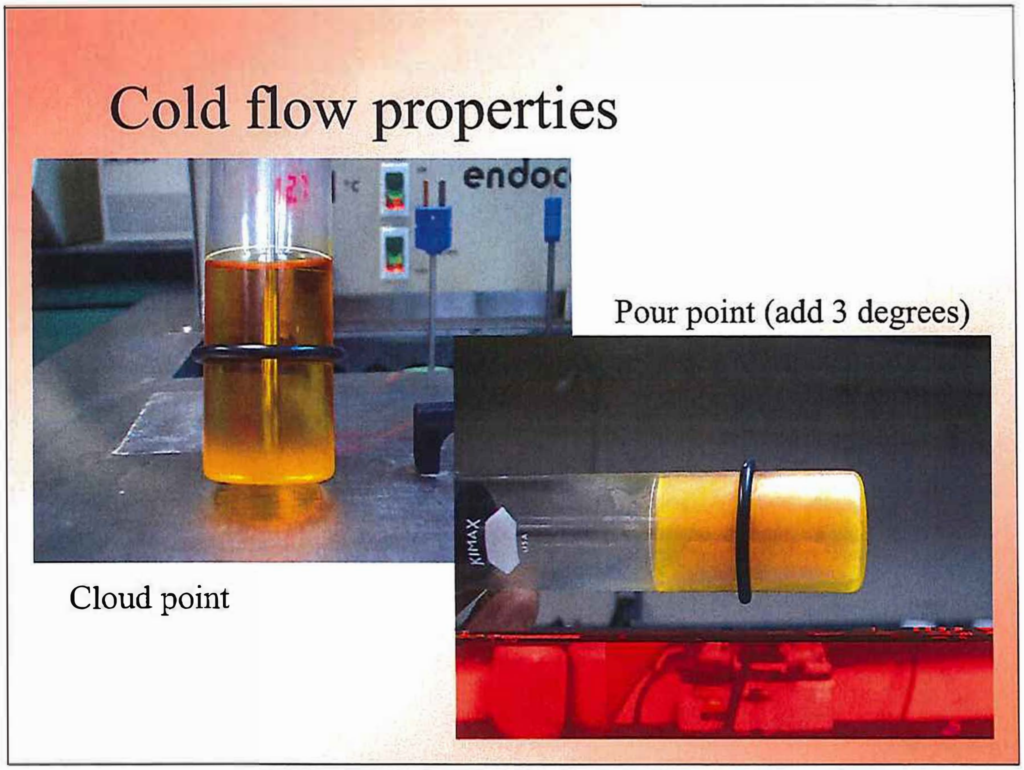
There isn't much that can be done about saturation level. The transesterification reaction does not seem to be affected significantly by the saturation level of the feedstock. However, saturated feedstocks produce biodiesel with a high cloud point and may not be acceptable at low operating temperatures. This can be improved by blending with less saturated feedstocks, blending with #1 or #2 diesel fuels, or using cold flow additives. These additives do not lower the cloud point but they inhibit the agglomeration of crystals and thus allow the crystals to stay small enough to pass through fuel filters. This can lower the operability temperature of the vehicle considerably.



Biodiesel from a saturated feedstock

Saturated feedstocks will produce biodiesel that can start to gel at temperatures as high as ambient. One approach to dealing with this problem is ***winterization***. This involves cooling the fuel slowly to allow some crystals to form. Then, these crystals are filtered out and the balance of the fuel is cooled further to encourage more crystal growth. By this means it is possible to separate a large portion of the saturated compounds, which could be used in higher temperature applications, and produce a low cloud point biodiesel.

The disadvantage of winterization is that it entails a large yield loss. When separating saturates, you usually lose at least an equivalent amount of other material.



Cold flow properties

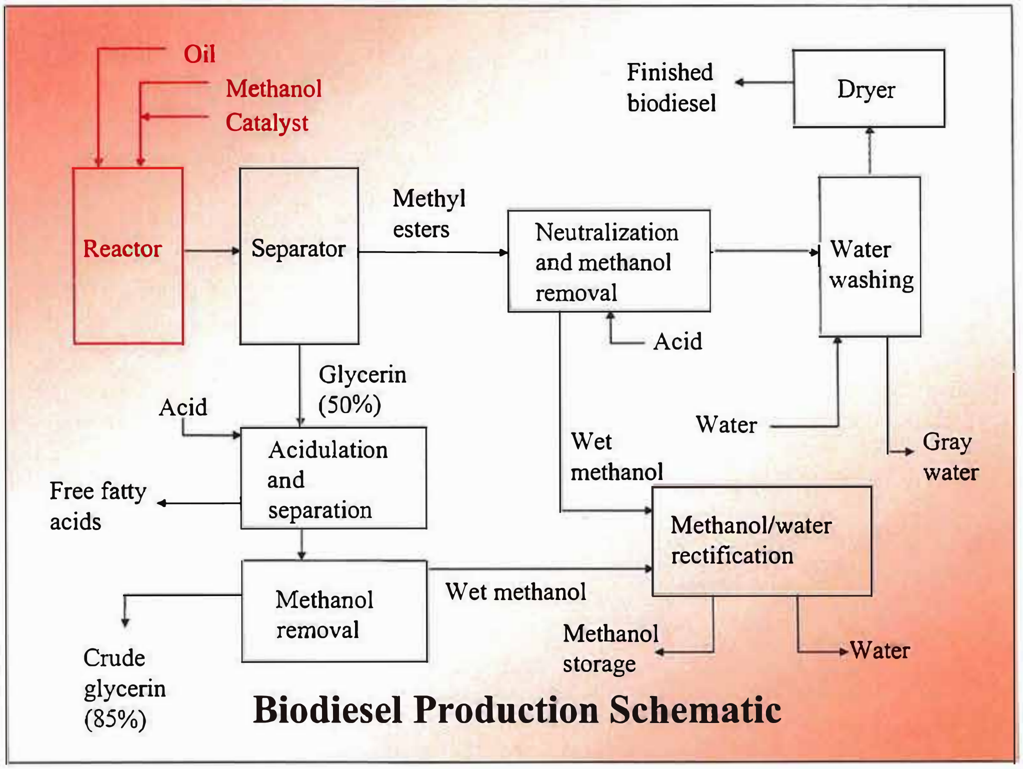
Pour point (add 3 degrees)

Cloud point

When the fuel is cooled, the cloud point is the temperature when the first crystals are observed as a slight cloudiness, usually near the bottom of the container.

The pour point is found by continuing to cool the fuel until it won't flow, then adding 3°C.

Other tests that attempt to identify the temperature when filters will plug are the cold filter plugging point (CFPP) and the low temperature filter test (LTFT).



Biodiesel Production Schematic

We will use this schematic as a guide to the biodiesel production process. Essentially all commercial biodiesel plants will have some version of each of these processes although they may use different equipment for each process or do the processes in different ways.

The first discussion will focus on the Reactor portion of the schematic.

Consider only transesterification

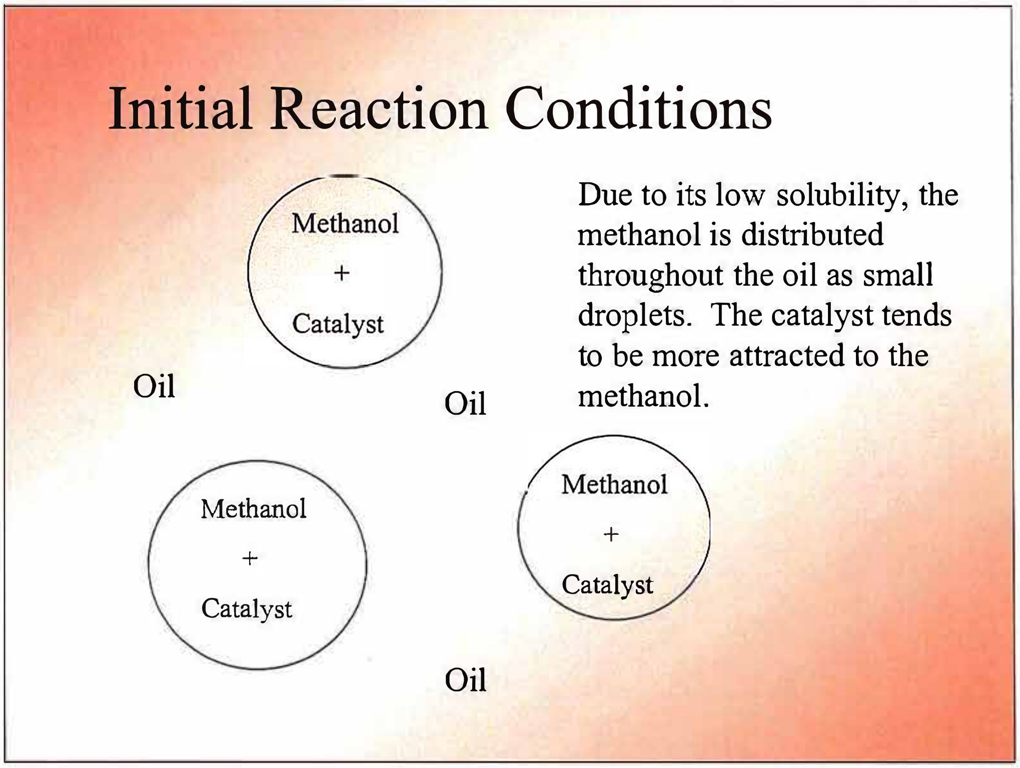
(high free fatty acids feedstocks will be discussed later)

- The reaction is reversible:

Triglycerides + methanol ↔ biodiesel + glycerin

- As long as we have excess methanol present, we are forcing the reaction to the biodiesel side. The ability to remove glycerin would also help move the reaction to the right.

Start with a detailed look at the reaction processes.



Initial Reaction Conditions

Methanol
+
Catalyst

Oil

Oil

Methanol
+
Catalyst

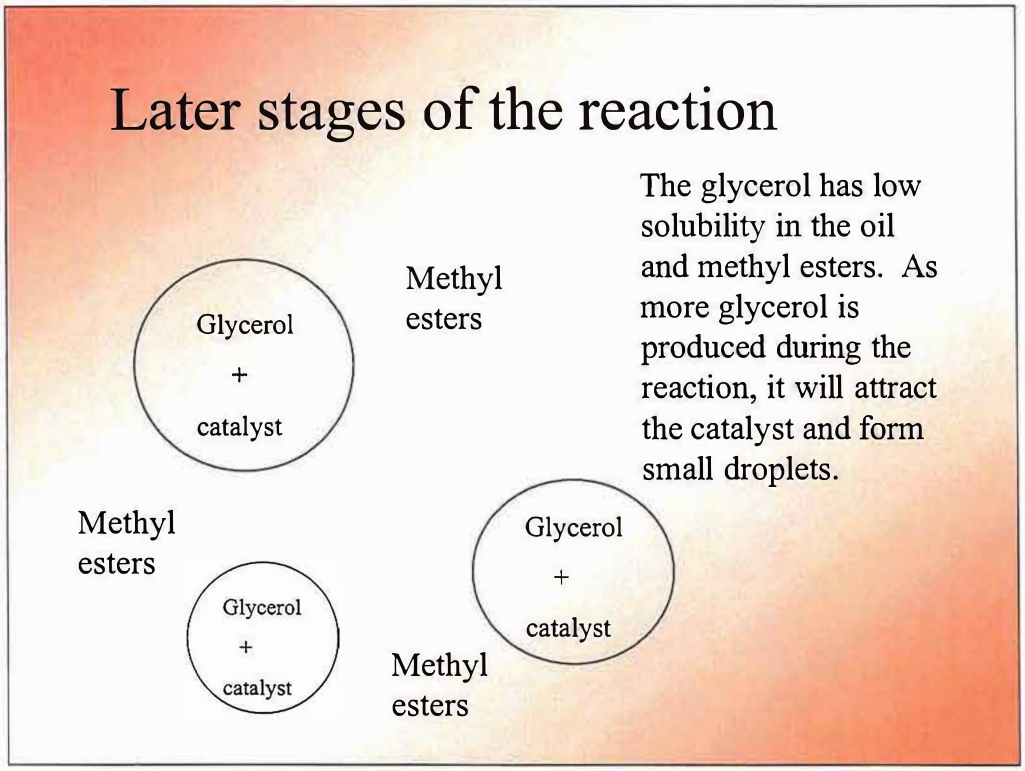
Methanol
+
Catalyst

Oil

Due to its low solubility, the methanol is distributed throughout the oil as small droplets. The catalyst tends to be more attracted to the methanol.

The catalyst is attracted to the polar phase in the system, which is the methanol.

Agitation is needed to keep the methanol distributed as small droplets throughout the oil.



Later stages of the reaction

The glycerol has low solubility in the oil and methyl esters. As more glycerol is produced during the reaction, it will attract the catalyst and form small droplets.

Glycerol + catalyst

Methyl esters

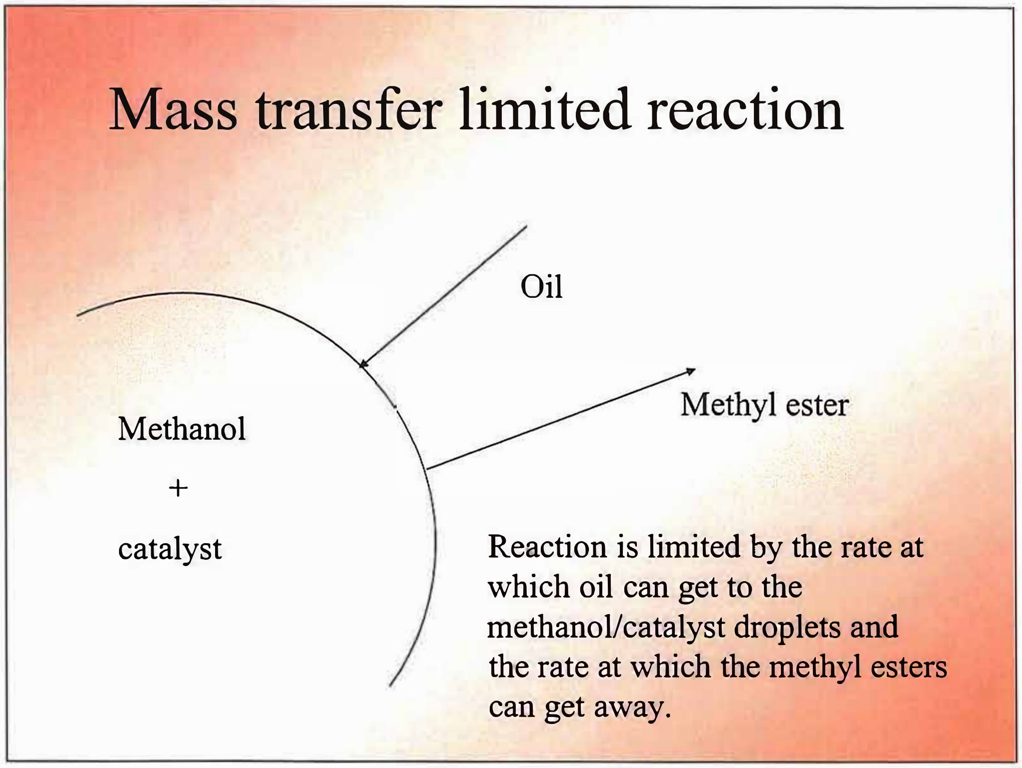
Methyl esters

Glycerol + catalyst

Glycerol + catalyst

Methyl esters

Glycerol is polar so it attracts the catalyst.



Mass transfer limited reaction

Oil

Methyl ester

Methanol

+

catalyst

Reaction is limited by the rate at which oil can get to the methanol/catalyst droplets and the rate at which the methyl esters can get away.

This a simplified view of the process.

The real reaction is complicated by the fact that the conversion of a triglyceride to methyl esters is a multi-step process, with diglycerides and monoglycerides as intermediate products.

$$\begin{tikzcd}
\text{Triglyceride} \arrow[r] \arrow[d] & \text{Diglyceride} \arrow[r] \arrow[d] & \text{Monoglyceride} \arrow[r] \arrow[d] & \text{Glycerol} \\
\text{Methyl ester} & \text{methyl ester} & \text{methyl ester} &
\end{tikzcd}$$

As the diglycerides and monoglycerides are formed, they may stay near the droplet for continued reaction or they may move away and need to be reacted at a later stage.

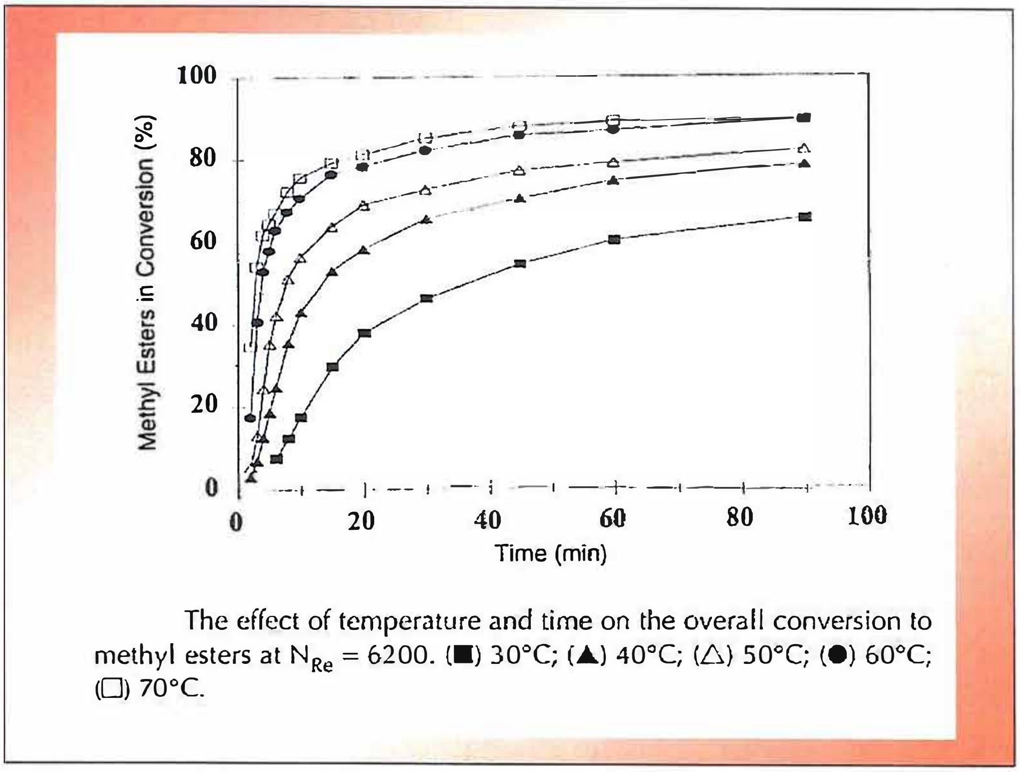
Also, when significant levels of diglycerides and monoglycerides are formed, they can assist in the formation of emulsions that alleviate the need for continued agitation.

Ma, F., L.D. Clements, and M.A. Hanna, "The Effects of Catalyst, Free Fatty Acids, and Water on Transesterification of Beef Tallow," Transactions of the ASAE, V. 41, No. 5, 1998, pp. 1261-1264.

Ma, F., L.D. Clements, and M.A. Hanna, "Biodiesel Fuel from Animal Fat. Ancillary Studies on Transesterification of Beef Tallow," Ind. Eng. Chem. Res., V. 37, 1998, pp. 3768-3771.

Reaction time

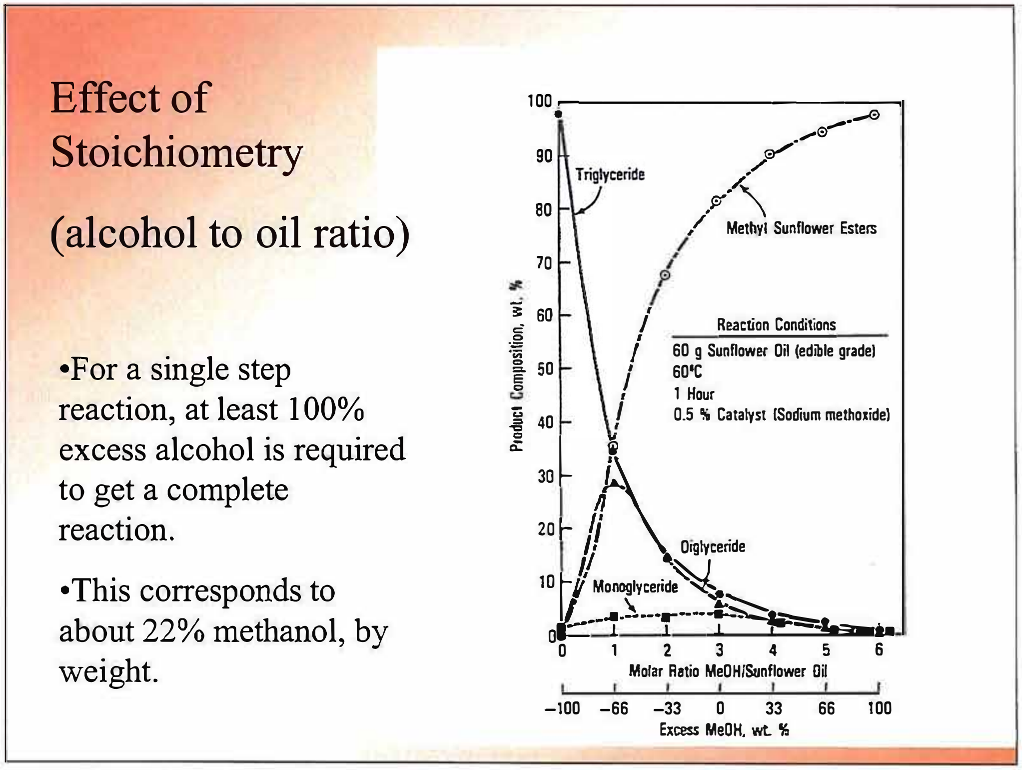
- Transesterification reaction will proceed at ambient (70°F) temperatures but needs 4-8 hours to reach completion.
- Reaction time can be shortened to 2-4 hours at 105°F and 1-2 hours at 140°F.
- Higher temperatures will decrease reaction times but require pressure vessels because methanol boils at 148°F (65°C).
- High shear mixing and use of cosolvents have been proposed to accelerate the reaction (discussed later)



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.

