Basic Chemistry of Biodiesel
A Curriculum for Agricultural Producers

Prepared by

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For the

National Center for Appropriate Technology

NCAT

With funding and cooperation from the

USDA Risk Management Agency

RMA

The Beauty of Transesterification:

Chemistry and Organic Chemistry

- Chemistry is the science of matter at the atomic to molecular scale, dealing primarily with collections of atoms (such as molecules, crystals, and metals).
- Chemistry deals with the interactions of these substances, and how their interactions on an atomic level correspond to substances we encounter in the world.
- Organic Chemistry is usually the study of the chemistry of Carbon and Hydrogen. The original name is derived from the misconception that all life is based on Carbon (which is not entirely true.) Biochemistry is the branch of chemistry that corresponds with all life processes.
- Fats and oils are organic compounds, and the biodiesel reaction falls under the field of Organic Chemistry

Source: Wikipedia

Elements, atoms and molecules, oh my...

- An element is a substance that cannot be separated into simpler substances by ordinary chemical means
- An atom is the smallest (a single) unit of an element.
- A molecule is the smallest unit of a combination of at least two atoms.
- A compound is a chemical substance made up of two or more elements, with a definite ratio determining the composition. Many compounds are composed of molecules.

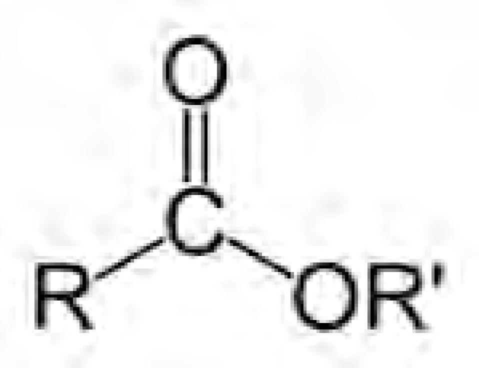
Organic Chemistry Terms & Definitions

- Acid- A corrosive substance that increases the concentration of hydronium ions (H_3O^+) in water. **pH lower than 7.**
- Base- A caustic substance that increases the concentration of hydroxide ions (OH^-) in water. **pH higher than 7.**
- Catalyst- A substance that facilitates a reaction between other substances by creating an alternate pathway for the reaction to occur.
- Alcohol- A substance containing hydroxyl compounds (-ROH).
- 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.

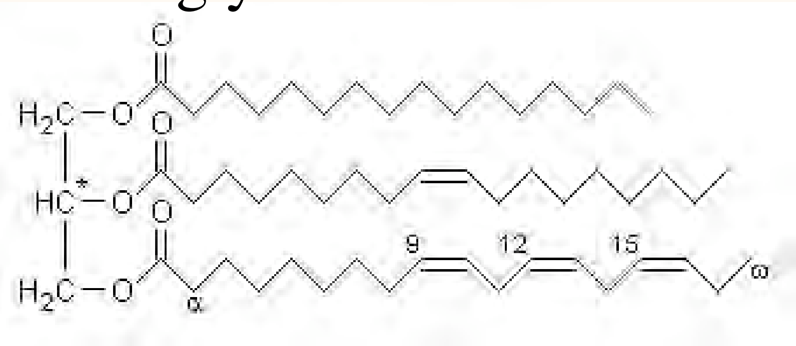
Fats & Oils - Definitions

- 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.

General Formula of an Ester

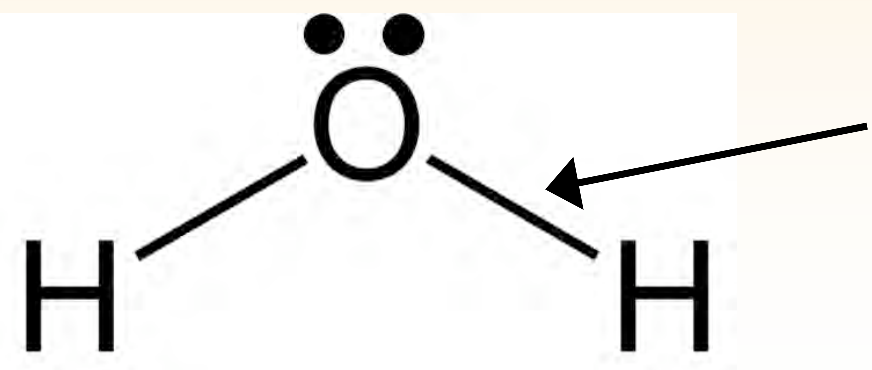


Triglyceride Formula



Chemical Bonds

- A chemical bond is the physical phenomenon of chemical species being held together by attraction of atoms to each other through sharing and exchanging of electrons.



