

Introduction to Oil Chemistry and Transesterification

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Atoms and Elements

- Elements are the fundamental substances that compose matter in the Universe.
 - Hydrogen, Carbon, Nitrogen, Silicon, Iron, Gold, etc.
- Atoms are the smallest particles of elements that can exist alone or in combination with other elements.
- Elements are defined by *atomic number*, which is the number of protons that exist in the nucleus of an atom of that element.
- Most of the mass of an atom is in its nucleus:
 - Protons: positively charged
 - Neutrons: no charge
- Surrounding the nucleus are negatively charged electrons, which are much smaller than either protons or neutrons.

Molecules and Compounds

- In theory, the number of electrons possessed by an atom is the same as the number of protons, however this usually does not result in a stable electron configuration.
- This instability is the basis for the formation of bonds between atoms and therefore groups of atoms called molecules.
- Compounds are distinct substances composed of molecules of two or more elements.
 - Carbon dioxide, methane, water

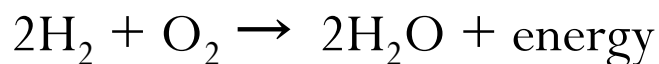
Chemical Bonds

- Result due to a tendency for atoms to exist in a low energy state.
 - Stable electron configuration → lowest energy state
- There are two main types of chemical bonds:
 - Covalent: electrons are shared between atoms
 - Sharing allows stable electron configuration and balance of charge, and binds the atoms together.
 - O₂ CO₂ N₂ CH₄ H₂O
 - Ionic: electrons are exchanged between atoms
 - Exchange allows stable electron configuration, and resulting imbalance of charge binds atoms together.
 - Atoms with a charge imbalance are called ions
 - Cation: Positively charged ion
 - Anion: Negatively charged ion
 - NaCl KOH

Chemical Reactions

- The result of rearranging of bonds to form different molecules.

- Example: Oxidation of Hydrogen



- Can occur spontaneously if the resulting compounds allow the atoms to exist in a lower energy state than the previous configuration. Spontaneous reactions release energy.

- Often times a chemical reaction may not result in a significant change in energy state, these are called reversible reactions.

- Example: Sodium carbonate formation



Stoichiometry

- Chemical reactions occur on a per-atom basis.
 - Understanding of reactions begins with balancing the equation:
$$2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$$
 - Note that the total number of elements on each side is the same.
 - This allows us to predict relative amounts of substances required and produced by a particular reaction.
- However, different atoms have different mass due to different amounts of protons and neutrons.
- A standard is required: Avogadro's Number
 6.022×10^{23} atoms = 1 mole of substance
- Molecular weight connects mass to number of atoms
 - 1 mole of Carbon \approx 12 grams
 - 1 mole of Sodium \approx 23 grams

Periodic Table of the Elements

Group →	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
↓ Period																		
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra		104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo
			Lanthanides	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
			Actinides	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

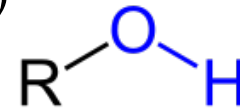
Organic Chemistry

- Branch of chemistry dealing with compounds containing the element carbon.
 - Carbon is very common and the basis for life
 - About 90% of known compounds
 - Can bond with up to 4 other atoms
 - Can form double or triple bonds with other atoms
- Organic compounds are generally composed of a carbon & hydrogen chain and a functional group containing other elements such as oxygen or nitrogen.

Nomenclature

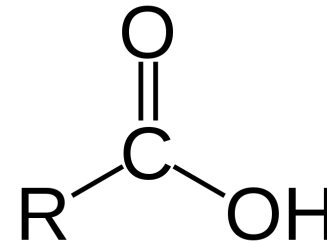
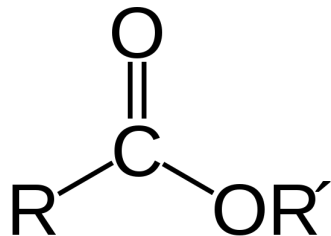
- Organized into classes based on functional groups.
- Three are important in biodiesel:

- Alcohols: Contain a hydroxyl group (OH)



- Carboxylic Acids: Contain a carboxyl group (COOH)

- Esters: Alcohol + Carboxylic Acid



Fatty Acids

- Are a type of organic acid, containing a carboxyl group.
- Are not “strong” acids, but still react with strong bases to form salts called soap.
- Length of carbon chain and types of bonds are *extremely* important in determining the physical properties of the fatty acid.
- Are strongly non-polar, and do not mix well with water, and are not good solvents of most salts.