Noureddini, H. and D. Zhu, “Kinetics of Transesterification of Soybean Oil,” JAOCS, V. 74, No. 11, 1997, pp. 1457-1463.

Roughly, a 10°C rise in reaction temperature will double the reaction rate.

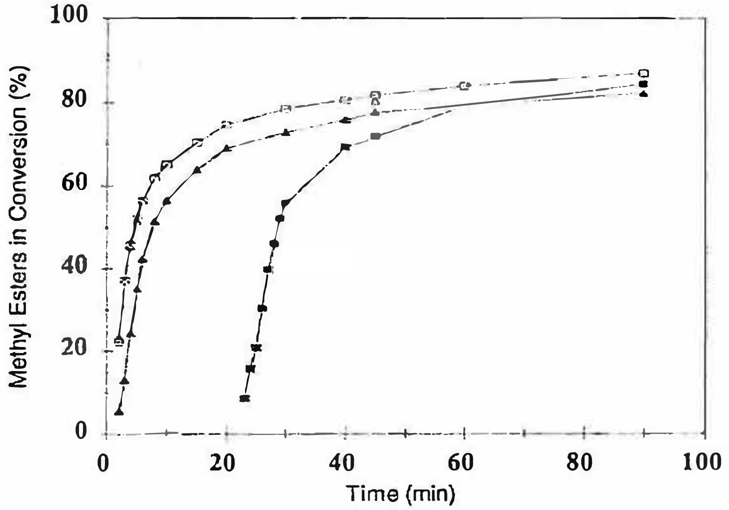


Effect of Stoichiometry

(alcohol to oil ratio)

- For a single step reaction, at least 100% excess alcohol is required to get a complete reaction.
- This corresponds to about 22% methanol, by weight.

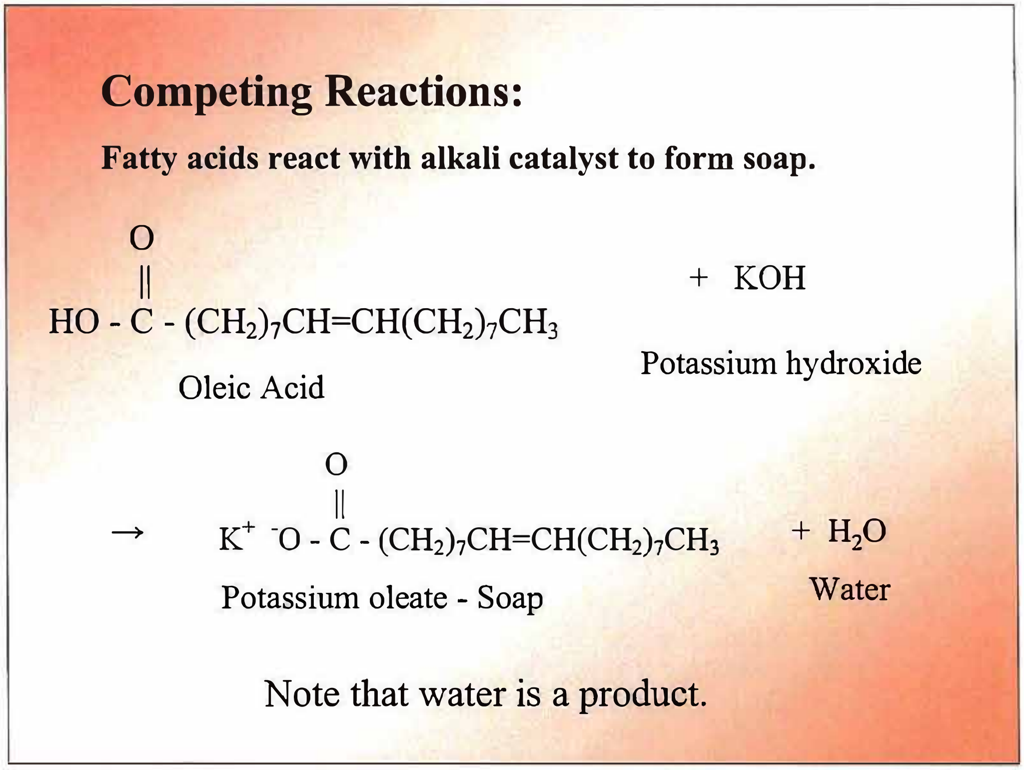
Freedman, B. and E.H. Pryde, “Fatty Esters from Vegetable Oils for Use as a Diesel Fuel,” from Vegetable Oil Fuels – Proceedings of the International Conference on Plant and Vegetable Oils as Fuels, published by American Society of Agricultural Engineers, Fargo, ND, August 2-4, 1982.



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.

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

Higher mixing rate provides faster reaction time.



Competing Reactions:

Fatty acids react with alkali catalyst to form soap.

$HO-\overset{\overset{O}{\|}}{C}-(CH_2)_7CH=CH(CH_2)_7CH_3$ + KOH

Oleic Acid

Potassium hydroxide

$\rightarrow K^+ \, {}^-O-\overset{\overset{O}{\|}}{C}-(CH_2)_7CH=CH(CH_2)_7CH_3$ + H_2O

Potassium oleate - Soap

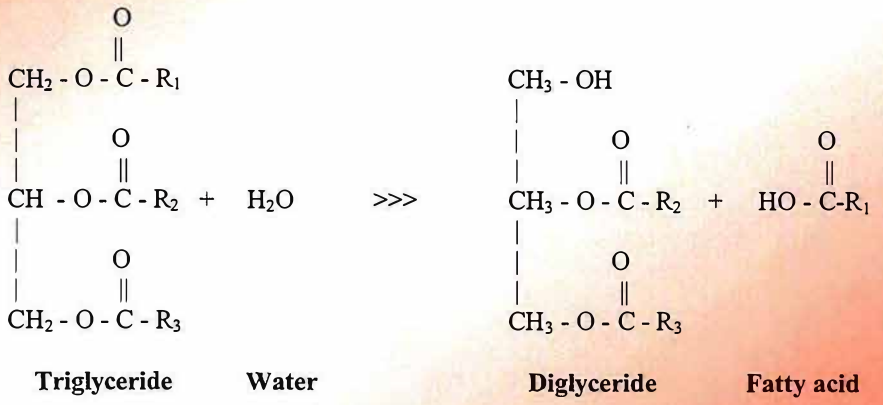
Water

Note that water is a product.

Fatty acids reacting with alkali to make soap also produces water. This water can in turn react with triglycerides and possibly esters to form additional free fatty acids.

Water is also a problem

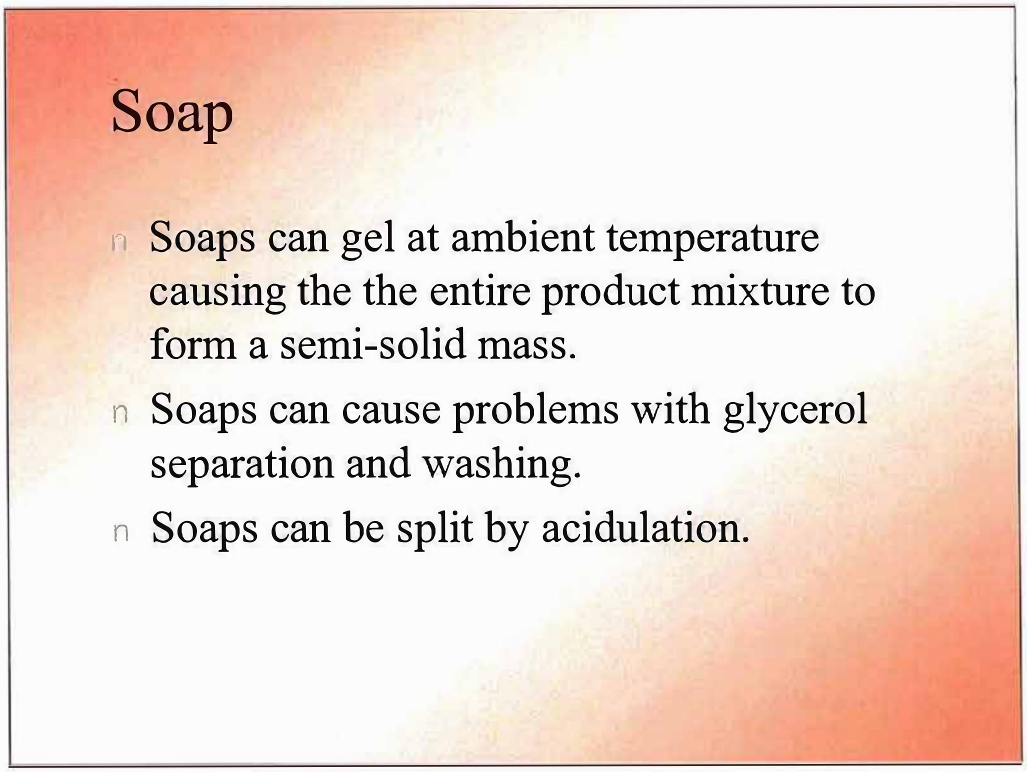
Water hydrolyzes fats to form free fatty acids, which then form soap.



$$\begin{array}{l} \overset{\displaystyle O}{\|} \\ CH_2 - O - C - R_1 \\ | \\ | \;\; O \\ | \;\; \| \\ CH - O - C - R_2 \\ | \\ | \;\; O \\ | \;\; \| \\ CH_2 - O - C - R_3 \end{array} + H_2O \;\; >>> \;\; \begin{array}{l} CH_3 - OH \\ | \\ | \;\; O \\ | \;\; \| \\ CH_3 - O - C - R_2 \\ | \\ | \;\; O \\ | \;\; \| \\ CH_3 - O - C - R_3 \end{array} + \begin{array}{l} O \\ \| \\ HO - C - R_1 \end{array}$$

Triglyceride **Water** **Diglyceride** **Fatty acid**

Enzymes may accelerate this reaction.



Soap

- Soaps can gel at ambient temperature causing the the entire product mixture to form a semi-solid mass.
- Soaps can cause problems with glycerol separation and washing.
- Soaps can be split by acidulation.

Soaps can be split be lowering the pH to 4.5 to 5.0 with a strong acid.

Soap + Acid → Free fatty acid + salt

This can be done with the methyl esters to reduce the tendency to form emulsions and make the fuel easier to wash. However, the free fatty acids will go into solution with the methyl esters and raise the acid value of the biodiesel. In most cases, the free fatty acids will still meet the specification.

Soap can be measured by AOCS Recommended Practice Cc 17-79.

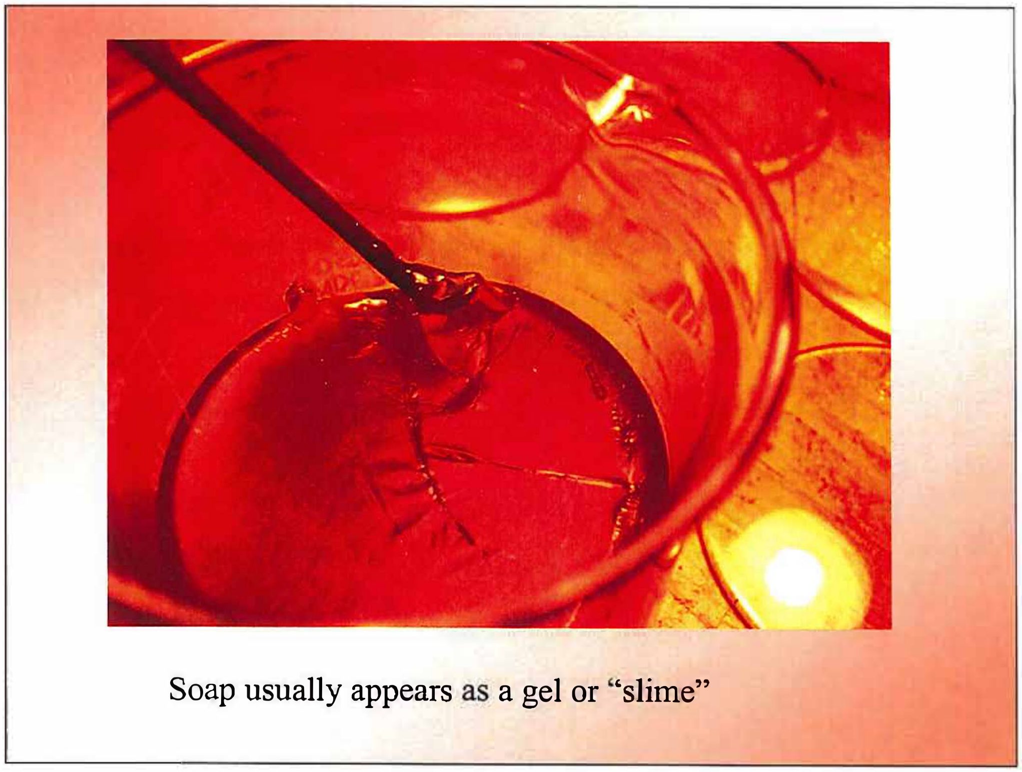
Soap

- Physical appearance: Usually clear, very viscous
- Methanol acts as a co-solvent to keep soap in solution with the methyl esters.
- High soap levels will cause high Sulfated Ash in biodiesel
- High FFA and water often go together (i.e trap grease, restaurant waste). Both contribute to soap formation.

White crystals floating in biodiesel, or white sludge layers at the bottom of a storage tank, are often thought to be soap. This is usually a mistake. These are probably monoglycerides of saturated fatty acids coming out of solution or possibly the saturated methyl esters themselves if their concentration is too high or the temperature is too low.

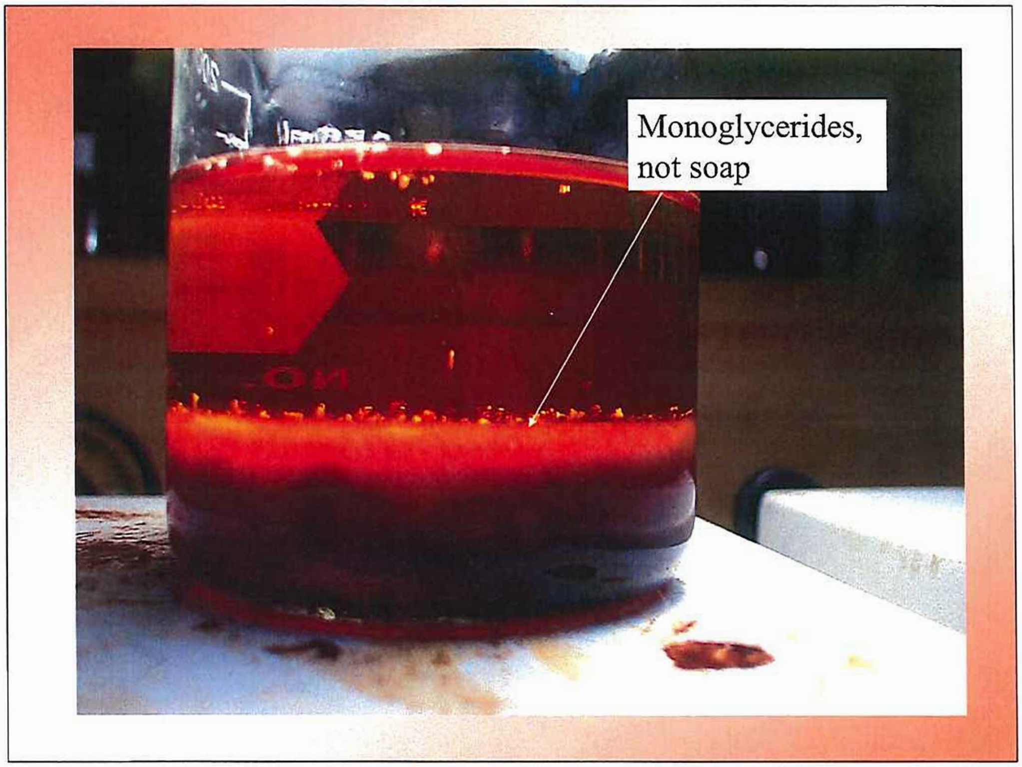
When it comes out of solution, soap will usually have the consistency of the skin that forms on the top of a can of paint that has been left open.

Soap can be measured using American Oil Chemists' Society method Cc 17-79. This method involves titrating with HCl solution to determine the amount of strong acid required to split the soap. Bromophenol blue is used as an indicator.



Soap usually appears as a gel or “slime”

Soap will plug filters, screens, and flash column packings.

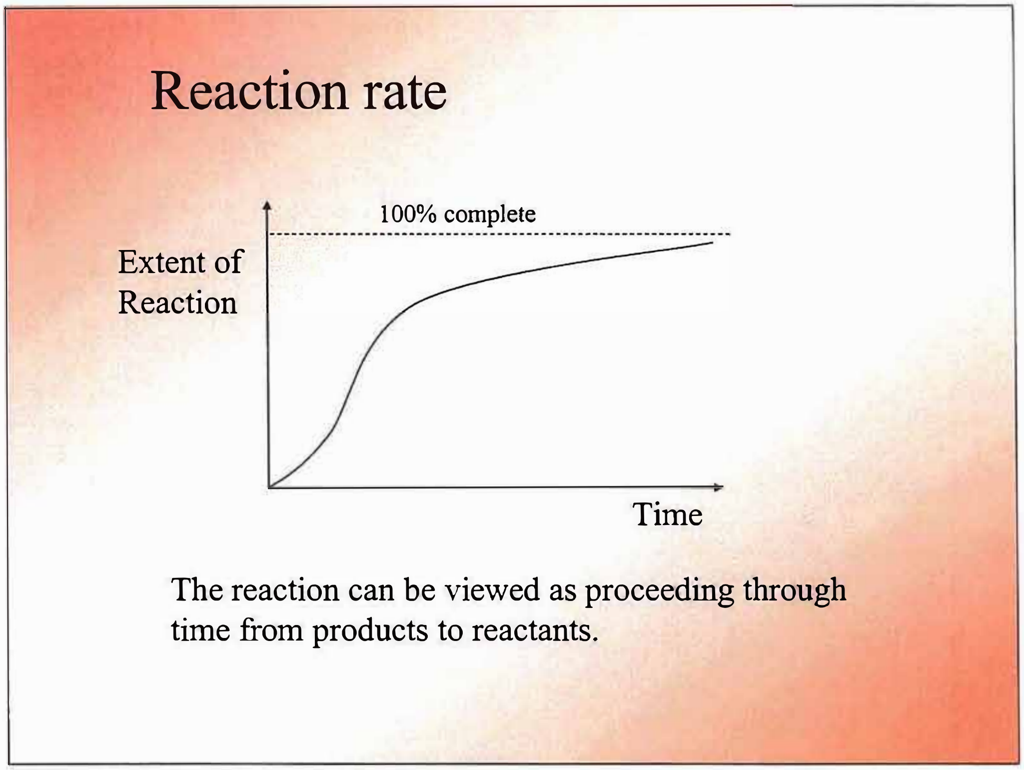

Monoglycerides, not soap

A white layer after the reaction is sometimes confused with soap. It is more likely to be monoglycerides of saturated fatty acids that have crystallized. These monoglycerides are a result of incomplete reaction.

The monoglycerides may occur with a high soap level. That is, high soap formation, caused by water or excessive free fatty acid level, may deactivate the catalyst (by converting it to soap) and thus cause an incomplete reaction.

Monoglycerides may be removed by reacting with additional alcohol and catalyst

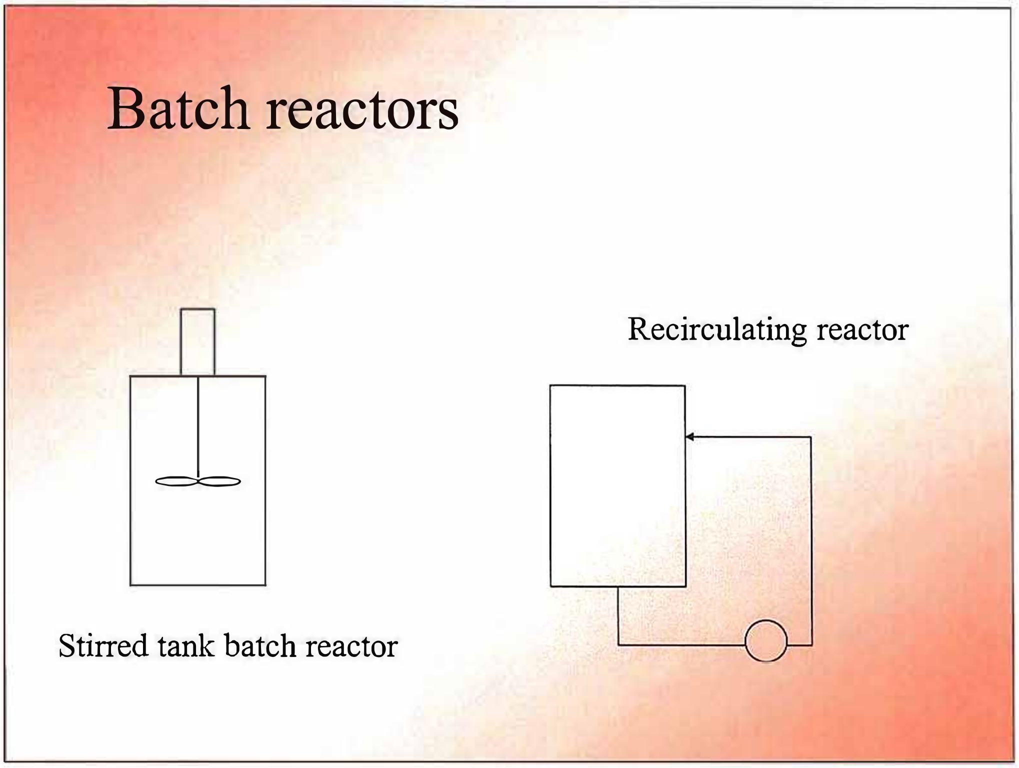
Soap can be washed out or split by acidulation.