A chemical bond between the hydrogen and oxygen atoms in water.

Fats & Oils - Saturation

- The level of saturation of an oil refers to the number of hydrogen atoms bonded to carbon, which is related to the number of double bonds between carbon atoms
- Why is this important? Because the level of saturation determines the characteristics of the fat or oil. For example, a fully saturated or monounsaturated oil will solidify at a higher temperature than a polyunsaturated oil.

Understanding Fatty Acid Composition

- Fats and Oils are generally composed of hydrocarbon (carbon and hydrogen atom) chains.
- The length and degree of saturation of the hydrocarbon chain affects the physical properties (viscosity, melting point, etc...) of the fat or oil.
- Fatty acids are generally designated in shorthand by: C:X in which the C corresponds to the number of carbon atoms in the chain and the X corresponds to the number of double bonds (thereby indicating the level of saturation.

  For example...

Oil or fat	14:0	16:0	18:0	18:1	18:2	18:3	20:0	22:1
Soybean		6-10	2-5	20-30	50-60	5-11		
Corn	1-2	8-12	2-5	19-49	34-62	trace		
Peanut		8-9	2-3	50-65	20-30			
Olive		9-10	2-3	73-84	10-12	trace		
Cottonseed	0-2	20-25	1-2	23-35	40-50	trace		
Hi linoleic Safflower		5.9	1.5	8.8	83.8			
Hi Oleic Safflower		4.8	1.4	74.1	19.7			
Hi Oleic Rapeseed		4.3	1.3	59.9	21.1	13.2		
Hi Erucic Rapeseed		3.0	0.8	13.1	14.1	9.7	7.4	50.7
Butter	7-10	24-26	10-13	28-31	1-2.5	.2-.5		
Lard	1-2	28-30	12-18	40-50	7-13	0-1		
Tallow	3-6	24-32	20-25	37-43	2-3			
Linseed Oil		4-7	2-4	25-40	35-40	25-60		
Tung Oil		3-4	0-1	4-15		75-90**		
Yellow Grease*	1.3	17.4	12.4	54.7	8.0	0.7	0.3	0.5

* Typical analysis: listed in Tat, M.E. and J.H. Van Gerpen, "Fuel Property Effects on Biodiesel," ASAE Paper 036034, American Society of Agricultural Engineering Annual Meeting, Las Vegas, NV, July 27-30, 2003.

** The dominant fatty acid in tung oil is a conjugated isomer of linolenic acid called eleostearic acid. The three double bonds in eleostearic acid are located at 9:10, 11:12, and 13:14 instead of at 9:10, 12:13 and 15:16 as in linolenic acid.

Peterson, C.L., "Vegetable Oil as a Diesel Fuel: Status and Research Priorities," ASAE Transactions, V. 29, No. 5, Sep.-Oct. 1986, pp. 1413-1422.
Linstromberg, W.W., Organic Chemistry, Second Edition, D.C. Heath and Company, Lexington, Mass., 1970.

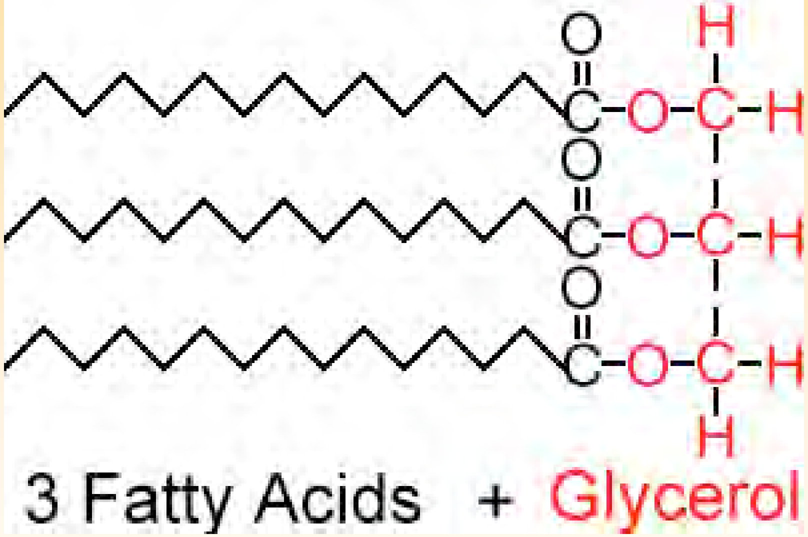
Chart 1. Composition of Various Oils and Fats.