Saturation

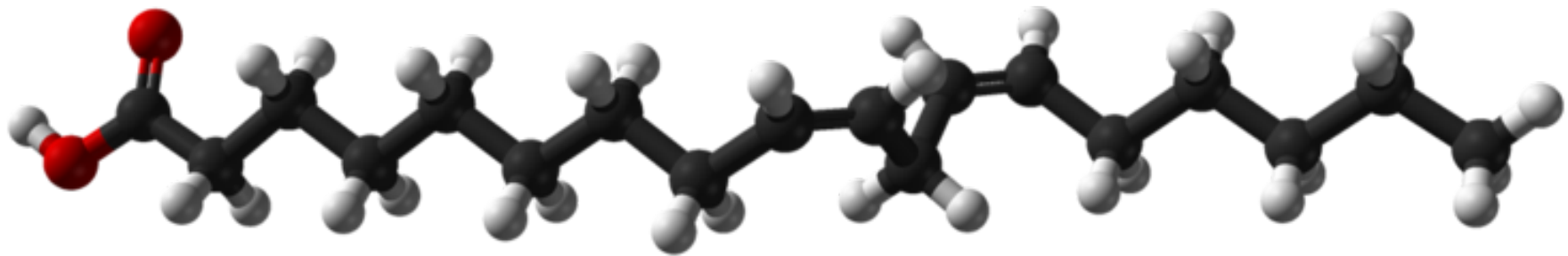
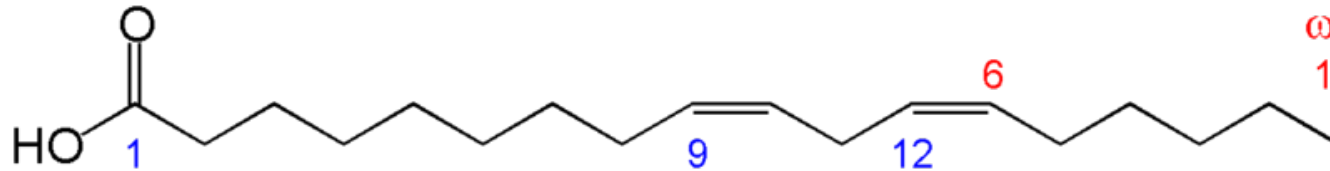
- Saturated fats do not contain double or triple bonds, hence are “saturated” with hydrogen.
 - Palmitic (16:0), Stearic (18:0)
- Saturated fats are most stable, but have much higher melting points than unsaturated fats.