Reaction rate

The reaction can be viewed as proceeding through time from products to reactants.

This view of the reaction progress is useful for both batch and continuous flow reaction systems.

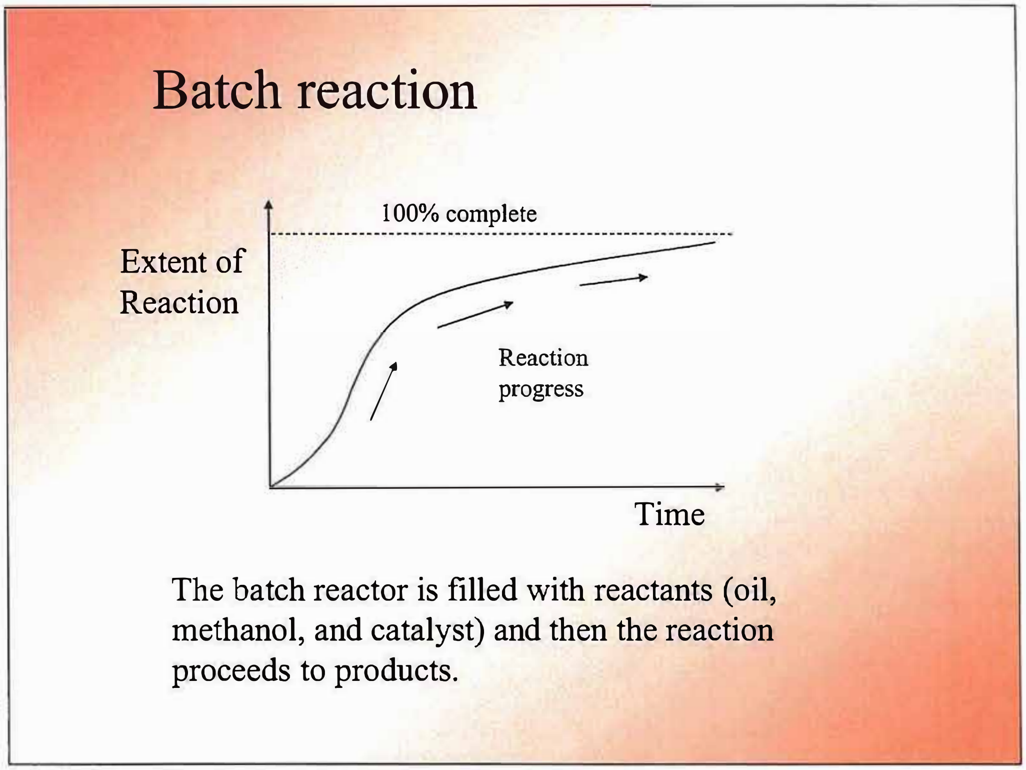


Batch reactors

Stirred tank batch reactor

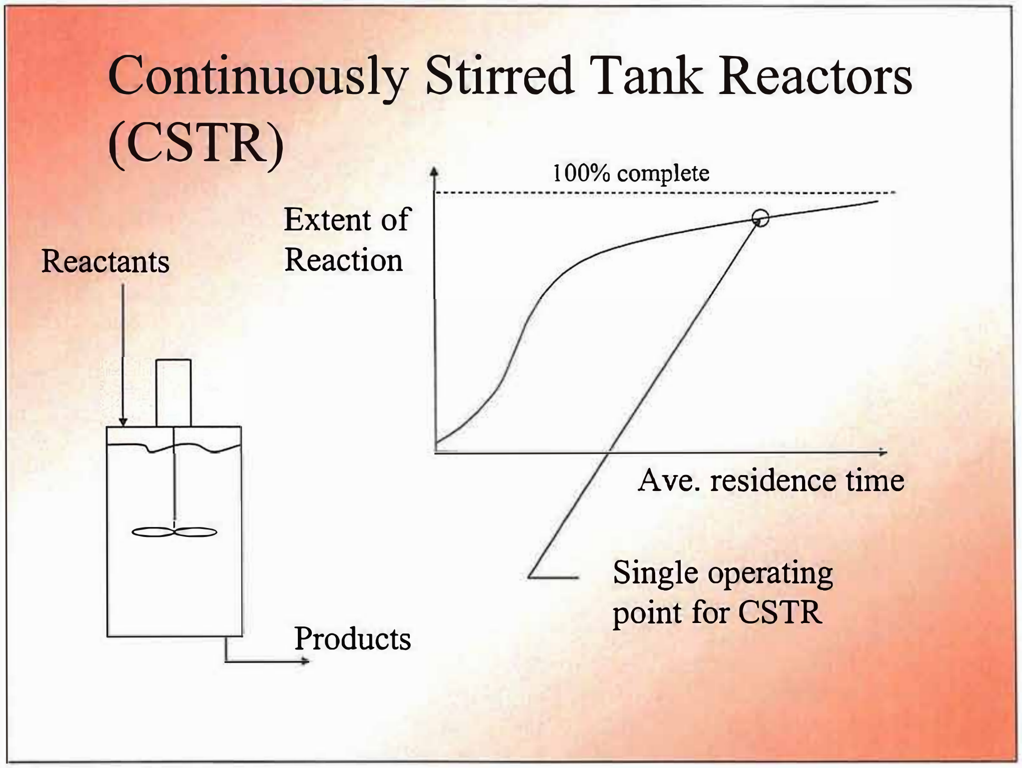
Recirculating reactor

Centrifugal pumps can provide high shear and enhance mixing. This is desirable early in the reaction. High shear mixing later in the reaction can extend glycerin settling times.



Batch reaction

The batch reactor is filled with reactants (oil, methanol, and catalyst) and then the reaction proceeds to products.



Continuously Stirred Tank Reactors (CSTR)

Reactants

Products

Extent of Reaction

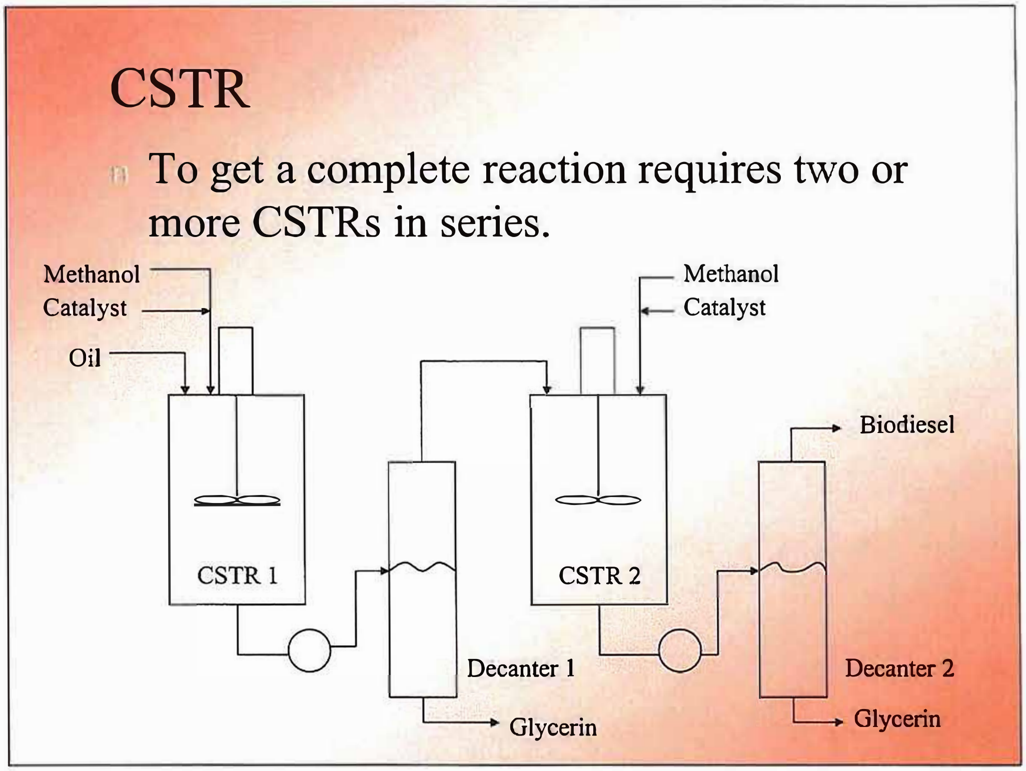
100% complete

Ave. residence time

Single operating point for CSTR

In the CSTR, reactants added continuously and products are removed continuously. The mixture is assumed to be perfectly mixed so the amount of products that might short circuit from the inlet directly to the outlet is small.

Rather than proceeding through a sequence of states in the reaction as is done with the batch reactor, the CSTR operates at steady state. The composition in the CSTR is fixed at a point along the reaction curve that is set by the average residence time of the reactants.



CSTR

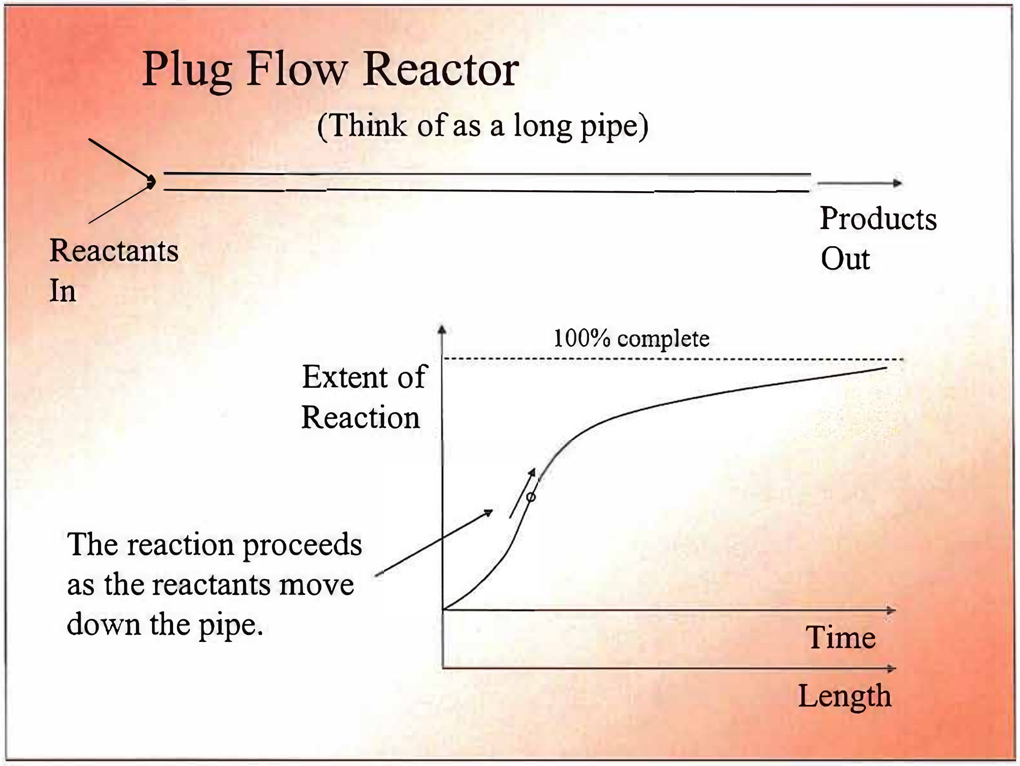
- To get a complete reaction requires two or more CSTRs in series.

Trying to have the reaction go entirely to completion in a single CSTR requires very long residence times. It is more efficient to stage the reactors so that one feeds into the next.

Glycerin removal between stages aids in reaction completion. In an equilibrium reaction, removal of one of the products of the reaction (in this case glycerin), tends to cause the equilibrium to shift more toward the product side.

Unfortunately, when the glycerin is removed most of the catalyst goes with it. More catalyst and methanol need to be added in the second CSTR.

Most of the water that enters the process with the oil and alcohol will come out with the glycerin from decanter 1. Glycerin from decanter 2 (following CSTR 2) will have low water content. This might be returned directly to CSTR 1 for recycling of methanol and catalyst with no further processing.



Plug Flow Reactor

(Think of as a long pipe)

The reaction proceeds as the reactants move down the pipe.

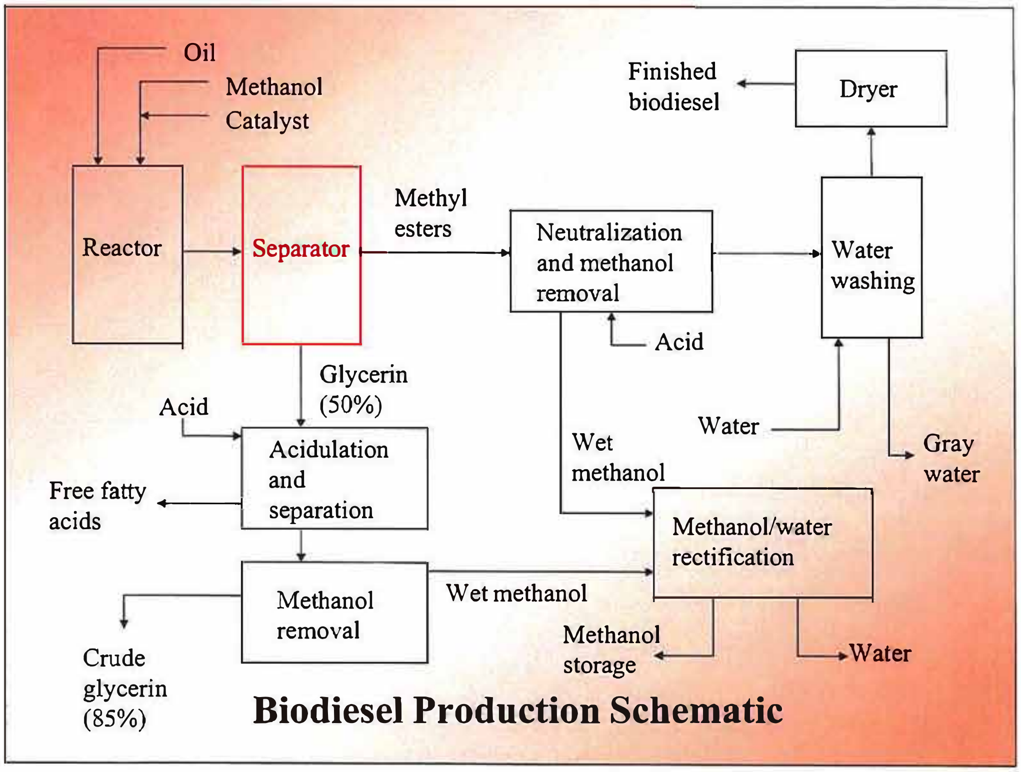
The pipe can be coiled to provide a smaller package.

If operating at high pressure, it is much cheaper to do the reaction in a pipe than a pressure vessel.

Plug flow systems have small operating volumes. There is relatively little product “in process.” This is desirable for frequent start-up and shut-down. However, it can be difficult to get the residence times needed for complete reaction to biodiesel. Usually high temperatures and pressures are required and long lengths of pipe.

Plug flow reactors have similarities to batch reactors in that the reaction reaches different degrees of completeness at different points along the pipe (instead of different points in time).

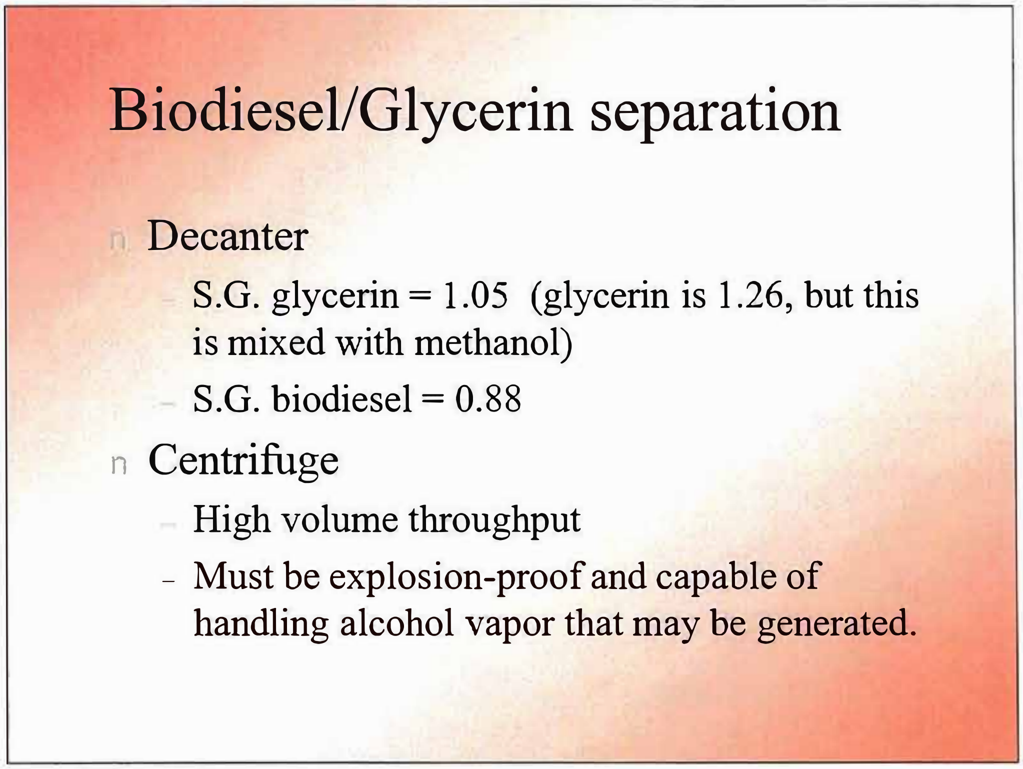
Plug flow reactors have been re-discovered many times for biodiesel production. An early example is given in Allen, H.D. and W.A. Kline, “Process for Treating Fats and Fatty Oils,” U.S. Patent 2,383,579 (1945).



Oil
Methanol
Catalyst
Reactor
Separator
Methyl esters
Glycerin (50%)
Acid
Acidulation and separation
Free fatty acids
Methanol removal
Crude glycerin (85%)
Wet methanol
Neutralization and methanol removal
Acid
Wet methanol
Methanol/water rectification
Methanol storage
Water
Water washing
Water
Gray water
Dryer
Finished biodiesel

Biodiesel Production Schematic

The separation process separates the biodiesel phase from the glycerin phase.

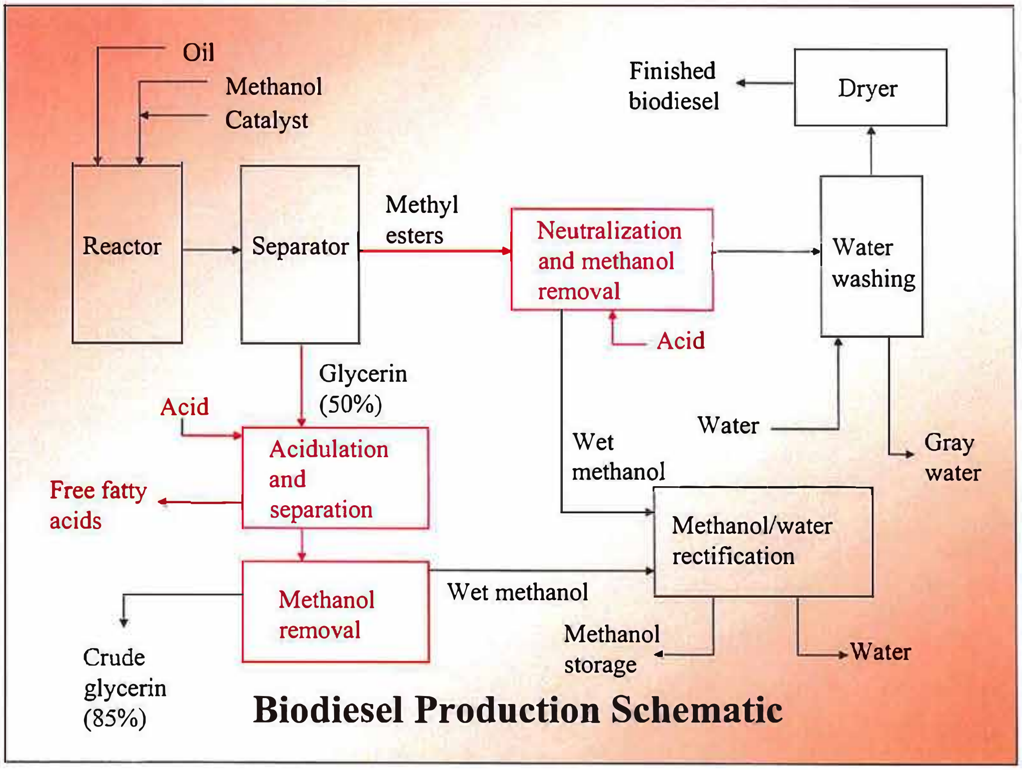


Biodiesel/Glycerin separation

- Decanter
  - S.G. glycerin = 1.05 (glycerin is 1.26, but this is mixed with methanol)
  - S.G. biodiesel = 0.88
- Centrifuge
  - High volume throughput
  - Must be explosion-proof and capable of handling alcohol vapor that may be generated.

Centrifuges are expensive. However, they eliminate the need for large decanter vessels that tie up large volumes of “in-process” material.

