Chemistry of Biodiesel: The beauty of Transesterfication

Organic Chemistry
Terms & Definitions

- Acid- A corrosive substance that liberates hydrogen ions (H^+) in water. **pH lower than 7.**
- Base- A caustic substance that liberates hydroxyl ions (OH^-) in water. **pH higher than 7.**
- Catalyst- A substance that facilitates or enables a reaction between other substances.
- Alcohol- A substance containing hydroxyl compounds.
- Ester- An acid bonded to an alcohol
- Esterification- Making an ester. Example: An acid bonds to an alcohol to form an ester.
- Transesterification- Transforming one type of ester into a different type of ester.

Fats & Oils - Definitions

- Fats & oils are esters (acids bonded to alcohols)
- The acids are know as Fatty Acids and are made up of hydrocarbon chains
- The fats and oils used to make biodiesel are known as triglycerides.
- A triglyceride means that three (tri) acids are bonded to an alcohol, in this case three fatty acids bonded to a glycerin.

Fats & Oils - Decomposition

- Fats and oils can decompose in the presence of water, heat accelerates this process
- When fats and oils break down they form mono-glycerides, di-glycerides and free fatty acids
- FFA or Free Fatty Acids are NOT esters….

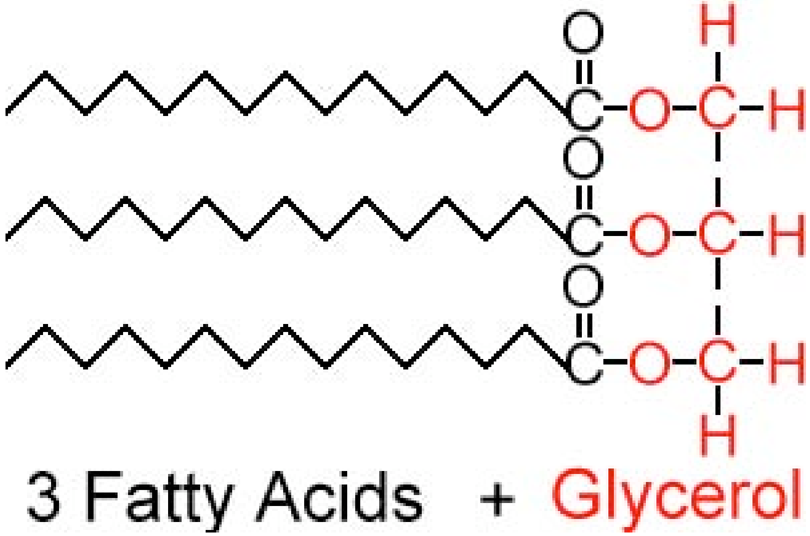
Fats & Oils - Saturation

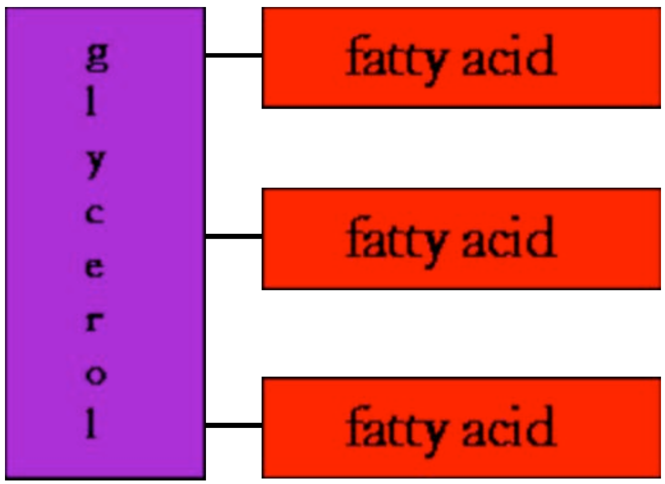
- Saturated fats and oils have more hydrogen bonded to the carbons so, a fully saturated fat would have four hydrogens bonded to every carbon (the maximum number of hydrogen carbon bonds possible)
- Why is this important? Because the level of saturation determines the characteristics of the fat or oil. For example, soy oil becomes a solid at lower temperatures than canola oil.
- Properties are determined by the fatty acid composition, or profile, of the fat or oil