Saturation

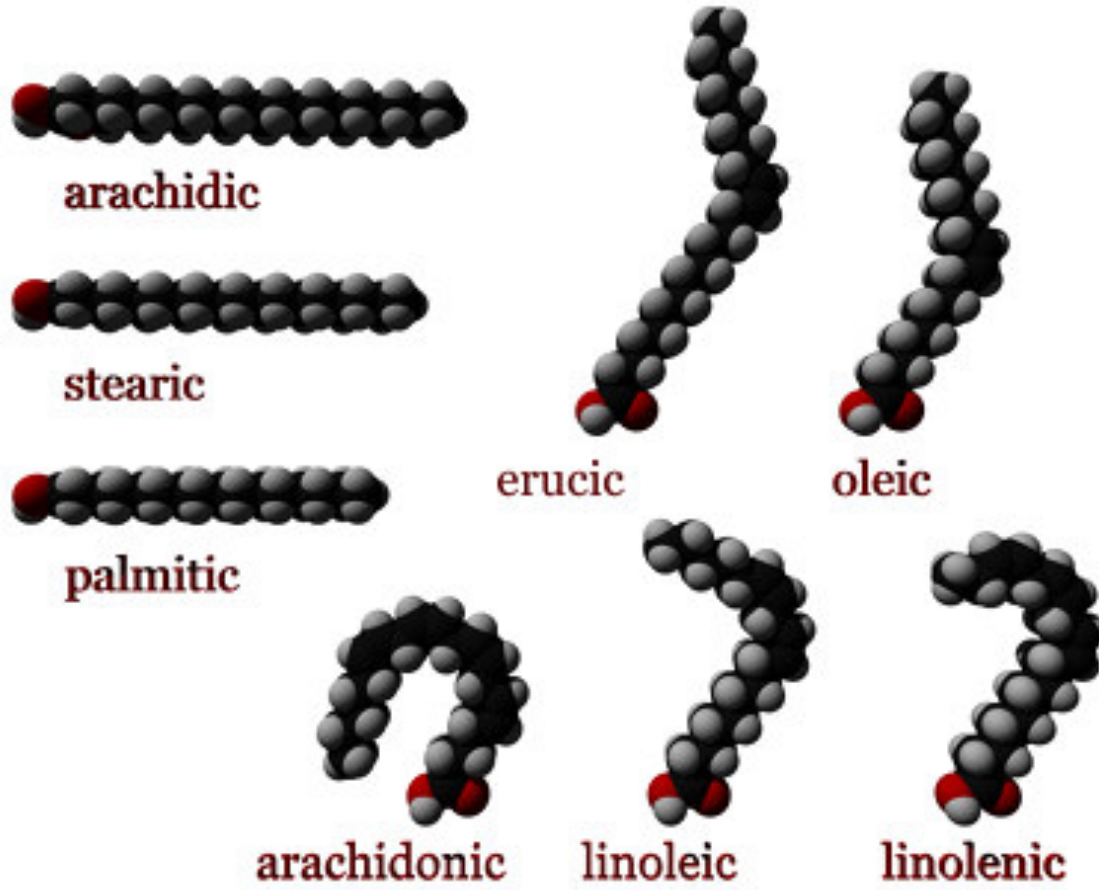
- Unsaturated fats contain double bonds, which lead to “kinks” in the molecule.
 - Oleic (18:1), Linoleic (18:2)
- These kinks cause the molecules to resist solidification and therefore they are liquid at lower temperatures.
- However, the double bonds are susceptible to oxidative degradation, which leads to the formation of undesirable compounds.

Fatty Acids

- Nomenclature:
 - Named based on the number of carbons (usually 16-22) and the number of double bonds (usually 0-3)
 - Both trivial and systematic names exist, although the systematic names may be long and complicated.
 - Linoleic Acid = *cis, cis-9,12-Octadecadienoic acid*



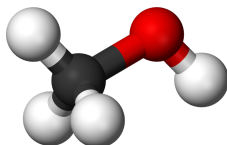
Fatty Acids



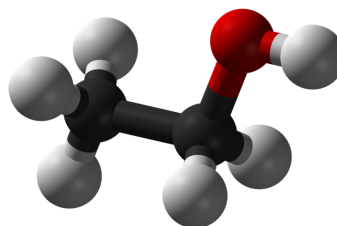
Alcohols

- Carbon chain plus one or more hydroxyl groups.
- Simple alcohols are most common.

- Methanol CH_3OH

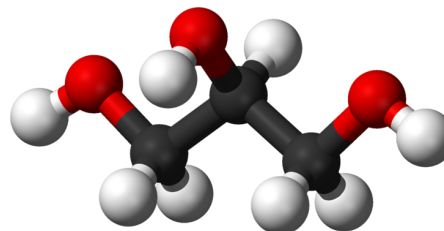


- Ethanol $\text{C}_2\text{H}_5\text{OH}$



- Glycerol is an alcohol, but somewhat more complex, containing 3 carbons and 3 hydroxyl groups.