Both decanters and centrifuges have difficulty with emulsions. Excessive soap can produce an emulsion that is difficult to break.



Biodiesel Production Schematic

Acidulation/neutralization

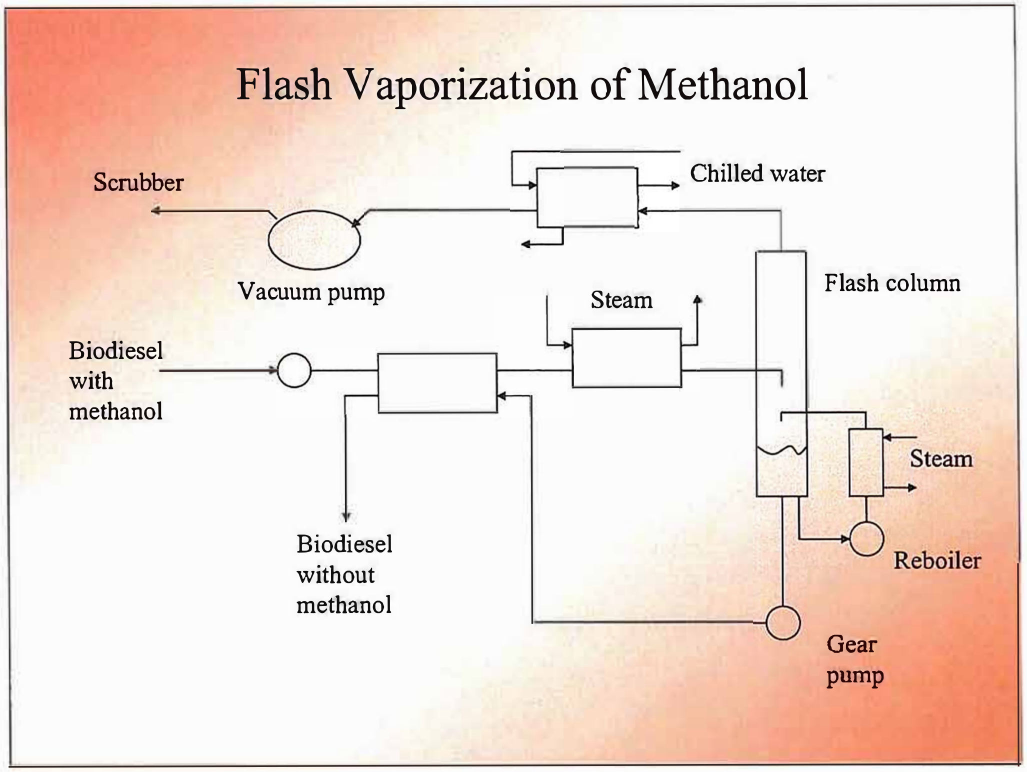
- Neutralization: Residual catalyst can be neutralized by acid addition.

  $NaOCH_3 + HCl \rightarrow CH_3OH + NaCl$

- Soaps can be split into free fatty acids and salt by acidulation (requires pH of 4.5-5.0).

  Soap + HCl → FFA + NaCl (salt)

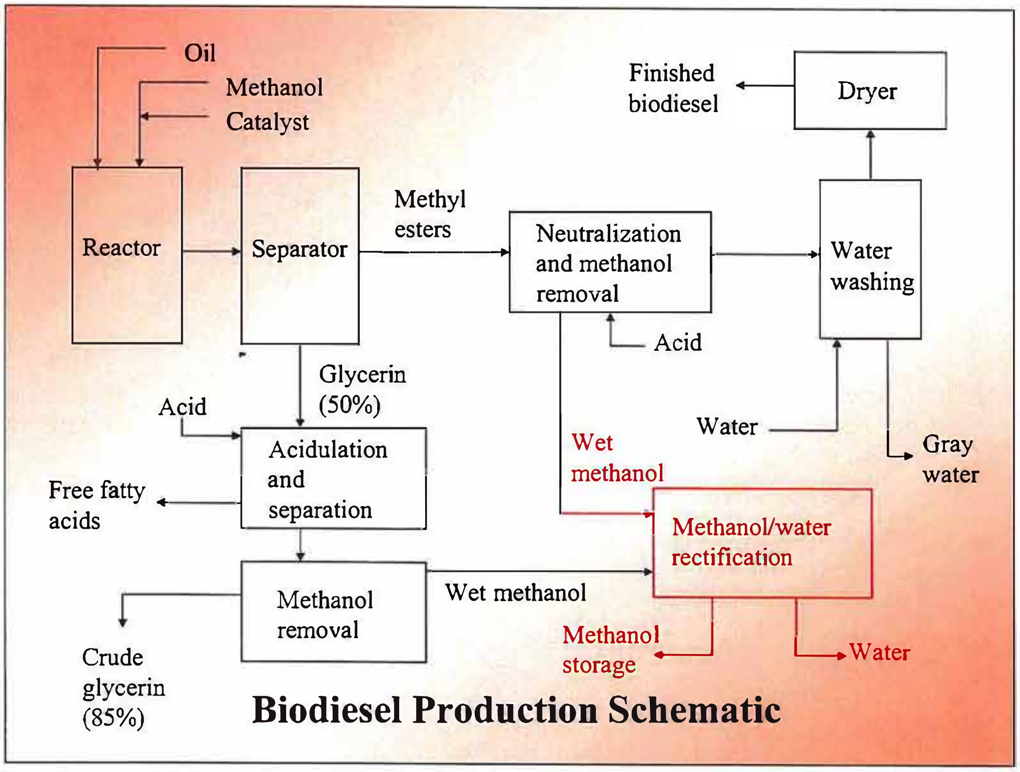
Eliminating soap can lessen the tendency to form emulsions during washing.



Flash Vaporization of Methanol

Methanol can be removed from the biodiesel by flash vaporization. Similar techniques can be used for glycerin but wiped film evaporators or falling-film evaporators might be more appropriate.

One issue that needs further research is whether it is necessary to do the methanol removal after separating the biodiesel and glycerin. On the plus side, it would be convenient to have a single flash process to remove the methanol. It has also been observed that the separation of biodiesel and glycerin is sharper and faster when the methanol is not present. This is probably due to methanol's slight co-solvent effect. On the negative side, when the methanol has been removed, there is no obstacle to a reversal of the transesterification reaction. The methyl esters and glycerin can react to form monoglycerides and methanol. The rate of this reverse reaction has not been determined and whether it results in significant formation of monoglycerides in the final products is not known.



Oil

Methanol

Catalyst

Reactor

Separator

Methyl esters

Neutralization and methanol removal

Acid

Water washing

Dryer

Finished biodiesel

Glycerin (50%)

Acid

Acidulation and separation

Free fatty acids

Water

Gray water

Wet methanol

Methanol/water rectification

Methanol removal

Wet methanol

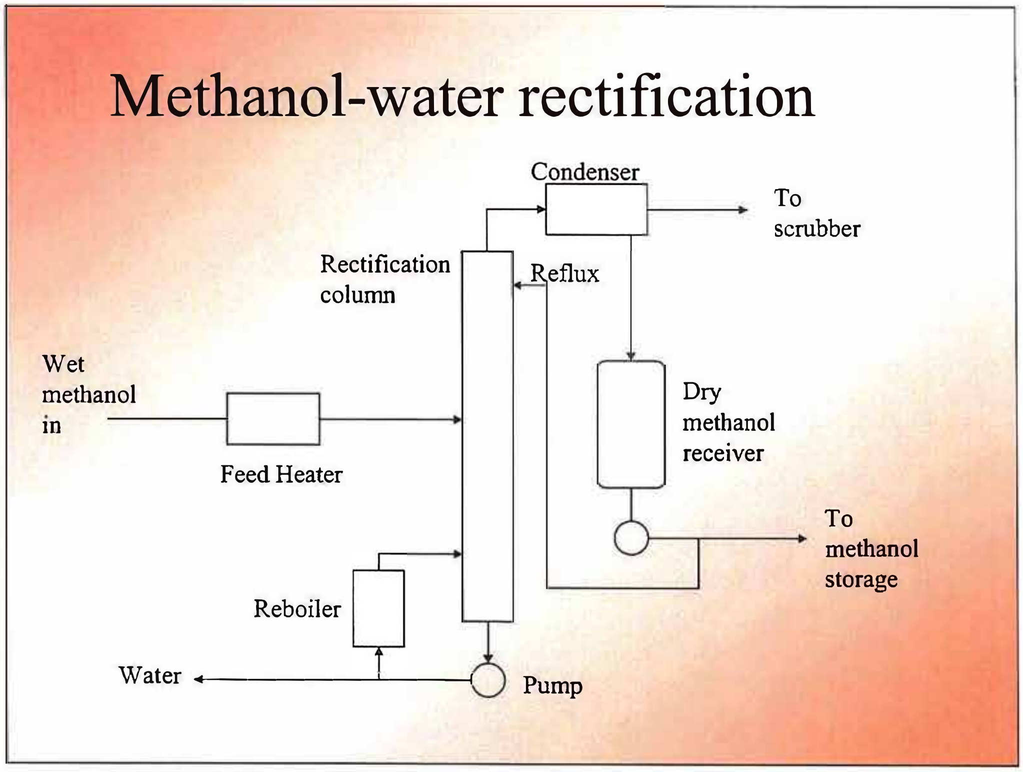
Crude glycerin (85%)

Methanol storage

Water

Biodiesel Production Schematic

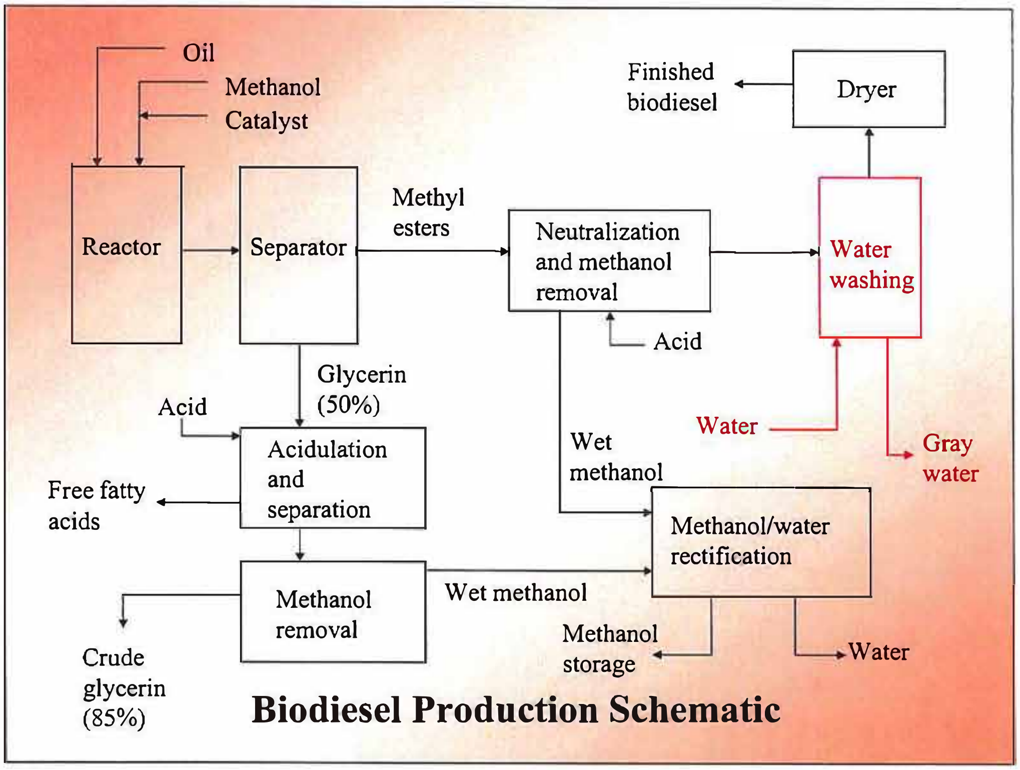
Consider methanol-water rectification.



Methanol-water rectification

Separation of the methanol and water requires a distillation column.

Even in the case where no water is added to the reaction, there will be some water coming in with the oil and this water will accumulate in the methanol if there is no means for its removal. Some water is produced by using hydroxide catalysts or during the acid-catalyzed esterification of high free fatty acid feedstocks. As discussed later, spent wash water might also be passed through the distillation column to allow it to be reused within the system.

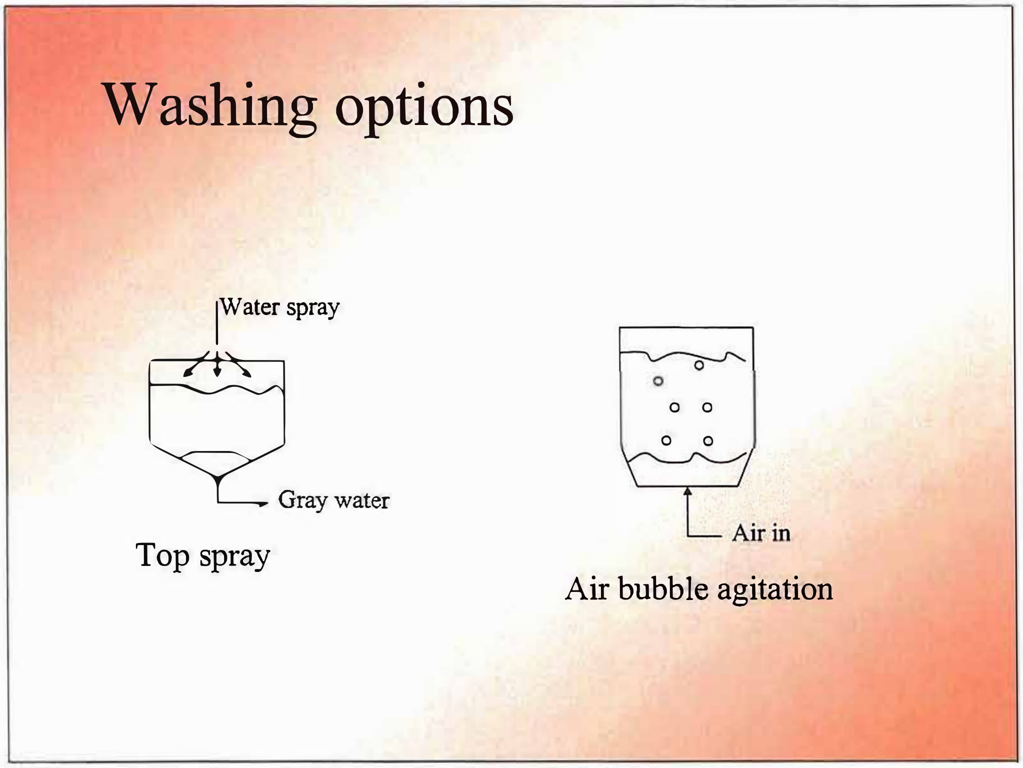


Biodiesel Production Schematic

Water washing

- Use softened, hot water (both the biodiesel and water at 60°C).
- Want to encourage contact between the biodiesel and water with “gentle” agitation.

It is preferable to use softened water to minimize the potential for mineral transfer (calcium, magnesium, and iron) to the biodiesel.

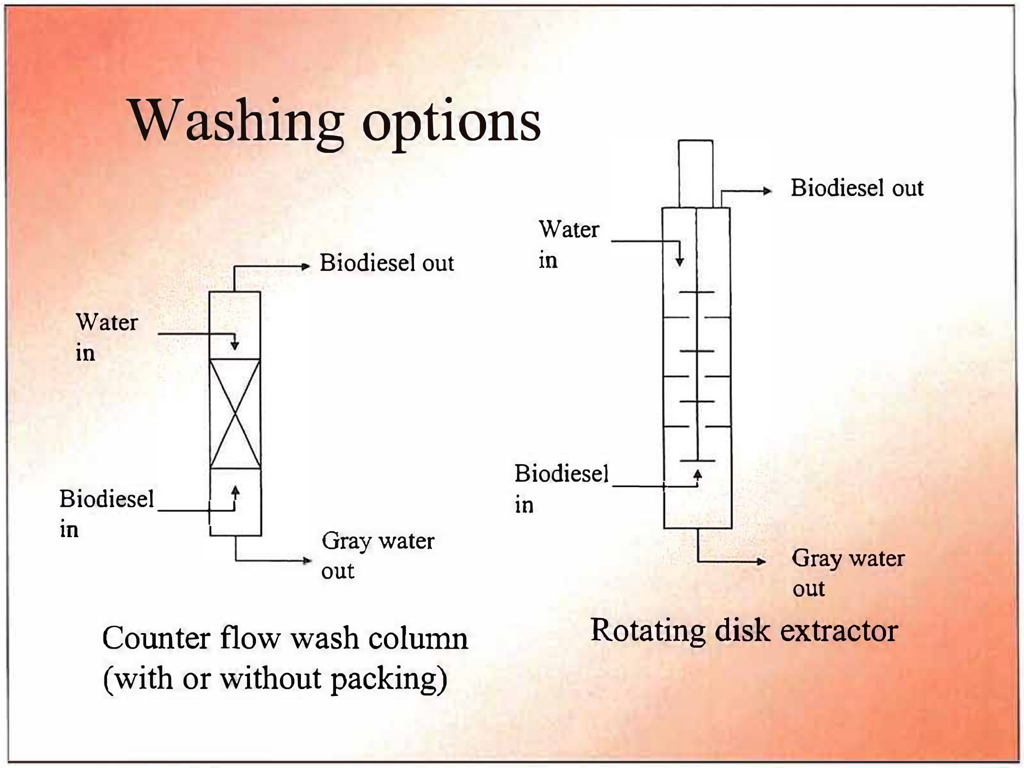


Washing options

Top spray

Air bubble agitation

Spray wash systems and air-agitated systems are best suited to batch processing.



Washing options

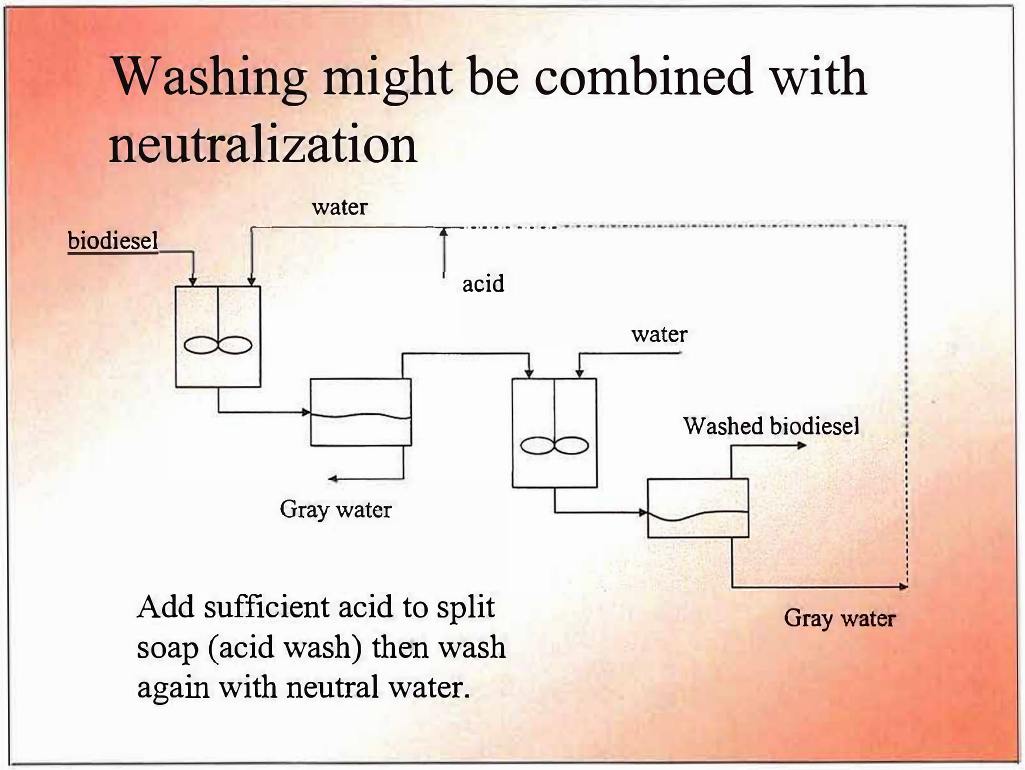
Counter flow wash column
(with or without packing)

Rotating disk extractor

These continuous flow wash columns are very prone to emulsion formation, especially if agitated. These systems are usually combined with acid addition for neutralization and soap splitting.

Without soap splitting, these water wash systems can consume a lot of water (1 gallon of water per gallon of biodiesel produced).

Most continuous wash systems would incorporate two or more of these columns.