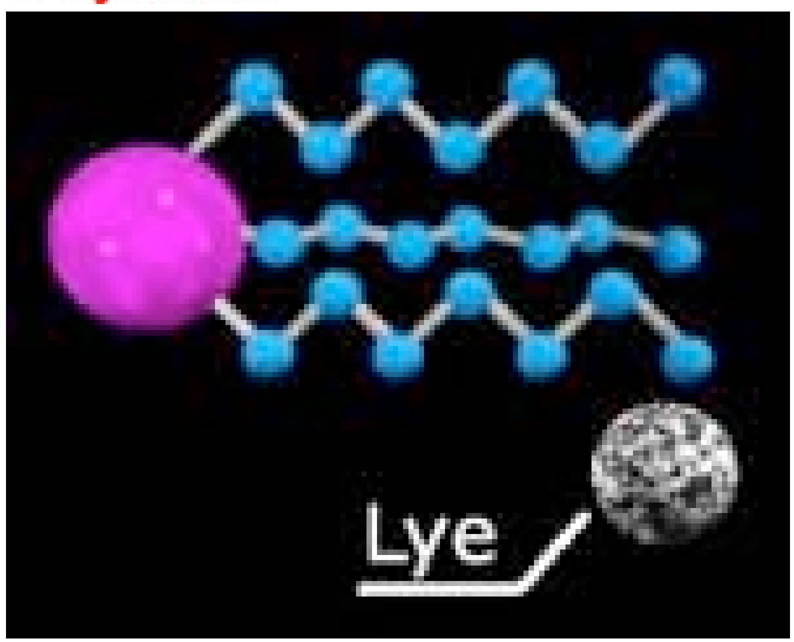
Fats & Oils - Hydrogenation

- Fats and oils can become more saturated by injecting hydrogen gas which bonds to available carbon receptors.
- This process is called hydrogenation and helps prolong shelf life by making the fat or oil more durable and resistant to decomposition.
- Hydrogenation of oils should not have a significant effect on the transesterification process.