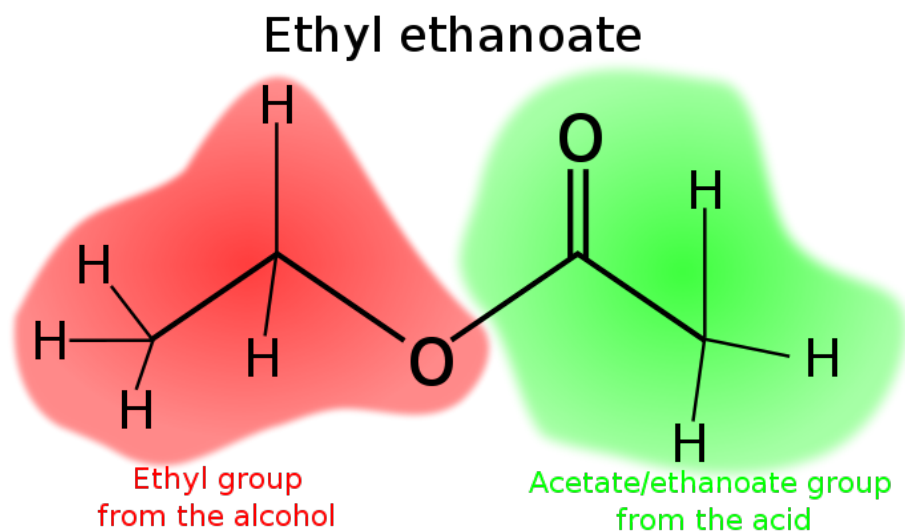
- $\text{C}_3\text{H}_8\text{O}_3$



- The alcohols relevant in biodiesel are strongly polar and mix well with water, and are good solvents of salts.

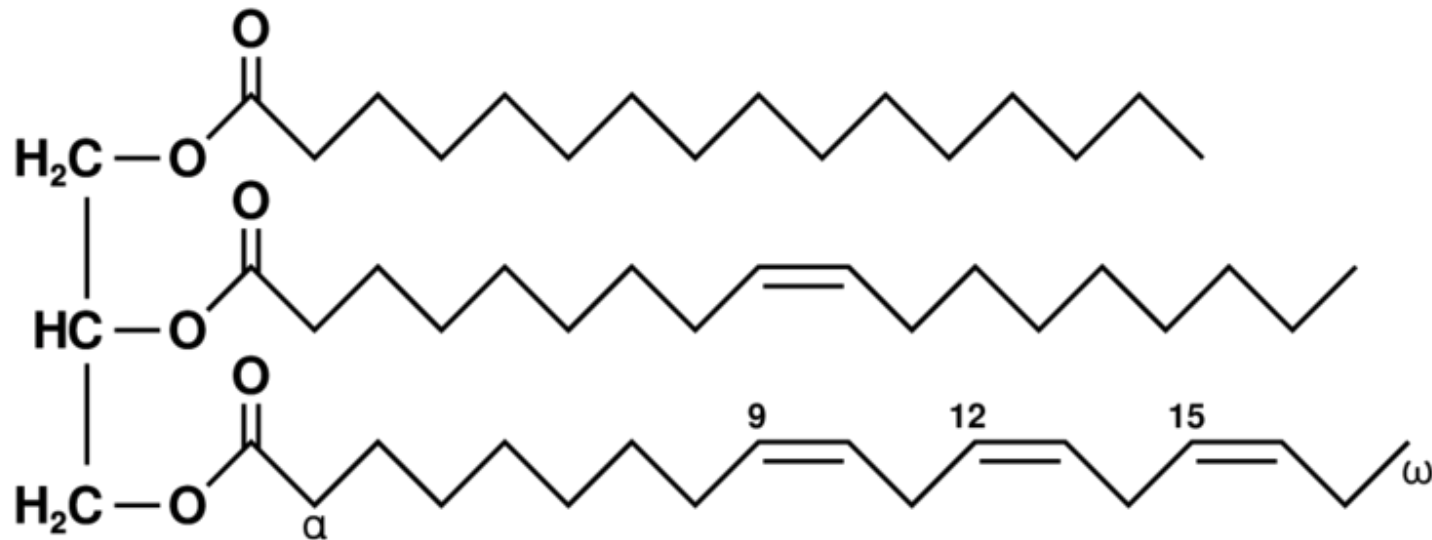
Esters

- Are the result of bonding an organic acid with an alcohol.
- Both vegetable oils and what we know as “biodiesel” are esters.
- Hence, the process of making biodiesel is called transesterification.