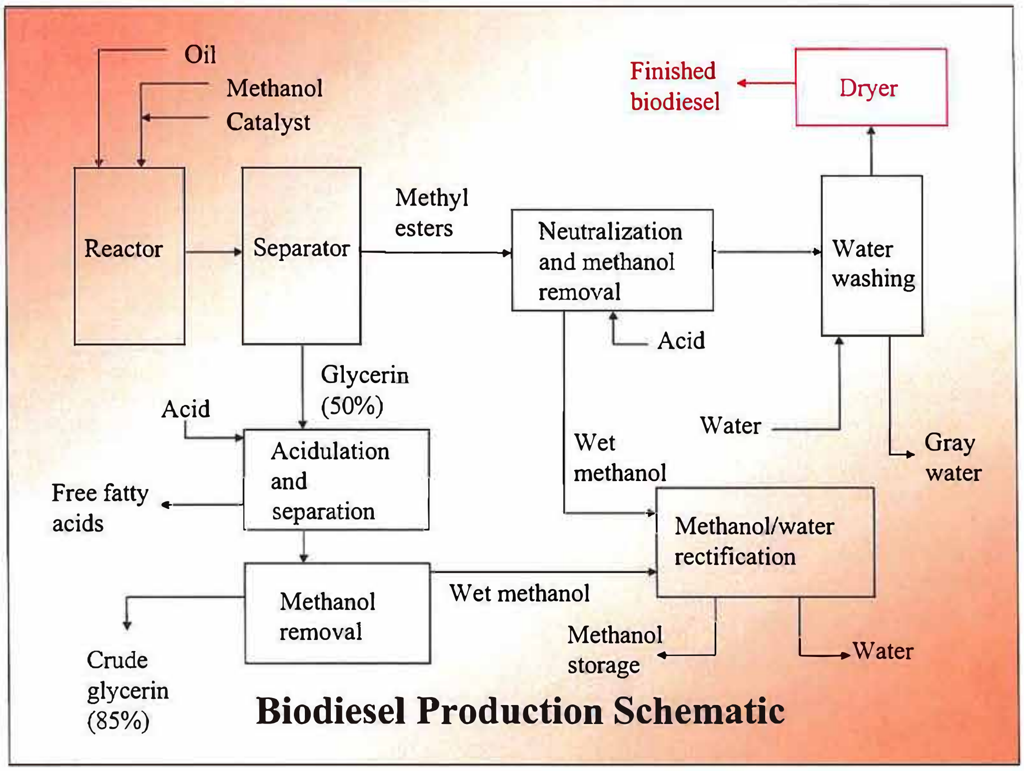


Washing might be combined with neutralization

Add sufficient acid to split soap (acid wash) then wash again with neutral water.

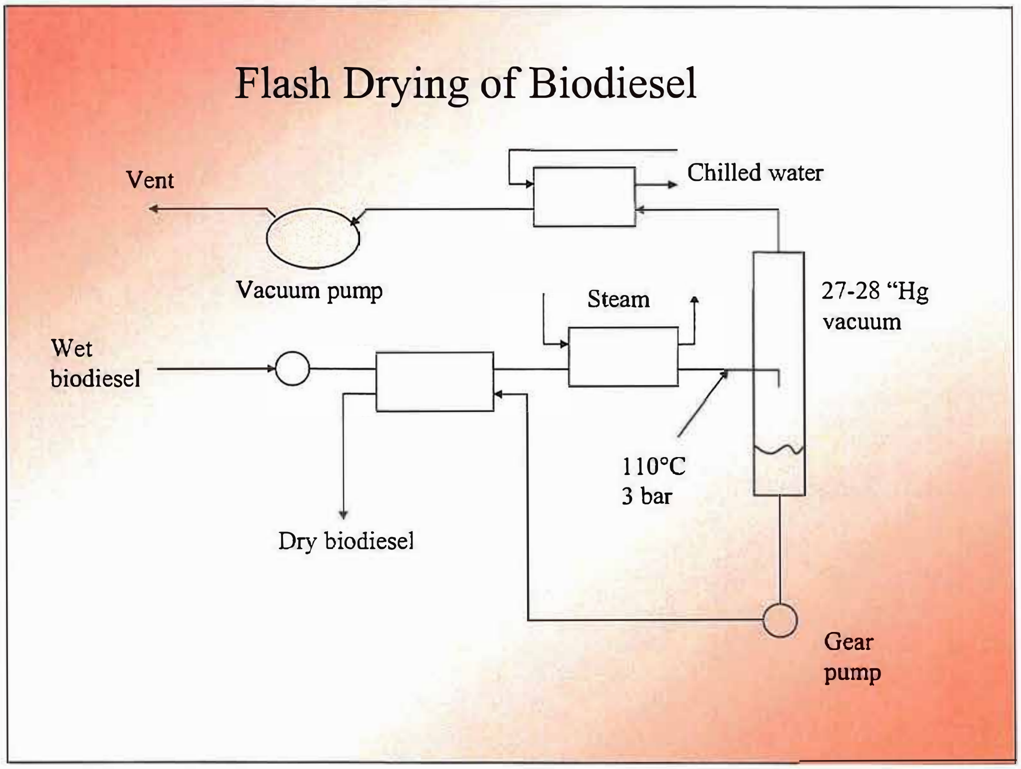
This approach can greatly reduce water consumption from 1 gallon of water per gallon of biodiesel to less than 0.1 gallon of water per gallon of biodiesel.

Note that gray water from second wash can be used as the supply water for the first wash (with acid addition). This is for water conservation.



Oil
Methanol
Catalyst
Reactor
Separator
Methyl esters
Neutralization and methanol removal
Acid
Water washing
Dryer
Finished biodiesel
Glycerin (50%)
Acid
Acidulation and separation
Free fatty acids
Wet methanol
Water
Gray water
Methanol/water rectification
Methanol removal
Wet methanol
Methanol storage
Water
Crude glycerin (85%)

Biodiesel Production Schematic



Flash Drying of Biodiesel

Drying of the biodiesel is a good idea to be sure that no suspended water droplets remain in the fuel that would prevent it from complying with the Water and Sediment specification in ASTM 6751.

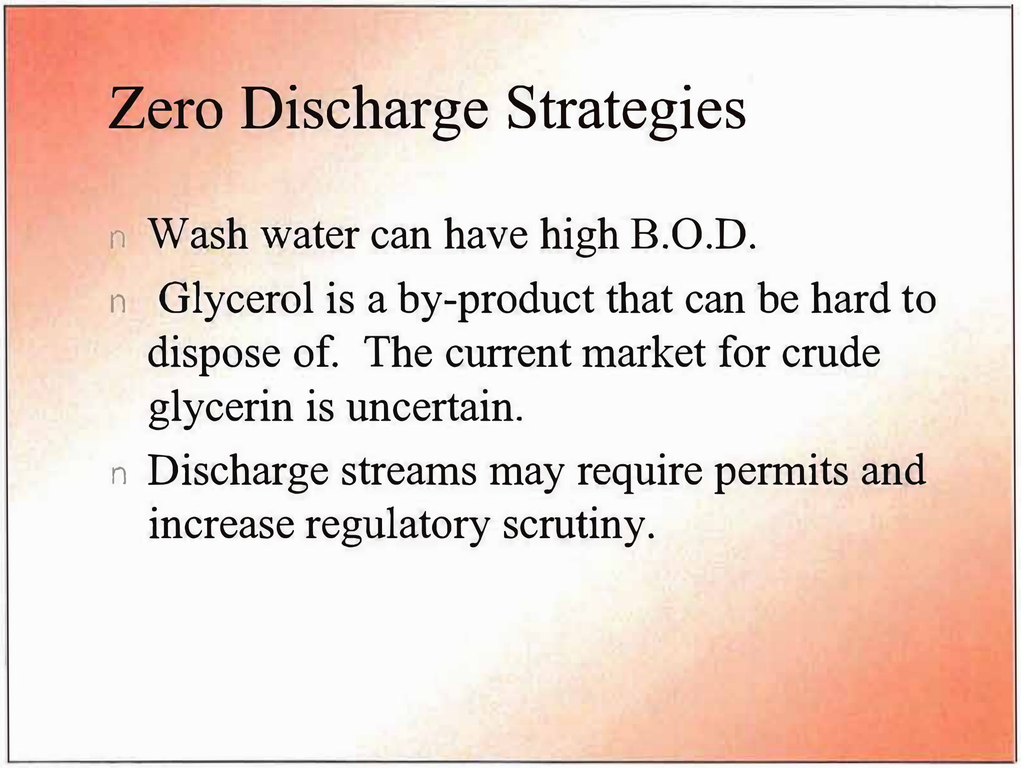
Biodiesel can absorb about 1500 ppm of water (compared with 50 ppm for diesel fuel). Water levels above this will be present as small droplets suspended in the biodiesel that make it cloudy.

Water in the fuel, even if dissolved, can contribute to fuel instability in long-term storage.

This drying system can share the vacuum source used in the drying system for the feedstock. It is not possible to share the entire system due to the potential for cross-contamination between the oil and the biodiesel.

Process Issues

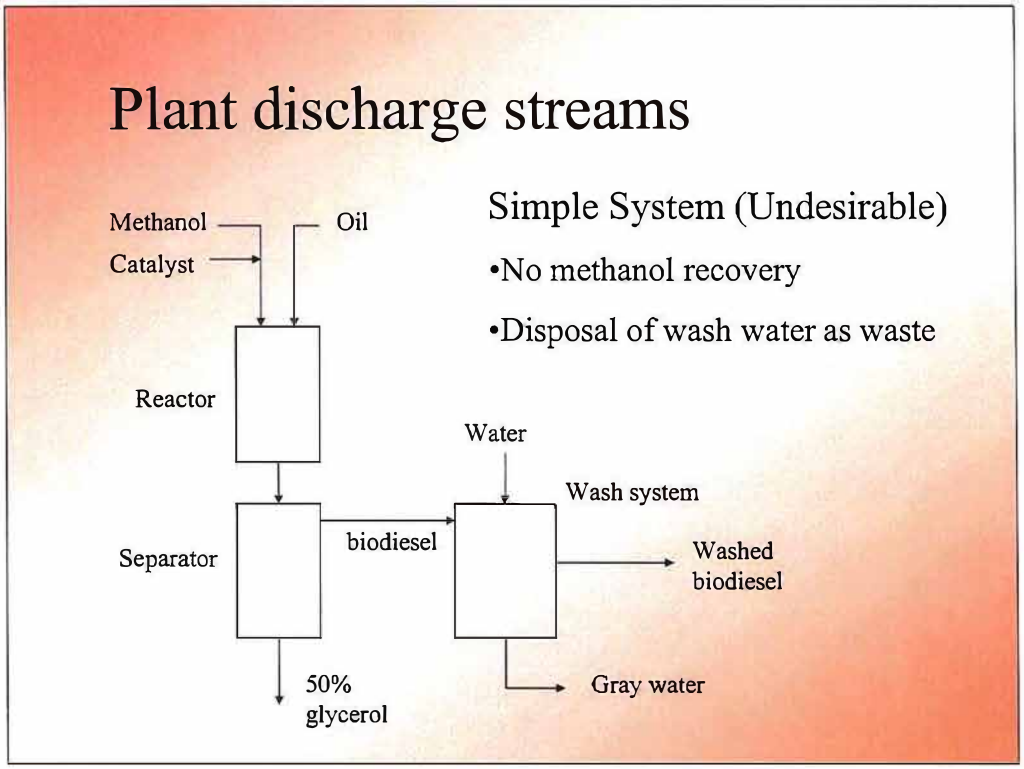
- Zero discharge strategies
- Processing low quality feedstocks
- Glycerin issues
- Continuous vs. batch processing
- Developing process options



Zero Discharge Strategies

- Wash water can have high B.O.D.
- Glycerol is a by-product that can be hard to dispose of. The current market for crude glycerin is uncertain.
- Discharge streams may require permits and increase regulatory scrutiny.

It is best to have no waste streams leaving the plant. Construction and operating permits are required for streams containing hazardous materials.



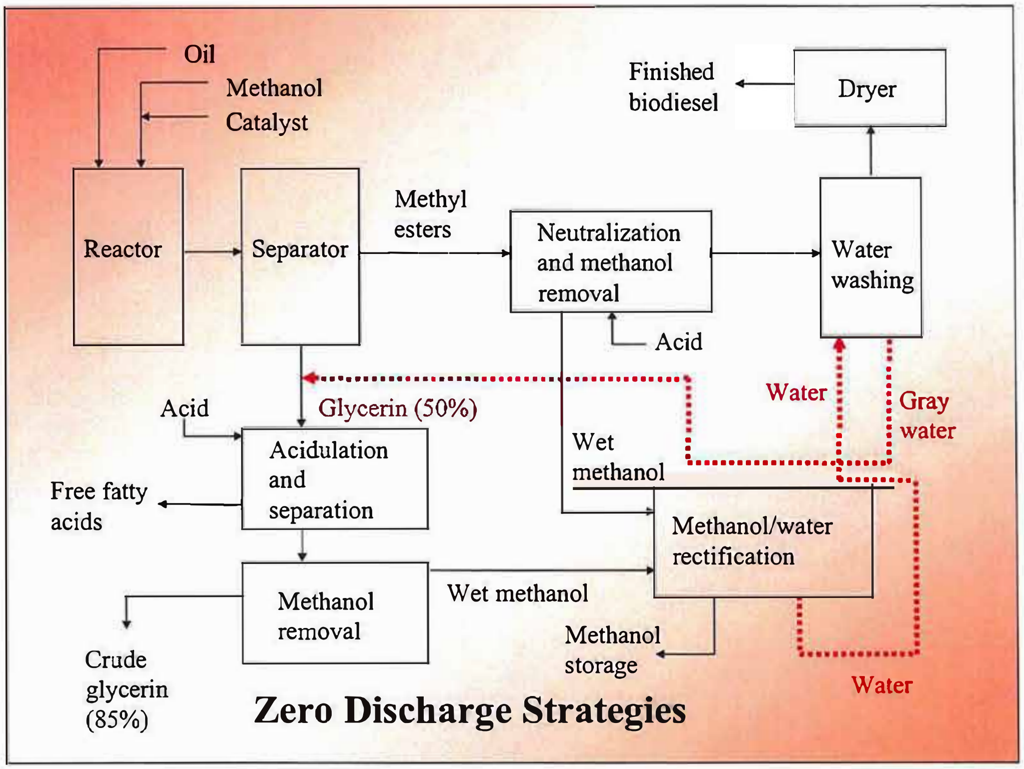
Plant discharge streams

Simple System (Undesirable)

- No methanol recovery
- Disposal of wash water as waste

The 50% glycerol will consist approximately of: 50% glycerol, 40% methanol, 10% soaps, salts, catalyst, and other contaminants. The methanol content makes it hazardous waste and very flammable. There is virtually no market for glycerol in this condition.

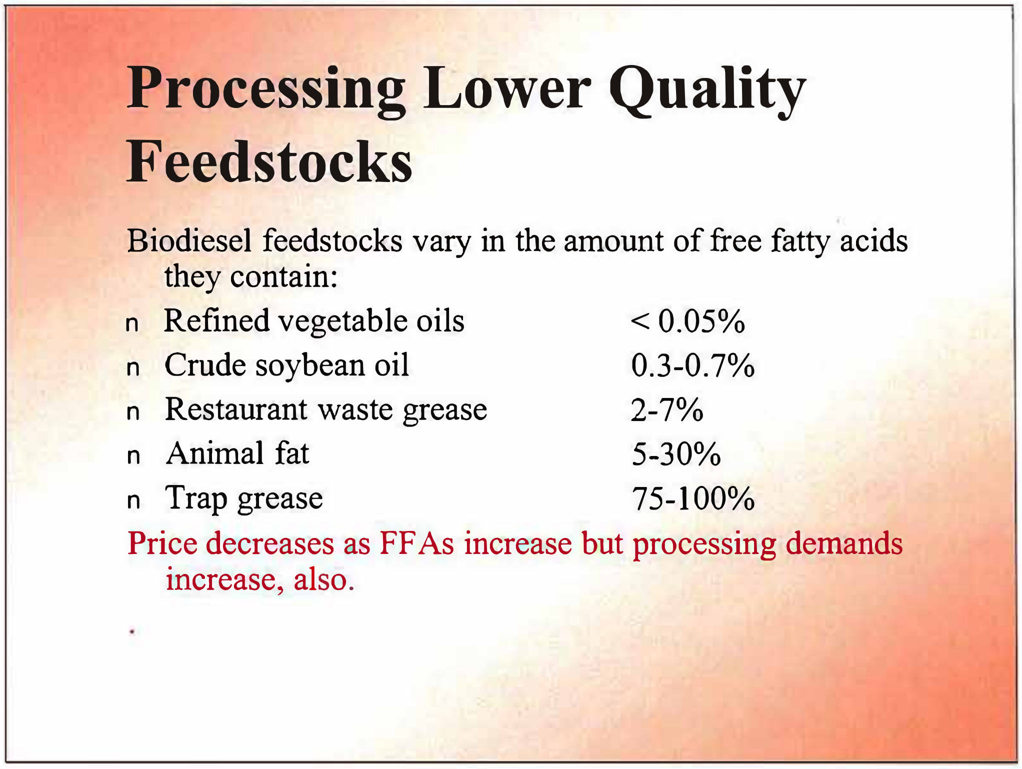
The gray water from this system will contain methanol, soap, some free glycerol, and small amounts of oil and methyl ester. With no neutralization of the biodiesel, the amount of water required will be 1-2 gallons of water/gallon of biodiesel produced. The waste water will have very high BOD (biological oxygen demand) and be a challenge to the capacity of a municipal sewage treatment system.


Oil
Methanol
Catalyst
Reactor
Separator
Methyl esters
Neutralization and methanol removal
Acid
Finished biodiesel
Dryer
Water washing
Water
Gray water
Acid
Glycerin (50%)
Acidulation and separation
Free fatty acids
Wet methanol
Methanol/water rectification
Methanol removal
Wet methanol
Methanol storage
Water
Crude glycerin (85%)

Zero Discharge Strategies

Zero Discharge Strategies

1. Recover methanol. Removing it from the biodiesel and glycerin streams and then separating any water that may have collected is expensive. The value of the methanol may not justify it for smaller plants, but waste disposal is the more serious issue.
2. Gray water from water washing processes can be added to the glycerin stream. The salts, soap, glycerin, and residual methyl esters will be mixed with the glycerin. Water will be extracted with the methanol and separated in the rectification process and recycled for washing. Soap will be split by acidulation and the free fatty acids recovered for recycling in the process or sale. Salts will go into the crude glycerin stream. Neutralization is an important part of keeping the wash water requirement low. Claims have been made that wash water can be as little as 3-10% of biodiesel flow.



Processing Lower Quality Feedstocks

Biodiesel feedstocks vary in the amount of free fatty acids they contain:

Refined vegetable oils	< 0.05%
Crude soybean oil	0.3-0.7%
Restaurant waste grease	2-7%
Animal fat	5-30%
Trap grease	75-100%

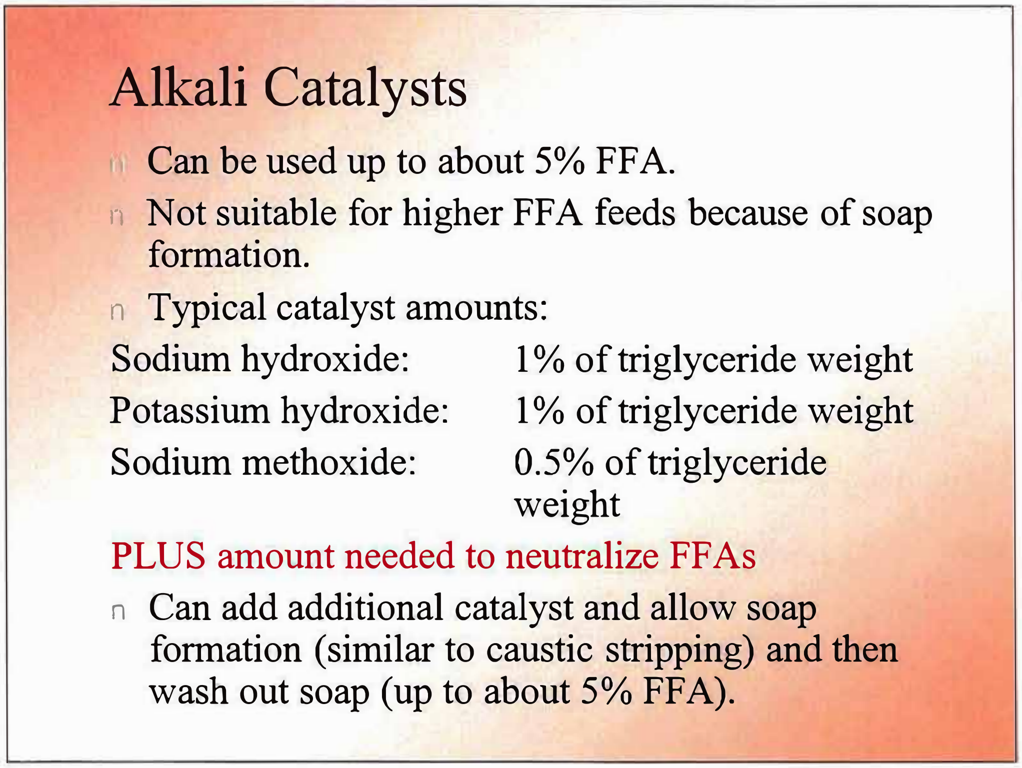
Price decreases as FFAs increase but processing demands increase, also.

The type of processing needed by the feedstock is most strongly dependent on the free fatty acid (FFA) level.

Refined vegetable oils can be transesterified directly with no concern for FFAs.

Crude oils containing less than 1% FFAs will also usually not be a problem. However, a portion of the catalyst will be consumed by reaction with the FFAs to form soap. In fact this approach can be used up to about 5% FFA. The incremental amount of catalyst needed to neutralize the FFAs can be calculated and extra catalyst provided for this purpose. Above 5%FFA, the soap formation will start to inhibit methyl ester/glycerin separation and make water washing more difficult.

Above 5% FFA, some type of pretreatment to esterify the FFAs is recommended.



Alkali Catalysts

- Can be used up to about 5% FFA.
- Not suitable for higher FFA feeds because of soap formation.
- Typical catalyst amounts:

Sodium hydroxide: 1% of triglyceride weight

Potassium hydroxide: 1% of triglyceride weight

Sodium methoxide: 0.5% of triglyceride weight

PLUS amount needed to neutralize FFAs

- Can add additional catalyst and allow soap formation (similar to caustic stripping) and then wash out soap (up to about 5% FFA).