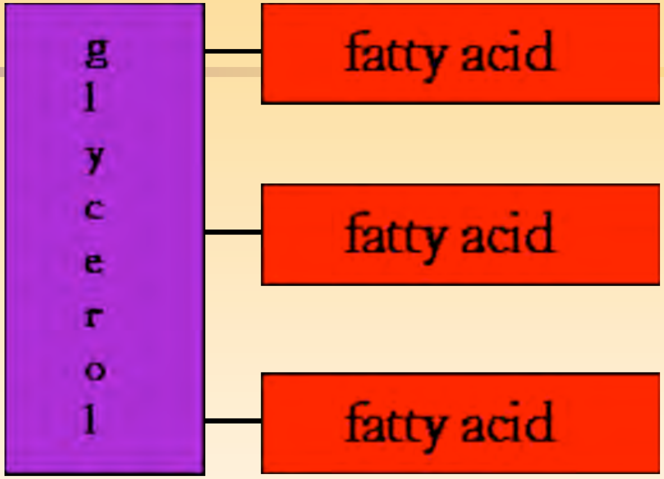
Source: Gerpen et al.

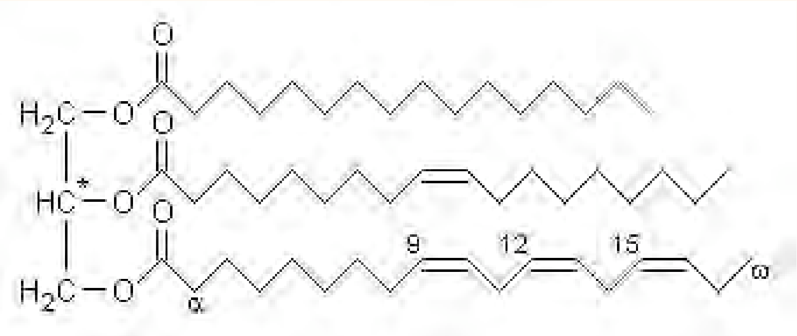
Properties of Various Fatty Acids

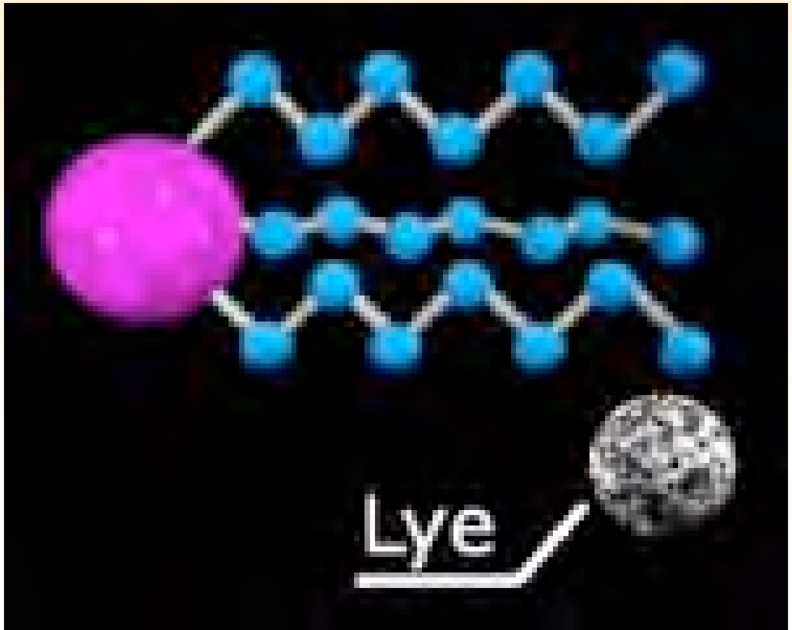
Fatty Acid	Abbreviation	Molecular Weight	Melting Point (°C)
Palmitic acid	C16:0	256.4	63
Stearic acid	C18:0	284.5	70
Oleic acid	C18:1	282.5	16
Linoleic acid	C18:2	280.4	-5
Linolenic acid	C18:3	278.4	-11