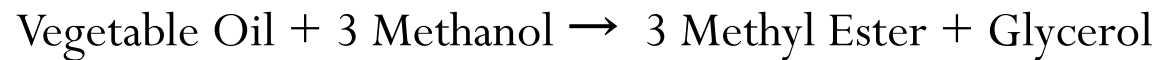
Vegetable Oil

- Vegetable oils are esters which contain 3 fatty acids bonded to a “backbone” of glycerol.
- Each of the 3 sites where there would be a hydroxyl group is replaced with a fatty acid.



Transesterification

- Simple Version:



- What we are basically doing is exchanging the glycerol with methanol, which only can bond with one fatty acid instead of three.
- This essentially breaks up the large vegetable oil molecule into three smaller methyl esters.
- The methyl ester has a similar energy content as the triglyceride but is less viscous and has a lower melting point.

Transesterification

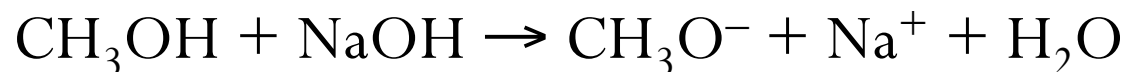
- It is important to note that the reaction is *reversible*.
 - This is a good thing because the overall energy content of the oil stays the same.
 - This is challenging because it can be difficult to encourage the reaction to complete.
 - The standard recipe calls for 100% excess methanol.
 - Heat + catalyst is required for reasonable reaction rates.

Transesterification

A Closer Look...

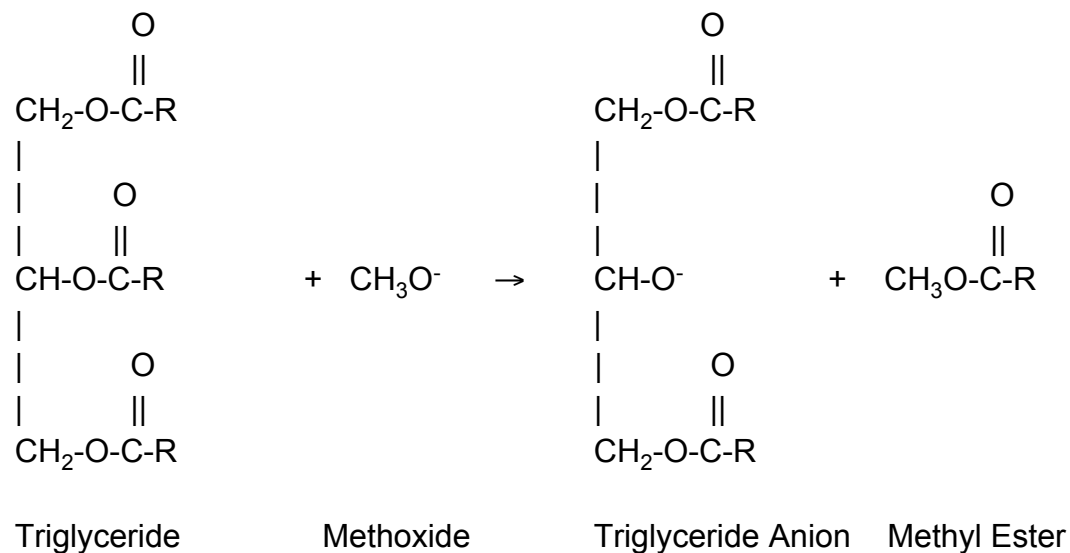
1. Reaction of catalyst with methanol to form methoxide.
2. Reaction of methoxide with triglyceride to form methyl ester and diglyceride anion.
3. Regeneration of catalyst.