The additional amount of alcohol needed to neutralize the FFAs can be calculated as:

Sodium hydroxide: [%FFA](0.144)

Potassium hydroxide: [%FFA](0.197)/0.86

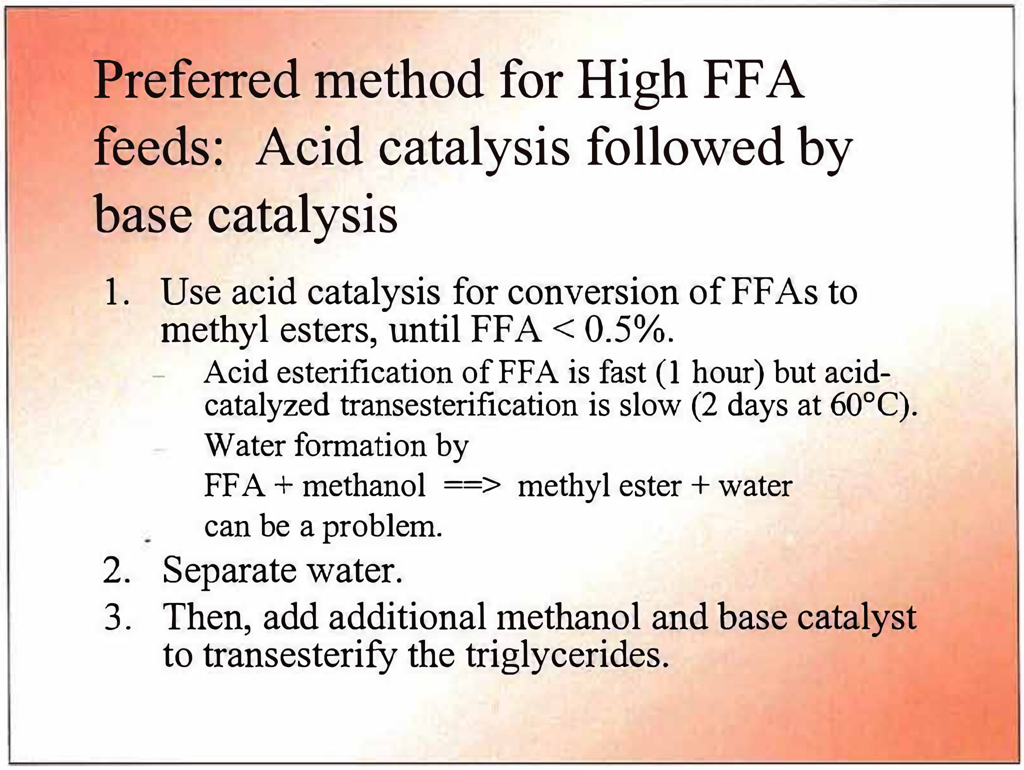
Sodium methoxide: [%FFA](0.190)

Note that common grades of potassium hydroxide are only about 86% KOH (balance is mostly water).

Example: When adding sodium methoxide to a feedstock with 3.5 % FFA, the amount of catalyst would be:

(3.5)(0.190) = 0.67 % of the triglycerides weight

Now, add to this the 0.5% needed to catalyze the reaction and the total amount of catalyst needed is 0.67 + 0.5 = 1.17% of the triglyceride weight.

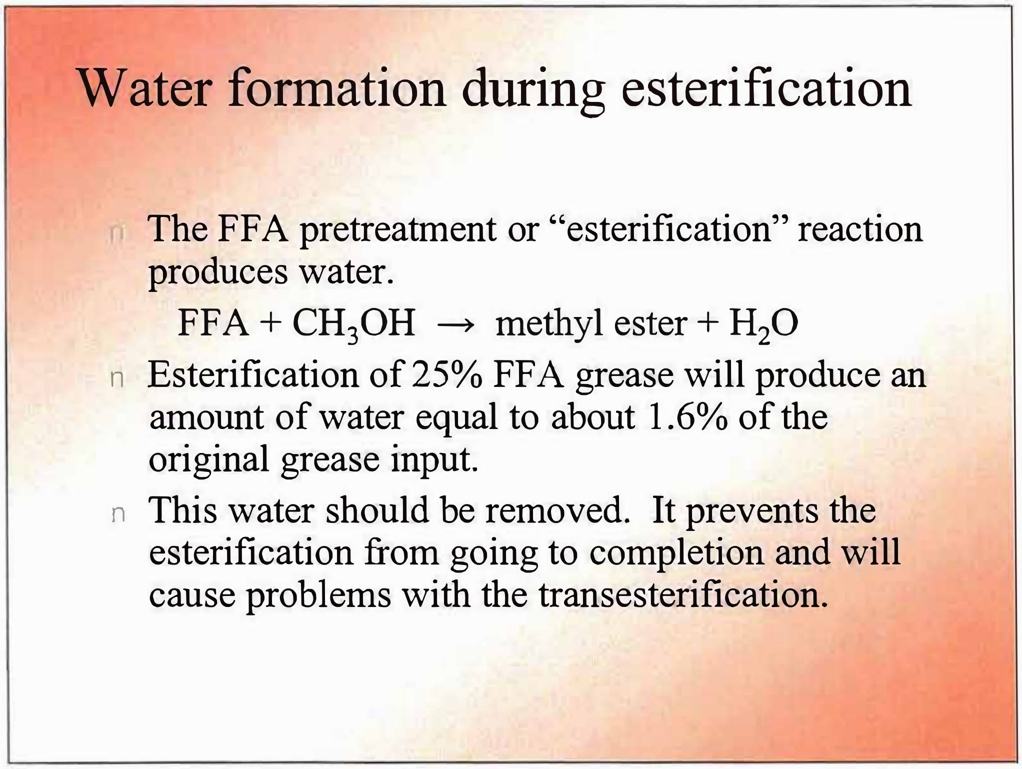


Preferred method for High FFA feeds: Acid catalysis followed by base catalysis

1. Use acid catalysis for conversion of FFAs to methyl esters, until FFA < 0.5%.
   - Acid esterification of FFA is fast (1 hour) but acid-catalyzed transesterification is slow (2 days at 60°C).
   - Water formation by
     FFA + methanol ==> methyl ester + water
     can be a problem.
2. Separate water.
3. Then, add additional methanol and base catalyst to transesterify the triglycerides.

Canakci, M. and J. Van Gerpen, 1999, "Biodiesel Production via Acid Catalysis," ASAE Transactions, 42(5):1203-1210.

Canakci, M. and J. Van Gerpen, 2001, "Biodiesel Production from Oils and Fats with High Free Fatty Acids," ASAE Transactions, 44(6):1429-1436.



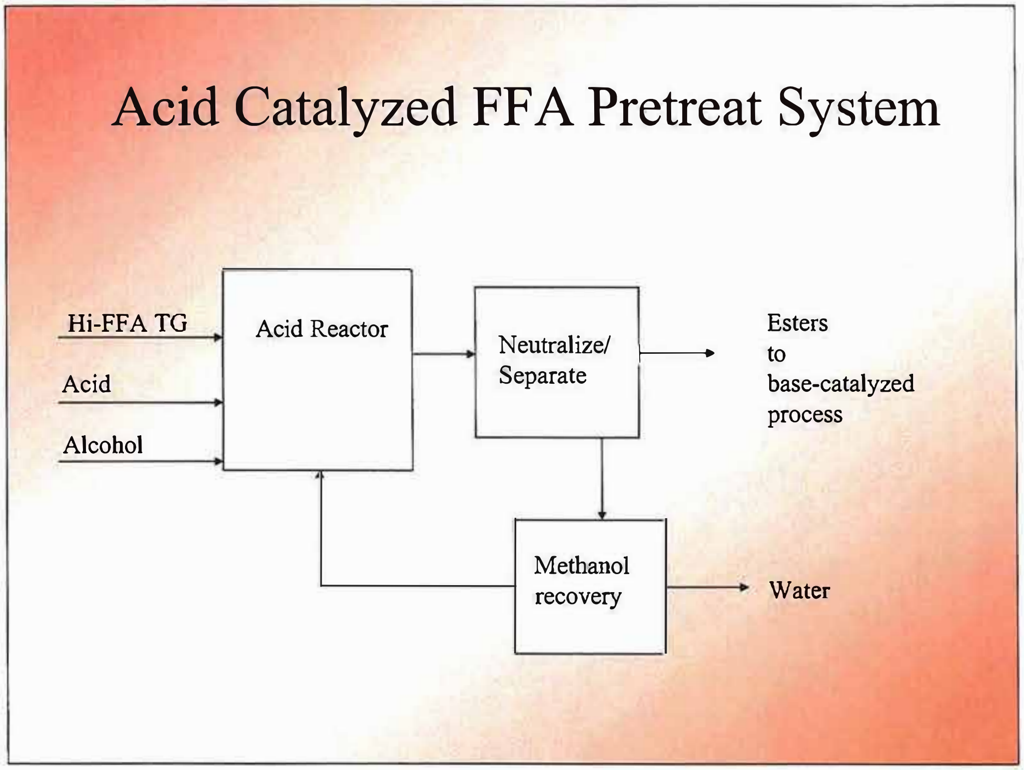
Water formation during esterification

- The FFA pretreatment or “esterification” reaction produces water.

  FFA + CH_3OH → methyl ester + H_2O
- Esterification of 25% FFA grease will produce an amount of water equal to about 1.6% of the original grease input.
- This water should be removed. It prevents the esterification from going to completion and will cause problems with the transesterification.

FFA + CH_3OH → methyl ester + H_2O

This translates into 0.063 g H_2O/g FFA produced during the esterification reaction. This will stop the esterification reaction (too much of one of the products). If the water is removed, the equilibrium for the reaction will cause it to go further in the direction of methyl ester formation. Unfortunately, it is difficult to remove the water without also removing the methanol.

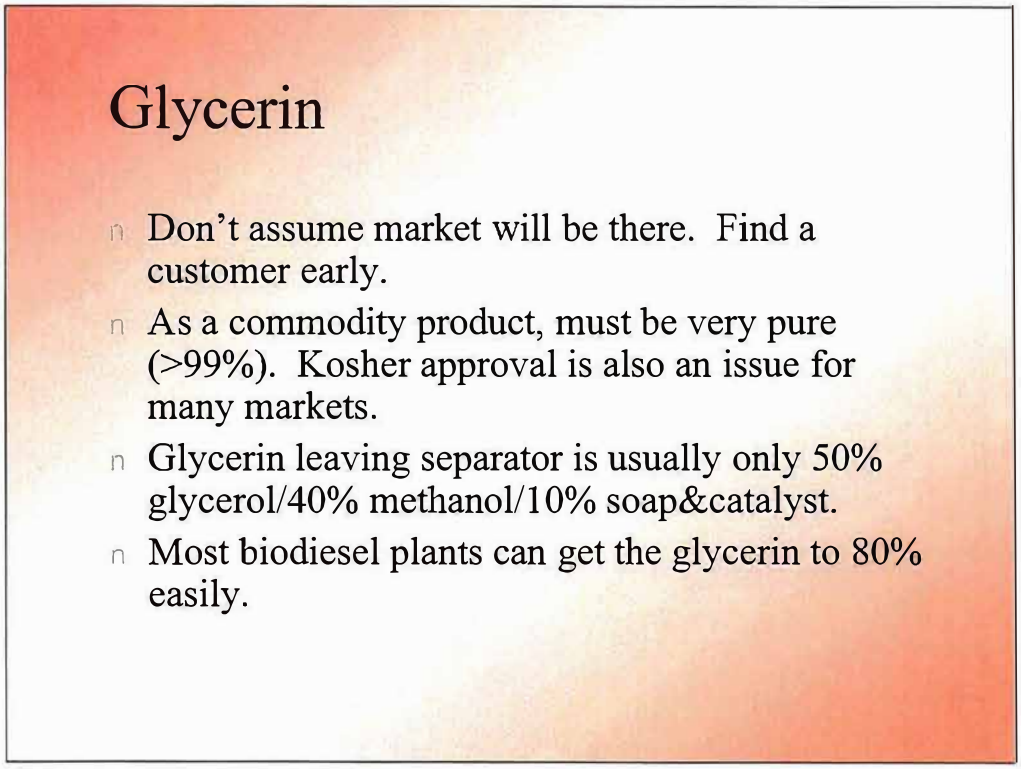


Acid Catalyzed FFA Pretreat System

The water can be removed be settling. Depending on the amount of excess methanol added, the methanol water mixture will form a separate phase on the top or the bottom of the oil phase. This phase will contain most of the water, a portion of the methanol, most of the sulfuric acid catalyst, and some dissolved triglycerides and esters. This material should be processed to recycle the triglycerides and oil. This could be done by neutralizing the acid, flashing off the methanol and water, and returning the non-volatile material to the acid-catalyzed process. An alternative is to use this material to neutralize the glycerin. This doesn't require any additional equipment and still recycles all of the different components of the mixture using the neutralization and methanol recovery equipment used for glycerin clean-up.

The water can also be removed by centrifugation, giving a phase that needs to be processed in the manner described above.

Finally, the water could be removed with a flash process. Virtually all of the methanol will be removed also, which requires fractional distillation to separate the methanol and water and then returning the methanol to the process.



Glycerin

- Don't assume market will be there. Find a customer early.
- As a commodity product, must be very pure (>99%). Kosher approval is also an issue for many markets.
- Glycerin leaving separator is usually only 50% glycerol/40% methanol/10% soap&catalyst.
- Most biodiesel plants can get the glycerin to 80% easily.

Glycerol, glycerin, and glycerine are generally used interchangably. Sometimes glycerol is used for the pure chemical and glycerin for actual products that contain different levels of impurities.

Glycerin from biodiesel plants using animal fats, restaurant waste, trap grease, etc. will not meet kosher requirements. It is possible for a vegetable oil-based plant to be kosher.

USP Specifications for Glycerol (USP, v. 24, 2000)

Purity: Contains not less than 99.0 percent and not more than 101.0 percent, by assay.

Color: When viewed downward against a white surface in a 50-ml color-comparison tube, is not darker than the color of a standard made by diluting 0.40 ml of ferric chloride CS with water to 50 ml and similarly viewed in a color-comparison tube of the same diameter as that containing the glycerol.

Specific gravity: not less than 1.249

Residue on ignition: Heat 50 g in an open, shallow 100-ml porcelain dish until it ignites, and allow it to burn without further application of heart in a place free from drafts. Cool, moisten the residue with 0.5 ml of sulfuric acid, and ignite to constant weight; the weight of the residue should not exceed 5 mg (0.01%).

Water: not more than 5.0%

Chloride: A 7.0-g portion shows no more chloride than corresponds to 0.10 ml of 0.020N hydrochloric acid (0.001%).

Sulfate: A 10-g portion shows no more sulfate than corresponds to 0.20 ml of 0.020 N sulfuric acid (about 0.002%).

Heavy metals: Mix 4.0 g with 2 ml of 0.1 N hydrochloric acid, and dilute with water to 25 ml; the limit is 5 ppm.

Chlorinated Compounds: Following specified reactions with morpholine, nitric acid and silver nitrate, the turbidity should not be greater than that of a blank to which 0.20 ml of 0.020 N hydrochloric acid has been added (0.003% of Cl).

Organic volatile impurities: Use gas chromatograph to identify 5 organic volatile impurities. Levels not to exceed: benzene, 2 μg/g; chloroform, 60 μg/g; 1,4-dioxane, 380 μg/g; methylene chloride, 600 μg/g; trichloroethylene, 80 μg/g.

Fatty acids and esters: Mix 50 g with 50 ml of freshly boiled water and 5 ml 0.5 N sodium hydroxide, boil the mixture for 5 minutes, cool, add phenolphthalein, and titrate the excess alkali with 0.5 N hydrochloric acid. Perform a blank determination. No more than 1 ml of 0.5 N sodium hydroxide should be consumed.

Glycerin clean-up

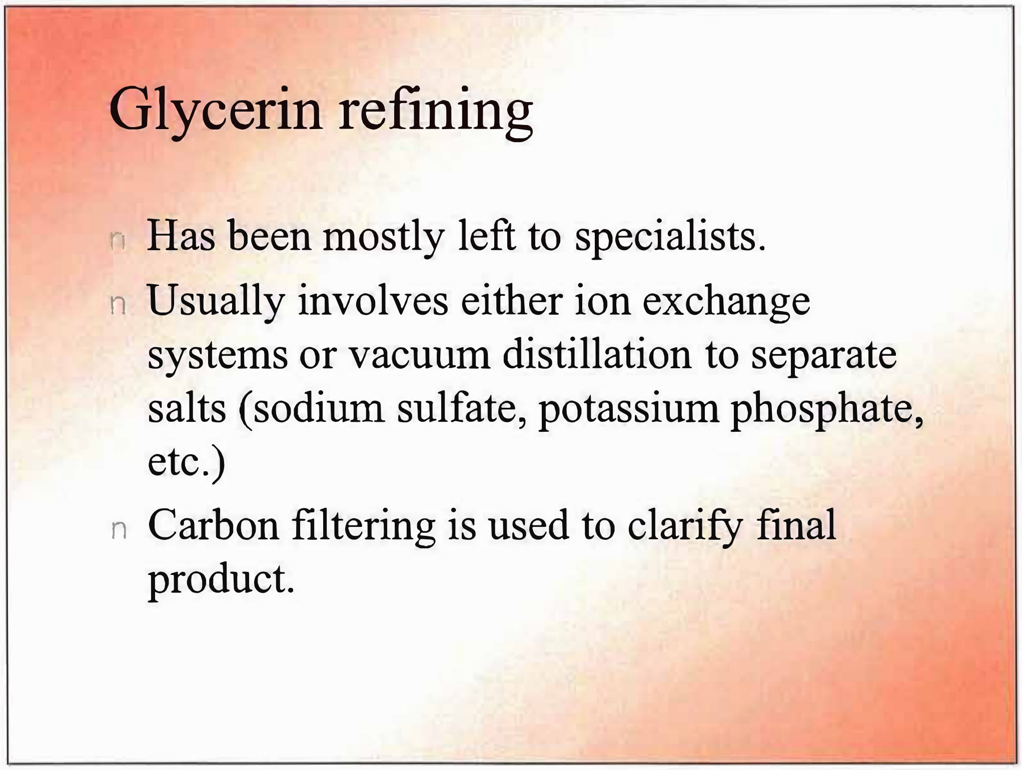
1. Add acid to split soap.

FFA will rise to the top, can be skimmed off and recycled or sold.

2. Methanol removal

Use flash process, or another type of evaporator.

3. Should yield 80-85% glycerin with 10-20% salts.



Glycerin refining

- Has been mostly left to specialists.
- Usually involves either ion exchange systems or vacuum distillation to separate salts (sodium sulfate, potassium phosphate, etc.)
- Carbon filtering is used to clarify final product.

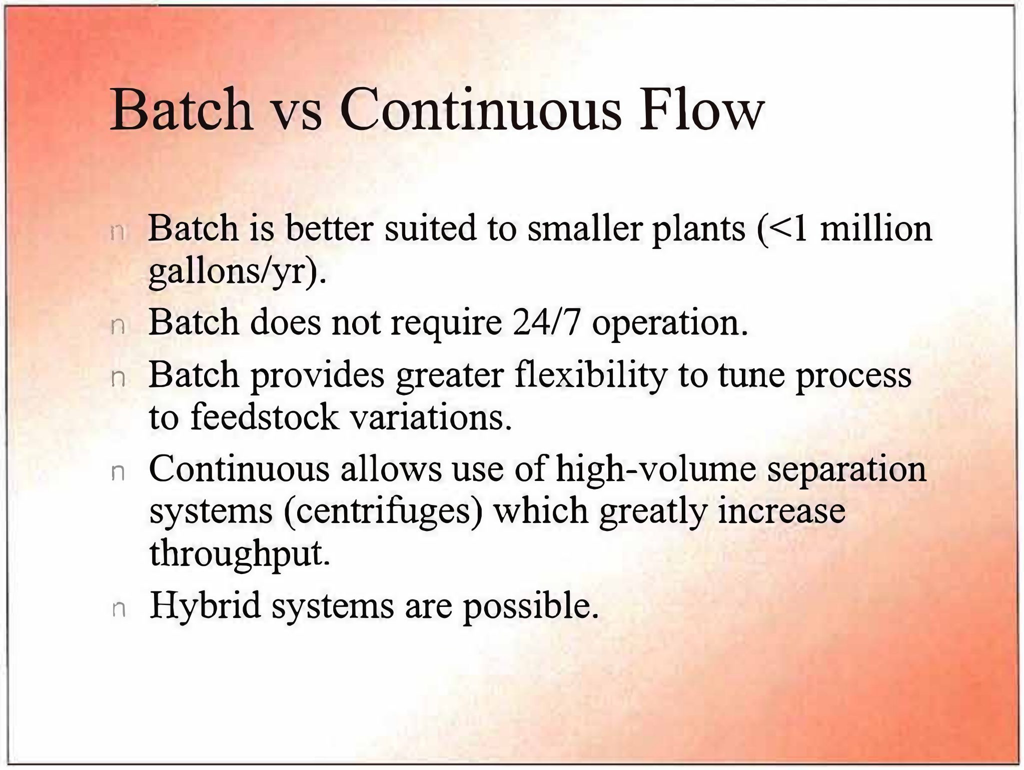
Glycerin disposal is a great concern for many biodiesel producers. The most promising avenues seem to be:

Antifreeze production (propylene glycol)

Anti-icers, de-icers

Animal feed (if methanol is < 1%)