The Infamous Triglyceride

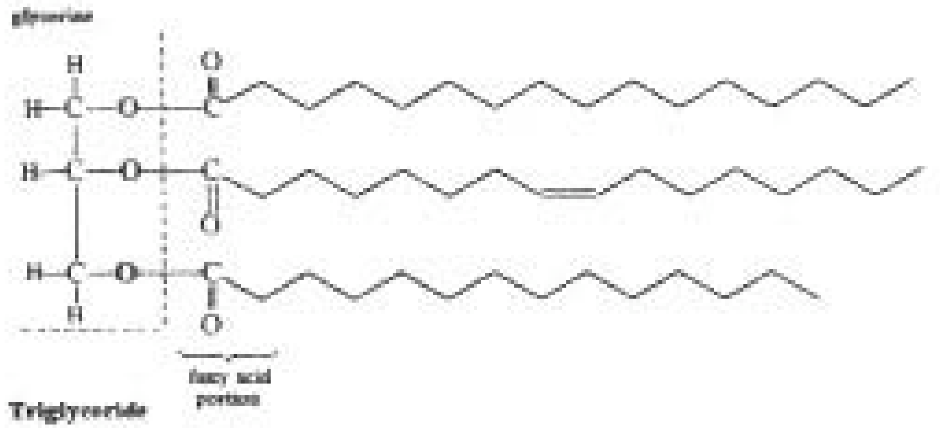




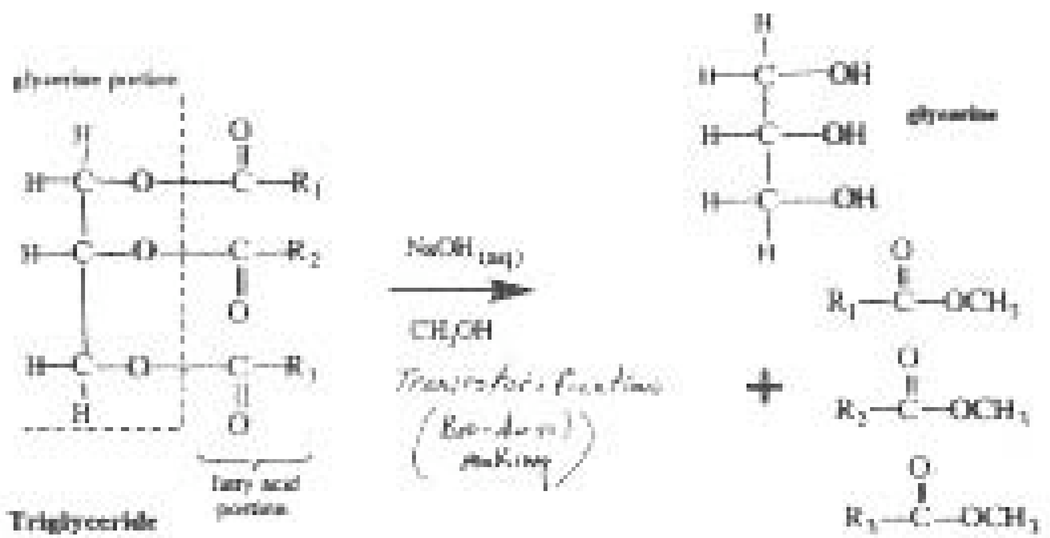


Biodiesel - Definition

- Biodiesel is most commonly a mono-ester of methanol but other alcohols like ethanol can also be used.
- You can call biodiesel a mono-alkyl methyl ester or methyl ester for short



During transesterification a basic catalyst breaks the fatty acids from the glycerin one by one. If a methanol contacts a fatty acid they will bond and form biodiesel. The hydroxyl group from the catalyst stabilizes the glycerin.



Rate of Reaction

- Transesterification can happen at ambient/70 degrees F, need 4-8 hours for completion
- Reaction is shortened to 2-4 hours at 105 degrees F
- Even shorter time 1-2 hours at 140 degrees
- Watch out! Methanol boils at 148degrees

Let's Make Biodiesel

Biodiesel Safety

CAUTION:
Wear proper protective gloves, apron, and eye protection and do not inhale any vapors --

Methanol can cause blindness and death, and you don't even have to drink it, it's absorbed through the skin.

Sodium or Potassium hydroxide can cause severe burns and death. Together these two chemicals form sodium methoxide or potassium methoxide. This is an extremely caustic chemical.

Wear a mask and full body covering for safety, that means chemical-proof gloves with cuffs that can be pulled up over long sleeves -- no shorts or sandals.

These are dangerous chemicals -- treat them as such! Always have a immediate access to running water when working with them. The workspace must be thoroughly ventilated.

No children or pets allowed.

More Biodiesel Safety

- Organic vapor cartridge respirators are more or less useless against methanol vapors.
- Professional advice is not to use organic vapor cartridges for longer than a few hours maximum, or not to use them at all.
- Only a supplied-air system, like a self contained breathing apparatus, will do.
- The best advice is not to expose yourself to the fumes in the first place.
- The main danger is when the methanol is hot -- when it's cold or at "room temperature" it fumes very little.
- All methanol containers should be kept tightly closed anyway to prevent water absorption from the air.
- It is best to transfer methanol from its container to the methoxide mixing container by pumping it, with no exposure at all.
- Making methoxide releases heat and causes methanol to get hot but keeping the container closed and properly vented prevents harmful fumes from contaminating the work space.