The Infamous Triglyceride









Properties of Two Alcohols Methanol and Ethanol

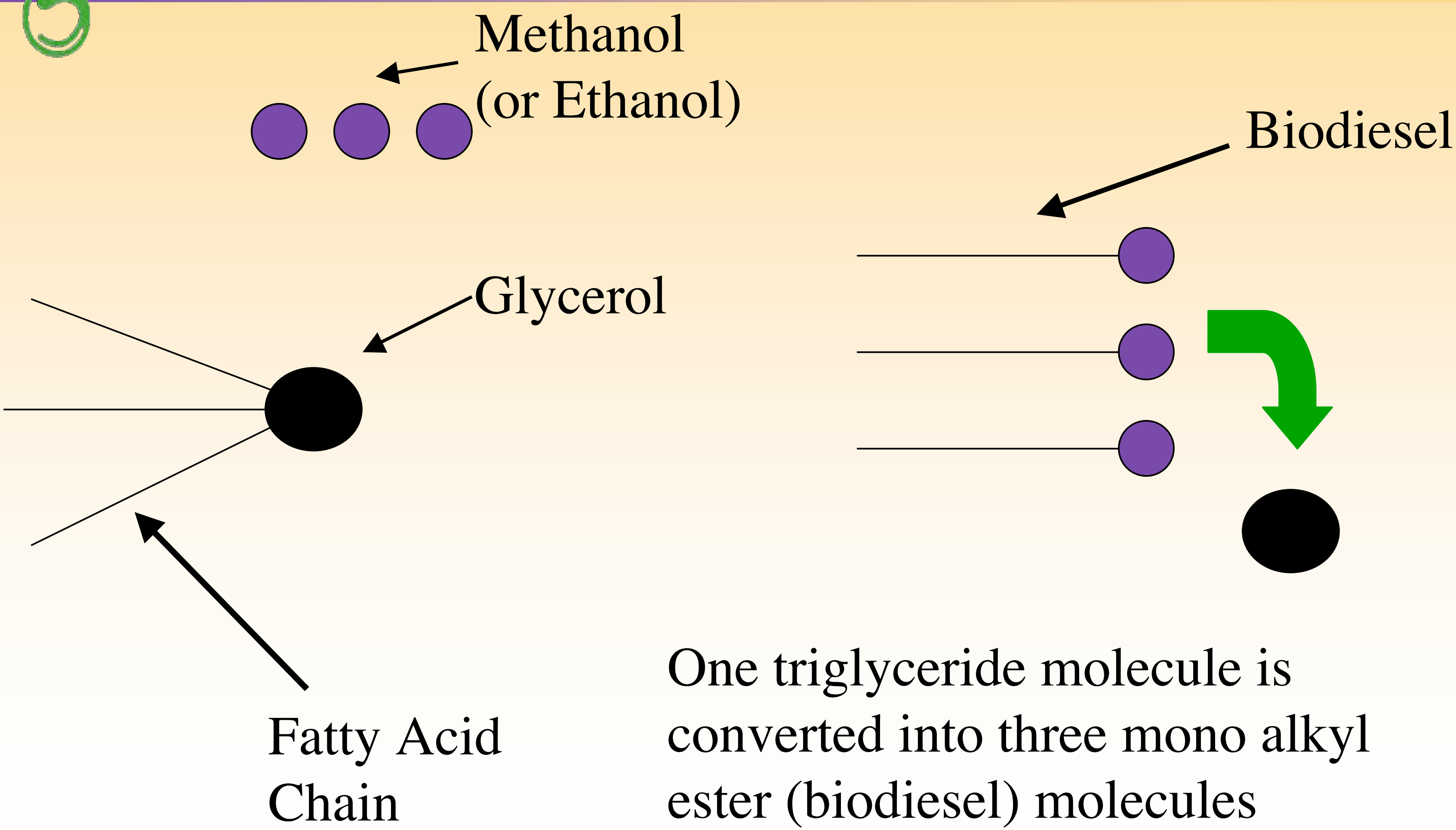
Alcohol	Formula	Molecular Weight	Boiling point (°C)
Methanol	CH_3OH	32.042	65 (148°F)
Ethanol	C_2H_5OH	46.069	78.5 (173°F)