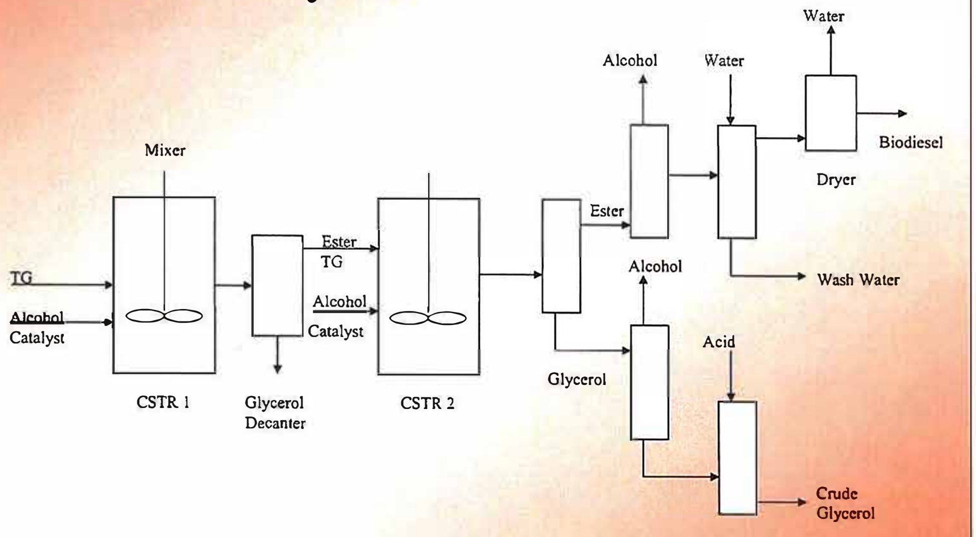
Composting accelerant

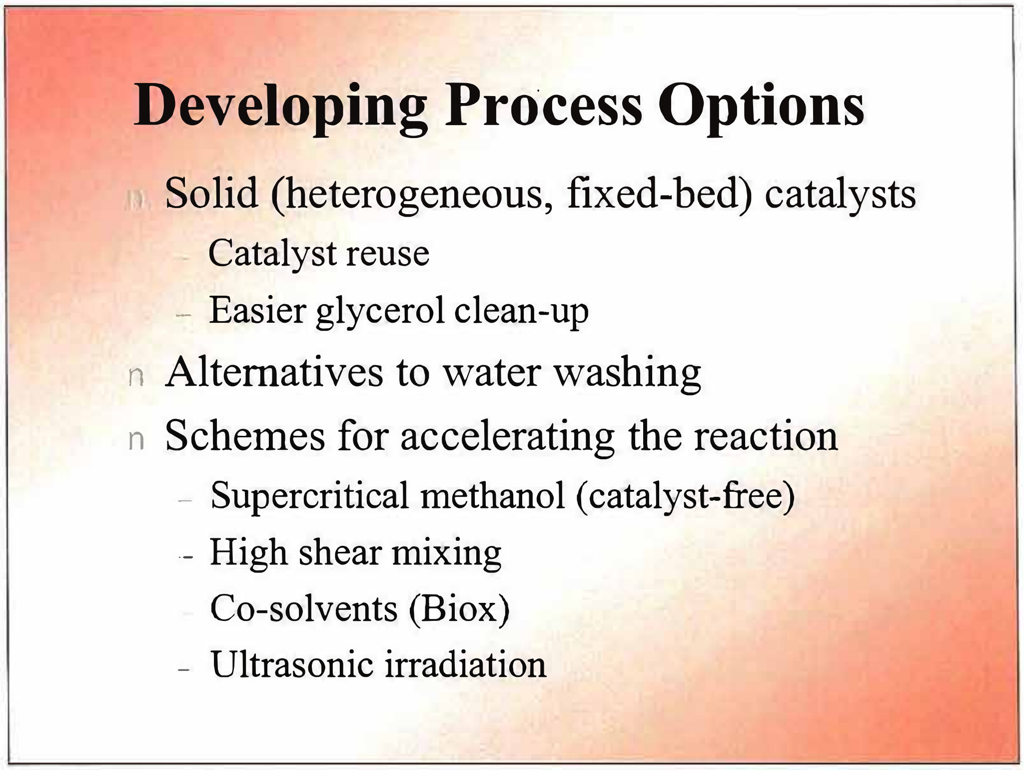


Batch vs Continuous Flow

- Batch is better suited to smaller plants (<1 million gallons/yr).
- Batch does not require 24/7 operation.
- Batch provides greater flexibility to tune process to feedstock variations.
- Continuous allows use of high-volume separation systems (centrifuges) which greatly increase throughput.
- Hybrid systems are possible.

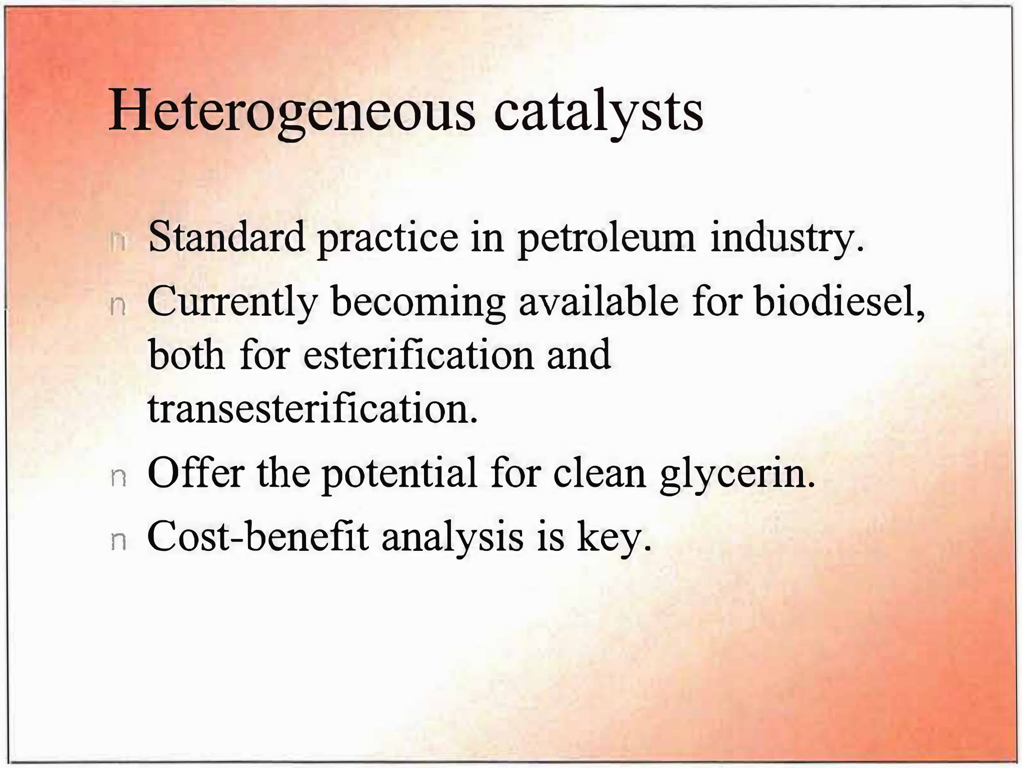
Hybrid Batch/Continuous Base Catalyzed Process





Developing Process Options

- Solid (heterogeneous, fixed-bed) catalysts
  - Catalyst reuse
  - Easier glycerol clean-up
- Alternatives to water washing
- Schemes for accelerating the reaction
  - Supercritical methanol (catalyst-free)
  - High shear mixing
  - Co-solvents (Biox)
  - Ultrasonic irradiation



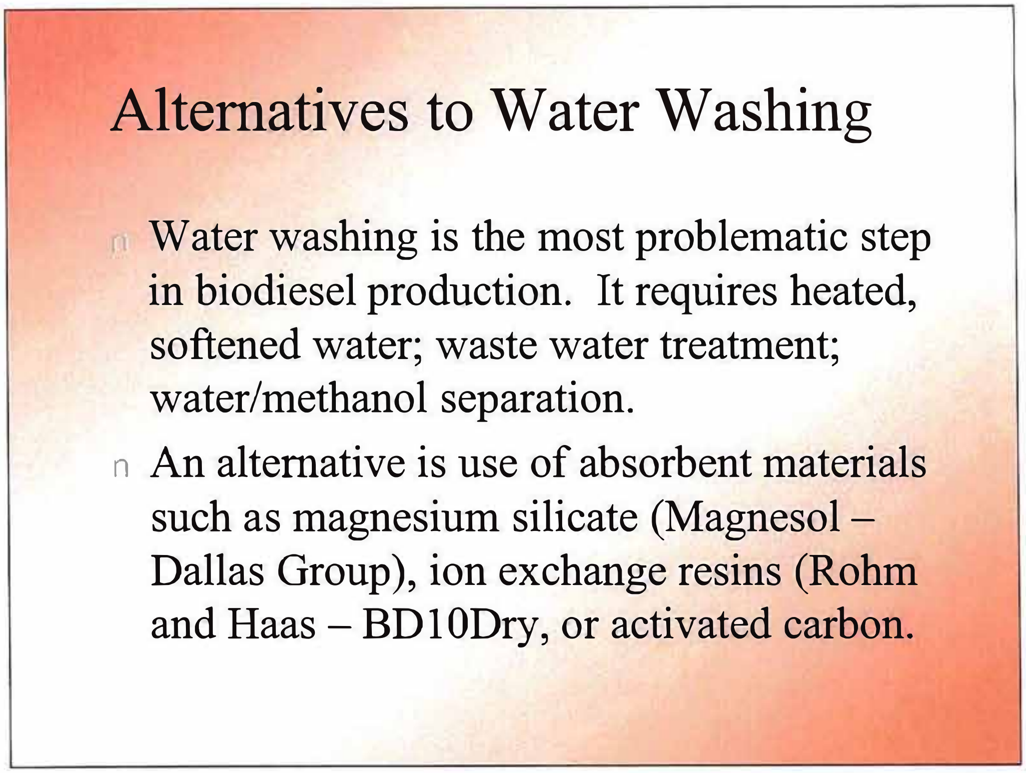
Heterogeneous catalysts

- Standard practice in petroleum industry.
- Currently becoming available for biodiesel, both for esterification and transesterification.
- Offer the potential for clean glycerin.
- Cost-benefit analysis is key.

Things to remember about heterogeneous catalysts:

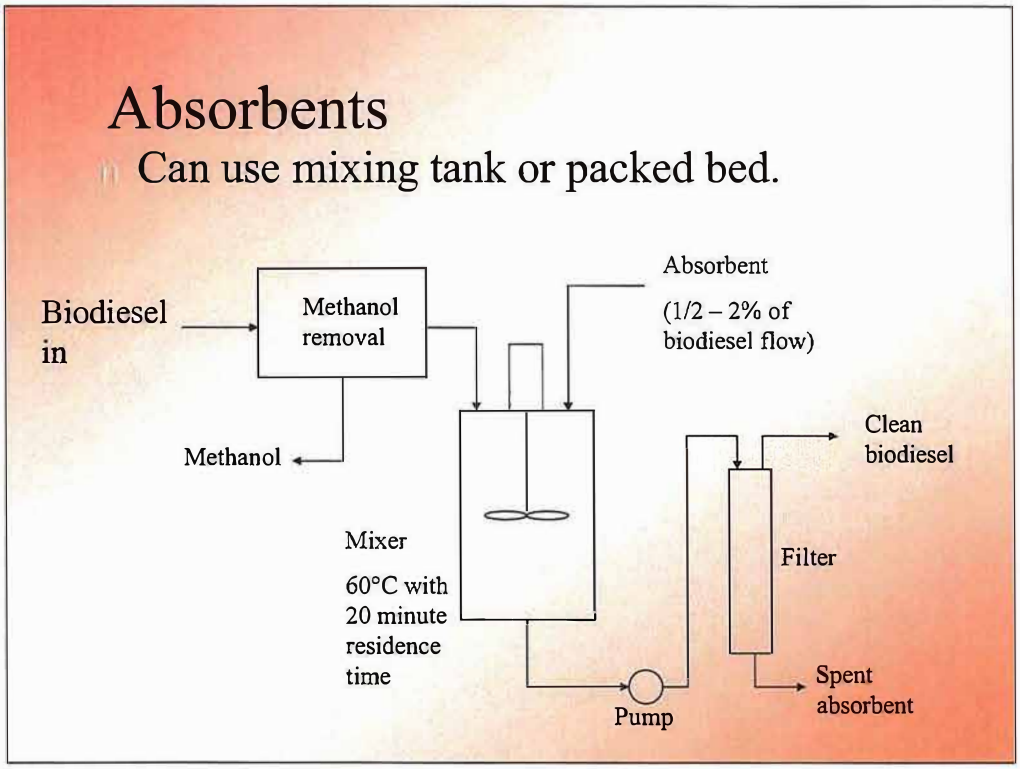
1. A heterogenous catalyst will never be as effective as a homogeneous catalyst at the same conditions (T and P). Most heterogeneous catalysts need high temperature.
2. If you have to go to high temperature, what pressure is needed to keep the methanol as a liquid? What added expense is needed to operate at that pressure?
3. What are the time requirements? This translates into bed size and flow rate requirements.
4. How long will the catalyst last? Can it be regenerated? How many times?
5. How tolerant is the catalyst to water, free fatty acids and other contaminants in the oil? Has the catalyst been tested with real feedstocks? Are the performance data the supplier provides for catalyst in powder form or for the pelletized form that will actually be used?
6. Heterogeneous catalysts will be proprietary products as opposed to KOH, NaOH, $NaOCH_3$ which are low-cost commodity products.
7. Currently, the primary incentive is to provide a cleaner glycerin product. Do you have a market for this glycerol, even if it is cleaner?

That said, it is a safe bet that in 10 years, all biodiesel will be made with heterogeneous catalysts.



Alternatives to Water Washing

- Water washing is the most problematic step in biodiesel production. It requires heated, softened water; waste water treatment; water/methanol separation.
- An alternative is use of absorbent materials such as magnesium silicate (Magnesol – Dallas Group), ion exchange resins (Rohm and Haas – BD10Dry, or activated carbon.

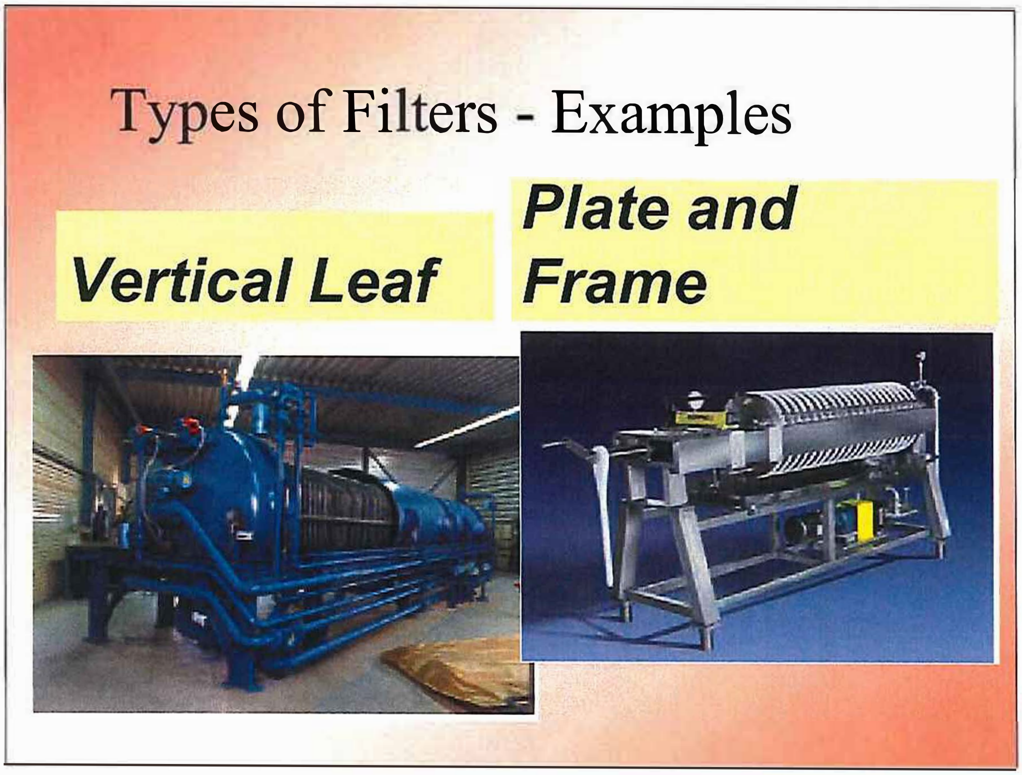


Absorbents

- Can use mixing tank or packed bed.

Some absorbents will remove polar compounds such as water, methanol, free glycerol, soap, and even monoglycerides and diglycerides. Methanol should be removed before processing or this can overwhelm the absorbent.

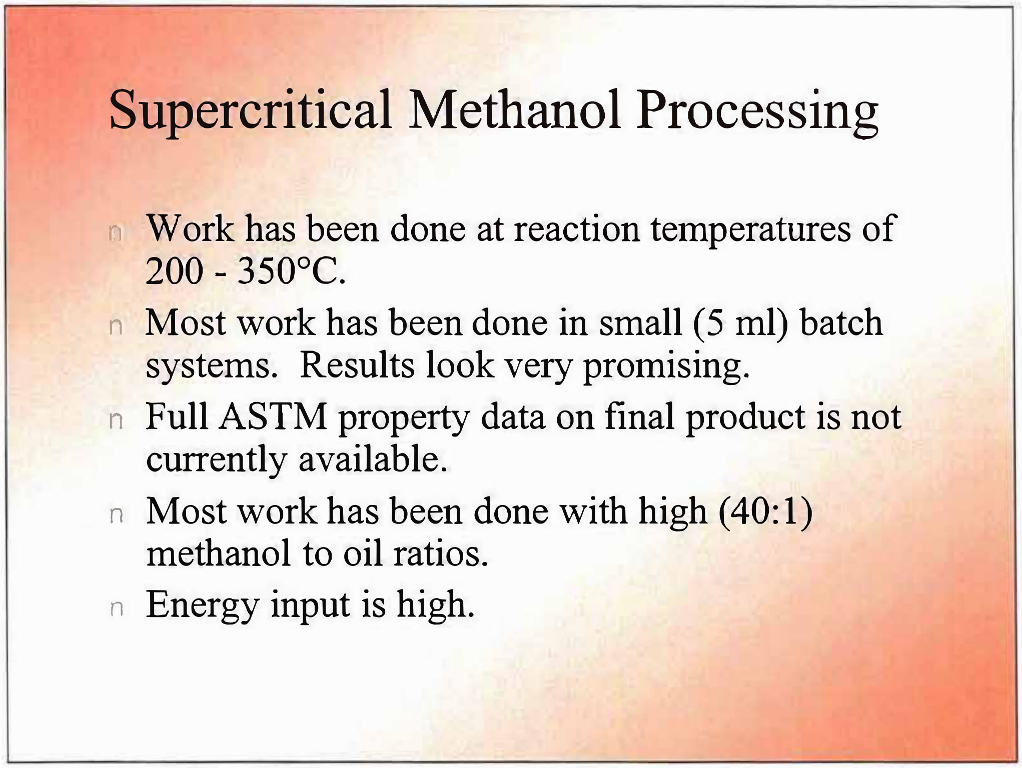
Some waste absorbent is not hazardous. It may have nutritional value (due to absorbed compounds) and could be added to animal feed (if methanol-free).



Types of Filters - Examples

Vertical Leaf

Plate and Frame



Supercritical Methanol Processing

- Work has been done at reaction temperatures of 200 - 350°C.
- Most work has been done in small (5 ml) batch systems. Results look very promising.
- Full ASTM property data on final product is not currently available.
- Most work has been done with high (40:1) methanol to oil ratios.
- Energy input is high.

Concerns with small batch studies include the potential for catalytic effects on the walls of the reaction vessels. Since these effects would not scale up to large size, the conversion might not either.

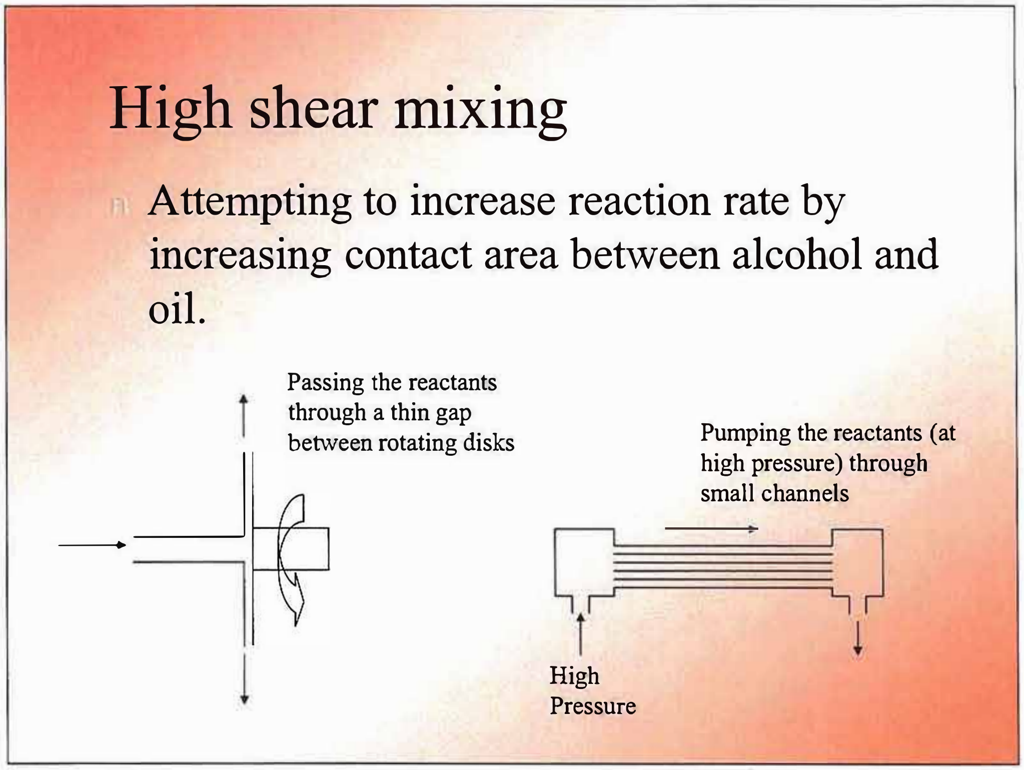
The temperatures that are proposed (up to 350°C) are above the temperatures where spontaneous decomposition of some of compounds, such as glycerin, are expected to occur. Whether the decomposition products exist in the fuel, and whether they will cause any harm, is still not known.