More on Potassium and Sodium Methoxide

- Treat either methoxide with extreme caution. Do not inhale any vapors.
- If methoxide gets splashed on your skin, it will burn you without your feeling it (killing the nerves) -- wash immediately with lots of water.
- Always have immediate access to running water when working with methoxide.
- methoxide is also very corrosive to paints.
- Sodium or Potassium hydroxide reacts with aluminum, tin and zinc. Use glass, enamel or stainless steel containers -- stainless steel is best.

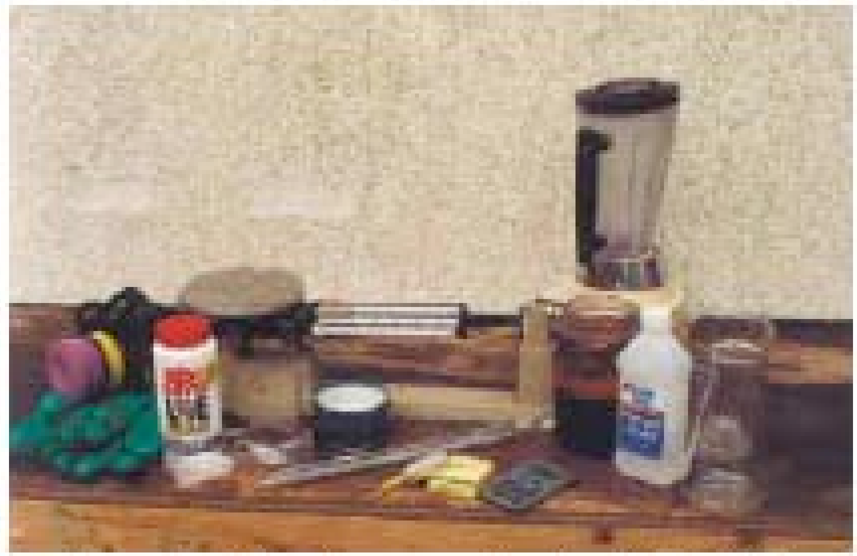
Sample Supplies for a Mini-Batch

Chemicals:

- New or used vegetable oil
- Isopropyl alcohol (>90% rubbing alcohol)
- Methanol
- Potassium hydroxide
- Distilled water

Other supplies:

- Paper towels, marker, masking tape
- 20ml beakers, 500ml beakers, 1500ml beakers
- Petri dishes for measuring KOH, eyedroppers with 1 ml graduations
- Mason jars



The equipment and supplies necessary to make a 1 liter test batch.

Understanding pH

Determining the pH of biodiesel:

Myth: It is not possible to truly determine the pH of biodiesel because it is not an aqueous solution (and pH is the measurement of hydrogen ions in water).

Fact: Biodiesel is hygroscopic and will always have a tiny bit of water (about 1,200 ppm) absorbed from the atmosphere, if from nowhere else. It is possible to measure its pH. We have had better luck with litmus paper and chemical indicators. It took too long to get a result using cheaper digital pH meters. Expensive laboratory meters work quite well.

Testing oil with digital meters--

There are special pH meters made for testing fossil oil products, and they're very expensive.

You don't need them for making biodiesel -- all regular pH meters should work in natural oils.

Measurement with electronic equipment takes about 30 seconds in water and up to two minutes in oils.

After measuring oils wash the electrode carefully with dishwashing soap and rinse thoroughly, first with tap water and finally with a little distilled water.

Never use solvents to clean an epoxy electrode -- solvents are only needed if you sample mineral oil products.