Source: JV Gerpen and G Knothe

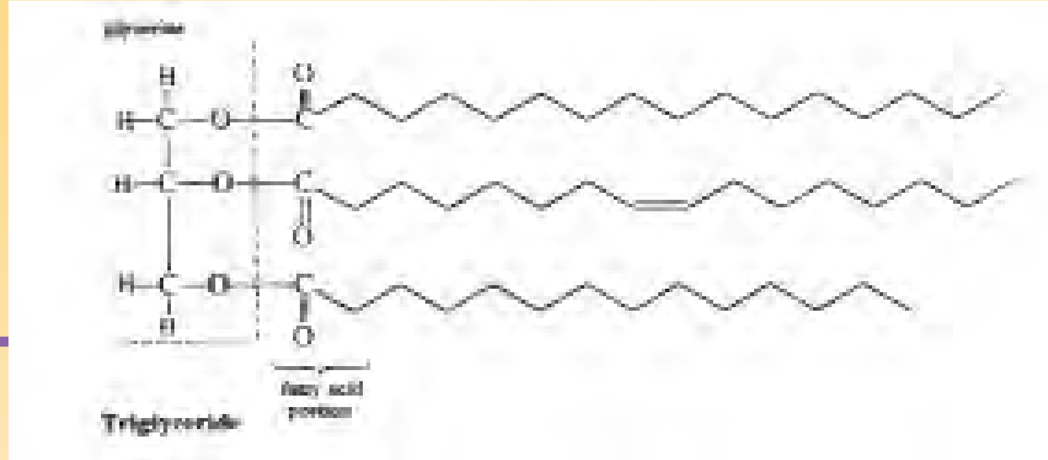
Biodiesel - Definition

- 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
- Biodiesel is a single fatty acid chain bonded to a methanol or ethanol molecule (usually methanol.)

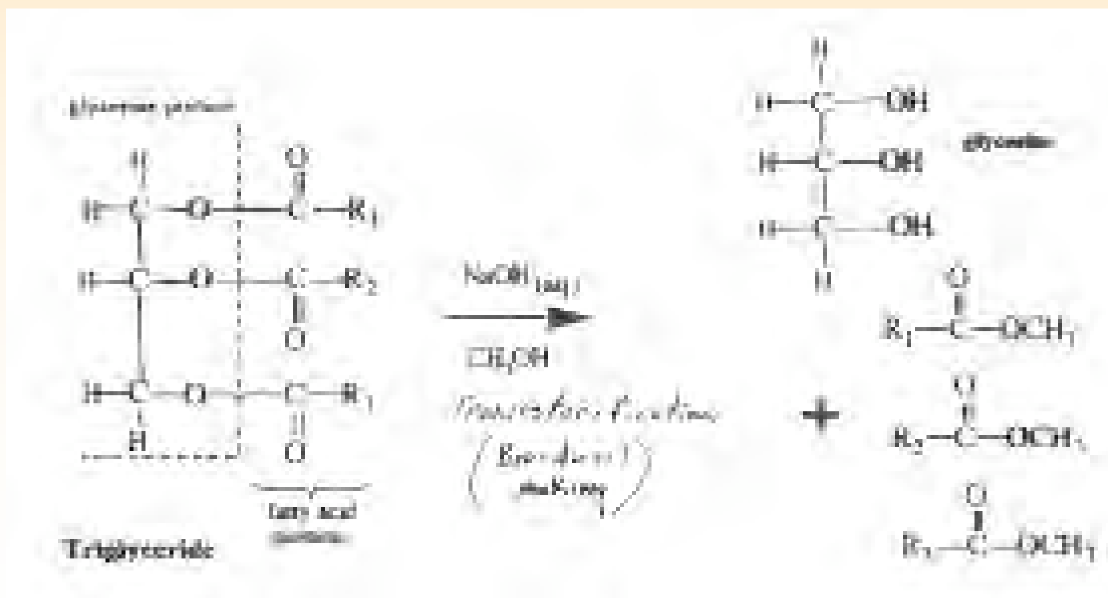
Transesterification (ie. the biodiesel reaction)



One triglyceride molecule is converted into three mono alkyl ester (biodiesel) molecules



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.