Reaction of Base Catalyst with Methanol



- Note
 - This reaction produces WATER!
 - The strong base disassociates into ions and forms a methoxide anion and a sodium cation.

Reaction of Methoxide with Triglyceride



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

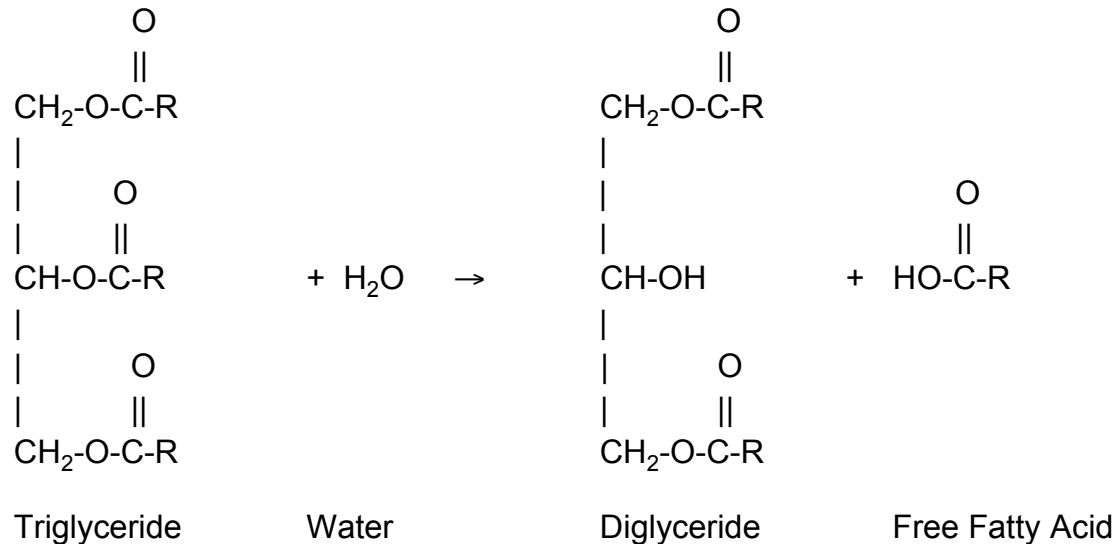
Reaction Optimization

- Reversible
 - Reaction can proceed in either direction
 - As long as there are excess *reactants*, the reaction is driven towards the *product* side.
 - Excess methanol \rightarrow more methyl ester
- Mass transfer limited
 - Reactants are not very soluble, and initially exist as tiny drops of methanol/catalyst suspended in oil.
 - Rate of reaction is limited by how quickly the methanol/catalyst can get to the oil and how quickly the methyl ester can escape.

Reaction Inhibitors

- Two side reactions that are bad:
 - Hydrolysis of Triglyceride to form Carboxylic Acid.
 - Reaction of Base Catalyst with Carboxylic Acid to form Soap.

Hydrolysis



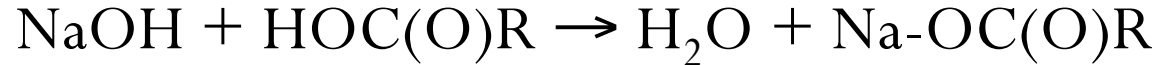
- High heat increases the rate of this reaction.
- It is particularly prevalent in deep fryers, and is the primary reason used cooking oil contains free fatty acids.
- It can also happen during biodiesel processing. The presence of a base catalyst facilitates this reaction in a similar way as it facilitates transesterification.

Soap Formation

- Soaps are salts of alkali metals and fatty acids.
- They possess both polar and nonpolar characteristics, and facilitate mixing between these types of substances.
- In biodiesel production, this means emulsification.