Titrating

- Titrating- a method of determining the concentration of a dissolved substance--vegetable oil--in terms of the smallest amount of a reagent--potassium hydroxide--is required to bring about a given effect--neutralize the FFAs.
- We will use a chemical pH indicator that changes color when the FFAs are neutralized

pH Indicators

- Phenolphthalein has a broad pH range where it changes color and as such is a great indicator for titrating biodiesel. It is colorless until 8.3, then it turns pink (magenta), and red at its maximum of pH of10.4.
- Phenol red, available at pool and spa supply stores, also works. It's range is not quite as good as phenolphthalein but it does the job in a pinch. It is colorless until 6.8, then it turns yellow, and red at its maximum pH of 8.2)
- For accurate titration you need to be able to measure pH 8.5.
- High quality oil (that means low FFA concentration) phenol red is usually fine but for higher FFA levels it is not as accurate.

Step 1: Titration

method of determining how much catalyst needed to neutralize the fatty acids in the used vegetable oil

1. Measure 1 gram of KOH onto a petri dish on a scale
2. Measure 1 liter of distilled water into a 1500ml beaker
3. Pour the 1 gram of KOH into the 1 liter of water
4. Label this beaker with a piece of masking tape & marker “KOH/Water solution-do no drink”
5. Measure 10 ml of isopropyl alcohol into a 20 ml beaker
6. Dissolve 1 ml of used vegetable oil into the isopropyl alcohol
7. Label this 20ml beaker “oil/alcohol solution”
8. Add 2 drops of pH indicator to the oil/alcohol solution
9. Use a graduated eyedropper or burette to drip the KOH/water solution into the oil/alcohol solution about 1 millimeter at a time
10. Swirl the vegetable solution as the KOH/water is added and **watch carefully** for a color change. The change will occur suddenly.
11. Record the quantity of KOH/water solution you add until the color of the oil/alcohol changes pink and holds for at least 5 seconds. (This represents a pH of between 8 and 9)**.**

Titration Equation

- Our base equation is:

$$7.0 \text{ g KOH} + L = X$$

Where L is the number of grams of KOH necessary to neutralize and react one liter of used vegetable oil and X the number of milliliters of KOH/water solution dropped into the oil alcohol mixture

- Modified equation to account for impurity of KOH:

$$(7.0 \text{ g KOH} / \% \text{ purity}) + L = X$$

Note: The above equations are for **1 liter** batches. Adjust for other volumes as necessary.

Step 2: Measure the Reactants

- 500 ml of filtered used oil into a large mason jar
- Perform under fume hood: 100ml of methanol into a small mason jar
- Make sure not to spill any on yourself or on your work space. If any methanol spills, clean the spill with a wet paper towel immediately.
- **L** grams (determined by titration) of KOH onto a petri dish on a scale

Step 3:
Dissolve the KOH in the Methanol

- Carefully pour the KOH into the methanol filled jar.
- Put the top securely on the jar and agitate until the KOH is completely dissolved in the methanol. There should be no visible flakes.
- The solution created is **potassium methoxide,** a strong caustic. Be very careful handling it.

Step 4: Mix the Reactants

- Continue to operate under the lab fume hood.
- Carefully pour the potassium methoxide on top of the vegetable oil in the large mason jar.
- Secure the lid on the large mason jar. Be sure it seals tightly.

- Shake vigorously for 15 minutes. You can take turns shaking so that everyone shares in the fun!

Step 5: Allow the Glycerin to Settle

- 75% of the separation will take place within the first hour after the reaction.
- Within 8 hours, the glycerin will fall to the bottom of the large mason jar
- The top layer should be methyl esters or **biodiesel**
- Label mason jar "biodiesel reaction in progress- do not drink"
- Wait at least 8 hours for the separation of biodiesel & glycerin.
- Separation can continue for another 24-36 hours

Step 6: Cleanup

- Wash all glassware with hot water and soap and place on paper towel to dry
- Put leftover methanol in a clearly labeled safety container/bottle
- Store leftover KOH in a cool, dry place
- Put leftover used oil in a dark container and store it in cool, dry place.
- Clean all equipment and containers. Do not use for food.
- Wash all glassware

Links

- www.me.iastate.edu/biodiesel
- www.biodieselcommunity.org
- www.biofuels.coop
- www.howfatworks.com