Kusdiana, D. and S. Saka, "Kinetics of Transesterification in Rapeseed Oil to Biodiesel Fuel as Treated in Supercritical Methanol," Fuel, V. 80, 2001, pp. 693-698

Saka, S. and K. Dadan, "Transesterification of Rapeseed Oils in Supercritical Methanol to Biodiesel Fuels," Proceedings of the 4th Biomass Conf. of the Americas, Oakland, CA, edited by R.P. Overend and E. Chornet, Aug. 29-Sept. 2, 1999.

Saka, S. and D. Kusdiana, "Biodiesel Fuel from Rapeseed Oil as Prepared in Supercritical Methanol," Fuel, V. 80, 2001, pp. 225-231.

Kusdiana, D., E. Minami, K. Ehara, and S. Saka, "Development of the Batch-Type and Flow-Type Supercritical Fluid Biomass Conversion Systems," 12th European Conf. on Biomass for Energy, Industry, and Climate Protection, 17-21 June 2002, Amsterdam, The Netherlands.



High shear mixing

- Attempting to increase reaction rate by increasing contact area between alcohol and oil.

Passing the reactants through a thin gap between rotating disks

Pumping the reactants (at high pressure) through small channels

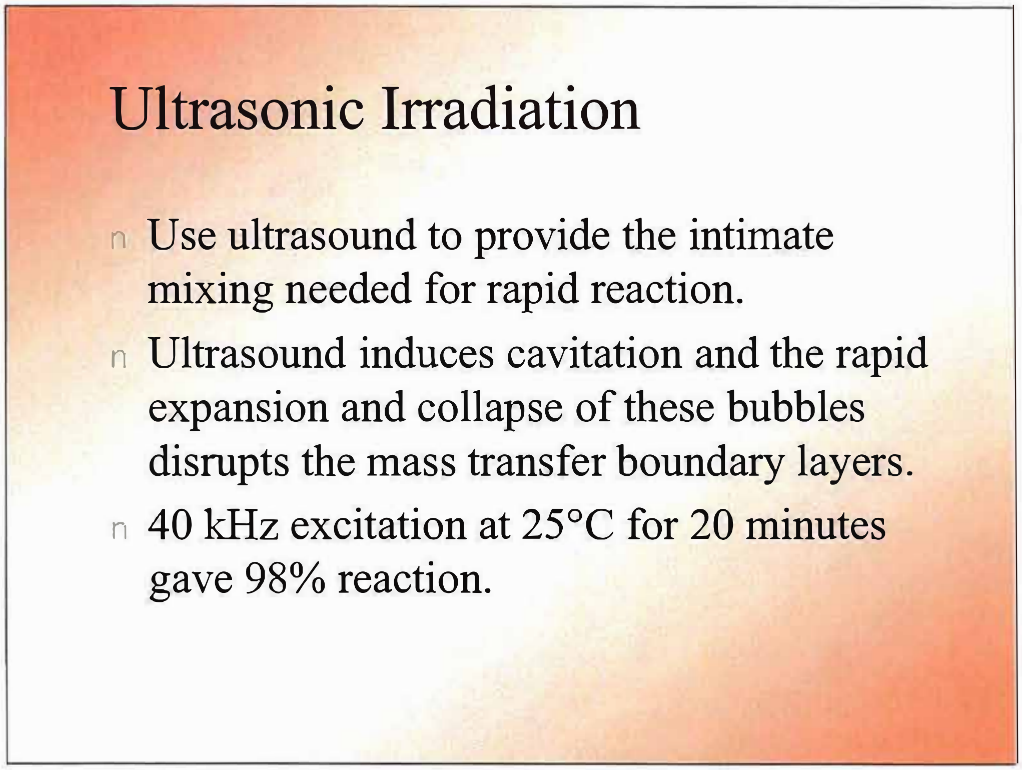
High Pressure

Noureddini, H., “High Shear Mixing Reactor for Glycerolysis,” Liquid Fuels, Lubricants, and Additives from Biomass, Proceedings of an Alternative Energy Conference, Ed. By B.E. Dale, American Society of Agricultural Engineers, Kansas City, MO, 16-17 June 1994.

Noureddini, H., D. Harkey, and V. Medikonduru, “A Continuous Process for the Conversion of Vegetable oils into Biodiesel,” Liquid Fuels and Industrial Products from Renewable Resources – Proceedings of the 3rd Liquid Fuels Conference, Nashville, TN, 15-17 Sept. 1996.

Noureddini, H. and D. Zhu, “Kinetics of Transesterification of Soybean Oil,” JAOCS, V. 74, No. 11, 1997, pp. 1457-1463.

Ergun, N. and P. Panning, “Method for Producing Fatty Acid Methyl Ester and Equipment for Realizing the Same,” U.S. Patent 6,440,057 (2002)

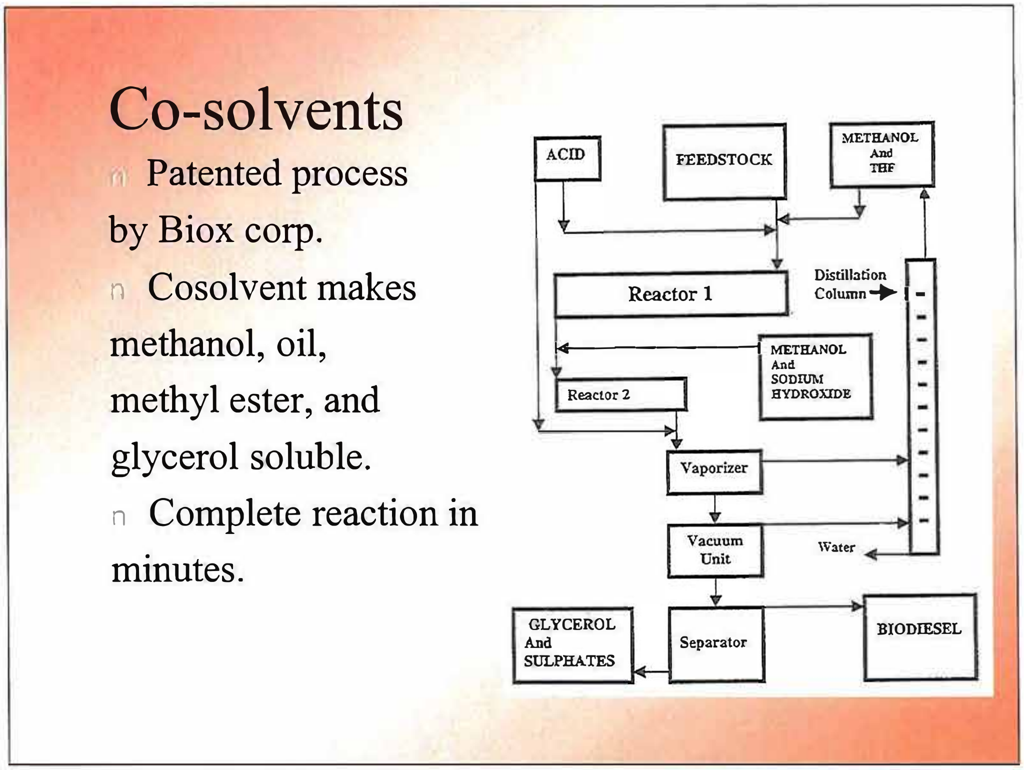


Ultrasonic Irradiation

- Use ultrasound to provide the intimate mixing needed for rapid reaction.
- Ultrasound induces cavitation and the rapid expansion and collapse of these bubbles disrupts the mass transfer boundary layers.
- 40 kHz excitation at 25°C for 20 minutes gave 98% reaction.

Stavarache, C., M. Vinatoru, R. Nishimura, and Y. Maeda, “Conversion of Vegetable Oil to Biodiesel Using Ultrasonic Irradiation,” Chemistry Letters (The Chemical Society of Japan), V. 32, No. 8, 2003, pp. 716-717.

Ergun, N. and P. Panning, “Method for Producing Fatty Acid Methyl Ester and Equipment for Realizing the Same,” US Patent No. 6,440,057, August 27, 2002.



Co-solvents

- Patented process by Biox corp.
- Cosolvent makes methanol, oil, methyl ester, and glycerol soluble.
- Complete reaction in minutes.

In addition to the ability to make the alcohol, oil, methyl esters, and glycerol soluble, an important criteria for the choice of co-solvent is having a boiling temperature that is close to the boiling temperature of methanol. This allows the co-solvent to be recovered and recycled with the alcohol. The co-solvent of choice is tetrahydrofuran (THF) although methyl t-butyl ether (MTBE) is also mentioned.

The technique can be used for both acid- and base-catalyzed reactions. Boocock shows how a two-step acid/base process can handle FFA levels up to 25%.

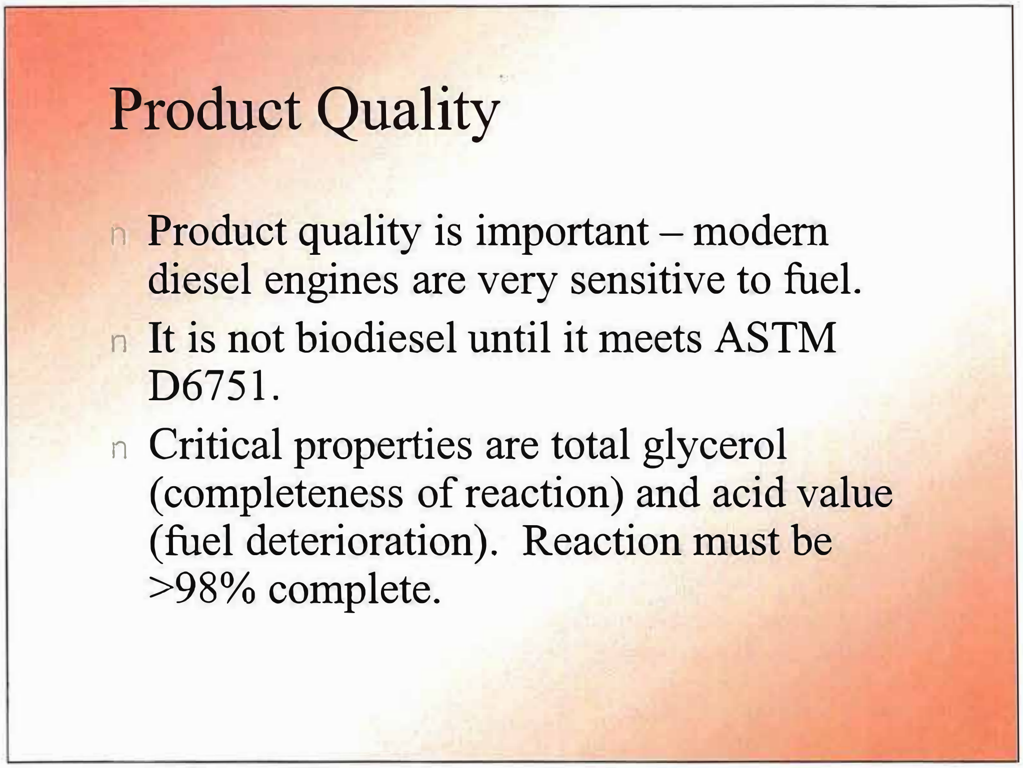
Boocock, D.G.B., S.K. Konar, and H. Sidi, “Phase Diagrams for Oil/Methanol/Ether Mixtures,” Journal of the American Oil Chemists’ Society, V.73, No. 10, 1996, pp. 1247-1251.

Boocock, D.G.B., S.K. Konar, V. Mao, and H. Sidi, “Fast One-Phase Oil-Rich Processes for the Preparation of Vegetable Oil Methyl Esters,” Biomass and Bioenergy, V. 11, No. 1, 1996, pp. 43-50.

Boocock, D.G.B., S.K. Konar, V. Mao, C. Lee, and S. Buligan, “Fast Formation of High-Purity Methyl Esters from Vegetable Oils,” Journal of the American Oil Chemists’ Society, V. 75, No. 9, 1198, pp. 1167-1172.

Boocock, D.G.B., S.K. Konar, V. Mao, and H. Sidi, “Biodiesel: Transesterification of Vegetable Oils Revisited: A Method for Increasing Base-Catalysed Methanolysis Rates,” Report from Biomass for Energy, Environment, Agriculture, and Industry, Proceedings of the 8th European Biomass Conference, Oct. 1994, pp. 1192-1197.

The concept of using a solvent was anticipated by Haller as described in *The Analyst*, 31(371):52 (1907).



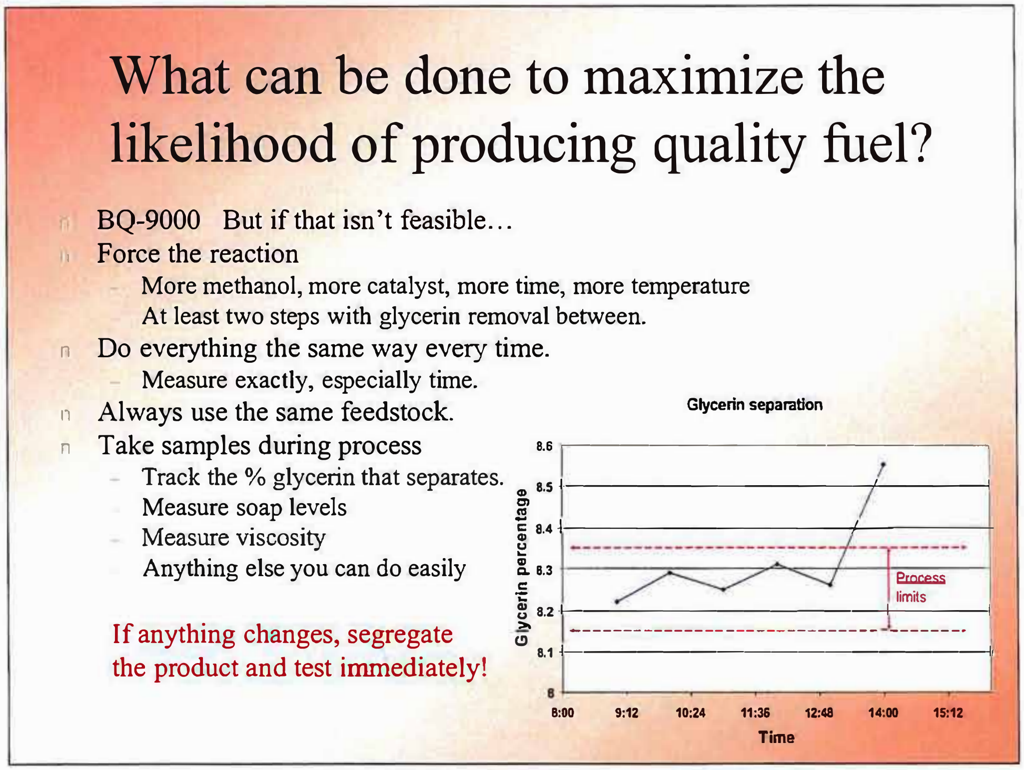
Product Quality

- 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.

BQ-9000 is a quality program that is based on ISO-9000 procedures to increase likelihood that a plant can provide quality fuel.

BQ-9000 does not guarantee that the fuel meets the specification but it guarantees that the producer is doing the right things to provide a quality fuel.

See www.BQ-9000.com



What can be done to maximize the likelihood of producing quality fuel?

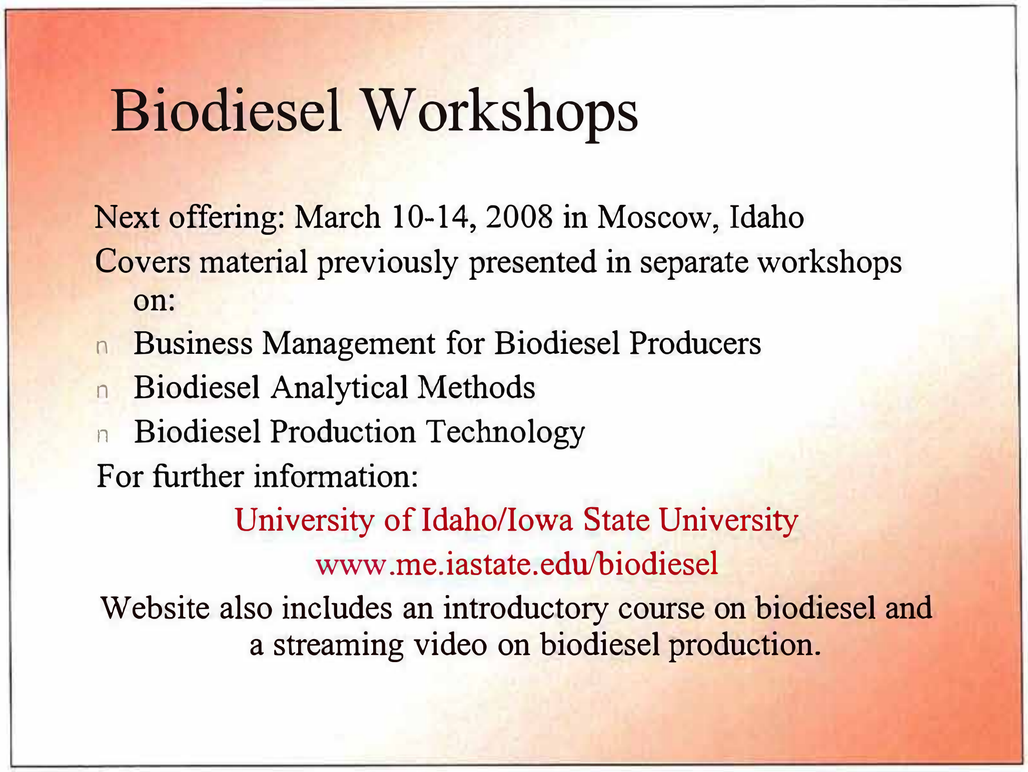
- BQ-9000 But if that isn't feasible…
- Force the reaction
  - More methanol, more catalyst, more time, more temperature
  - At least two steps with glycerin removal between.
- Do everything the same way every time.
  - Measure exactly, especially time.
- Always use the same feedstock.
- Take samples during process
  - Track the % glycerin that separates.
  - Measure soap levels
  - Measure viscosity
  - Anything else you can do easily

If anything changes, segregate the product and test immediately!

Use AOCS method Cc 17-79 to measure soap (titration with HCl to end point of bromophenol blue indicator)

Summary

- There are many technology options for biodiesel production.
- The technology choice is a function of desired capacity, feedstock type and quality, alcohol recovery, and catalyst recovery.
- Maintaining product quality is essential for the growth of the biodiesel industry.



Biodiesel Workshops

Next offering: March 10-14, 2008 in Moscow, Idaho

Covers material previously presented in separate workshops on:

- Business Management for Biodiesel Producers
- Biodiesel Analytical Methods
- Biodiesel Production Technology

For further information:

University of Idaho/Iowa State University

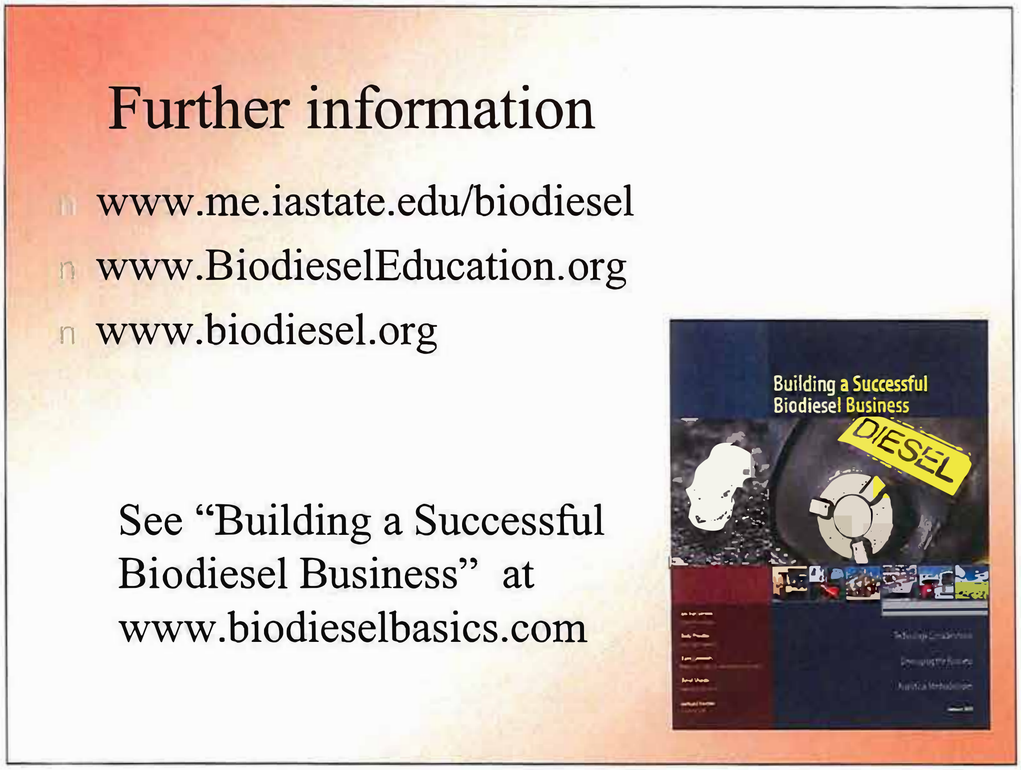
www.me.iastate.edu/biodiesel

Website also includes an introductory course on biodiesel and a streaming video on biodiesel production.

Currently planning workshop for:
March 10-14, 2008 in Moscow, Idaho

Will probably have additional workshops in July and October 2008, depending on demand.

Latest workshop schedule and information will be at www.me.iastate.edu/biodiesel



Further information

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

See "Building a Successful Biodiesel Business" at www.biodieselbasics.com