Moles and Molar Ratio

- A mole is the number of molecules required to equal the molecular weight of an element.
- In chemistry we generally look at chemical ratios in terms of the molar ratio of different compounds (stoichiometry).

Reversibility and Equilibrium

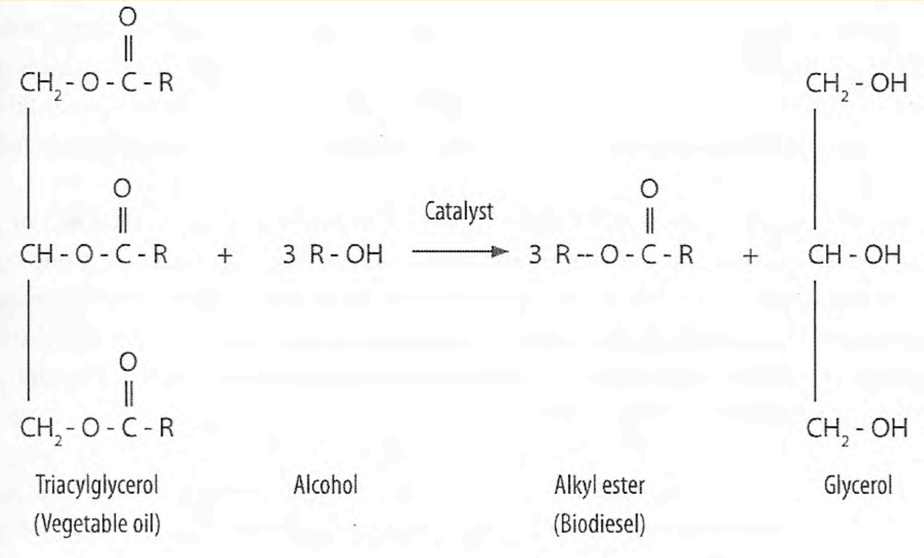
Chemical equilibrium is the state in which the concentrations of the reactants and products have no net change over time. Usually, this state results when the forward chemical reactions proceed at the same rate as their reverse reactions.

$$mA + nB \rightleftharpoons pC + qD$$

Source: Wikipedia

Excess Methanol

The stoichiometric ratio calls for 3 moles of alcohol per mole of triglyceride which would be about 10% by volume for methanol or , but...



The transesterification reaction.

We typically use double the stoichiometric ratio, or 6:1 moles of alcohol to triglyceride, to push the reaction to the products side.

Base Catalysts Used in Transesterification

Homogeneous alkaline Catalysis

- Sodium Hydroxide (Lye) NaOH
- Potassium Hydroxide (Potash) KOH
- Sodium Methylate CH_3ONa

Heterogeneous alkaline catalysis

- Can be reused and do not enter into reaction
- Calcium carbonate is promising, but requires high pressure and temperature

Rate of Reaction

- In the biodiesel process the rate of reaction is related to the temperature of reaction.
- At 70^{o}F, need 4-8 hours for completion
- Reaction is shortened to 2-4 hours at 105^{o}F
- Even shorter time 1-2 hours at 140^{o}
- Watch out! Methanol boils at 148^{o}
- **Ideal reaction temperature is 130-140^{o}F (55-60^{o}C)**

Fats & Oils - Decomposition and Degradation

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

Free Fatty Acids (FFAs)

- In highly degraded oil, the percentage of FFAs may be relatively high (over 5%). FFAs are not esters, and therefore cannot be converted into biodiesel through transesterification.
- The catalyst will react with the FFAs preferentially to create soap.
- This will lower yields, and can lead to emulsion problems during post-processing.
- If the FFA content is too high, the normal chemical process will **not** work.

Free Fatty Acids

- To determine oil quality (ie. FFA content) we can perform a titration to measure the acidity of the oil.
- Use excess catalyst to convert the FFAs into soap intentionally, and the remaining catalyst will be used in the biodiesel process.

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 Safety

- Treat 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.

Supplies for a sample 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

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.
- 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.
- Turmeric is also used as a pH indicator

Step 1: Titration

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:

$$7.0\ g\ KOH + L = X$$

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:

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

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
- Heat oil to 130F
- Perform under fume hood: 110ml 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