Soap Formation

- In the presence of free fatty acids, the reaction is straightforward

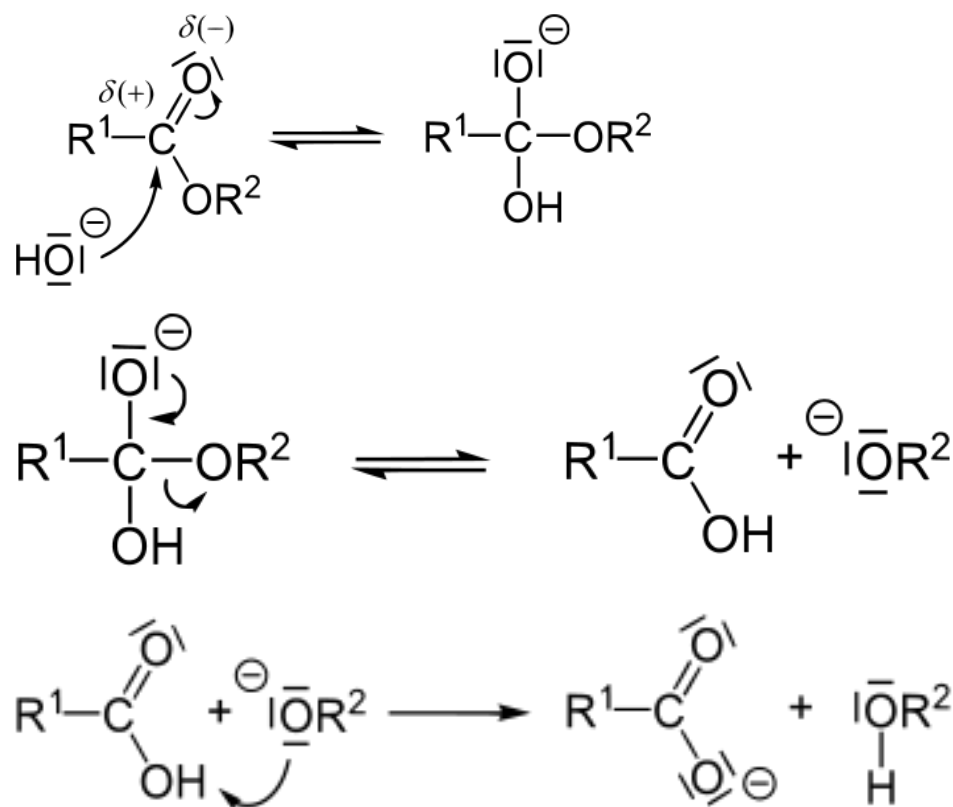


- Note:
 - Sodium (Na^+) is exchanged for a proton (H^+) in the free fatty acid, which then attaches to the hydroxyl (OH^-) left over to make water(!)
 - It can also bond with a methoxide (CH_3O^-) to make methanol. This is how free fatty acids “neutralize” the catalyst in biodiesel production.

Saponification

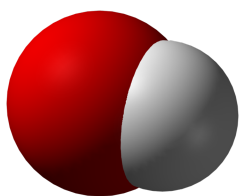
1. Hydroxyl anion attacks carbonyl group of the ester to form an orthoester.
2. Orthoester splits into a carboxylic acid and alkoxide.
3. Alkoxide is more basic than the conjugate base of carboxylic acid, so a proton is exchanged to form an alcohol.

Note: Recall that a carboxylic acid can associate with the alkali metal from the catalyst and make soap.

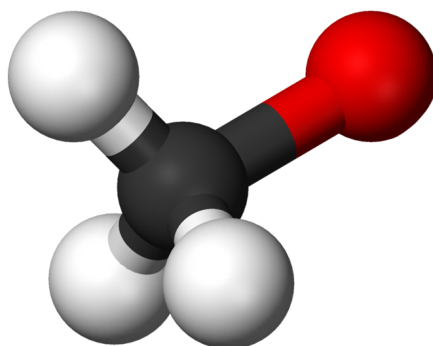


Saponification vs. Transesterification

- Saponification: hydroxide (OH^-) attacks the carbonyl group of the ester, resulting in a carboxylic acid and an alcohol.



- Transesterification: methoxide (CH_3O^-) attacks the carbonyl group of the ester resulting in a different ester and an alcohol.

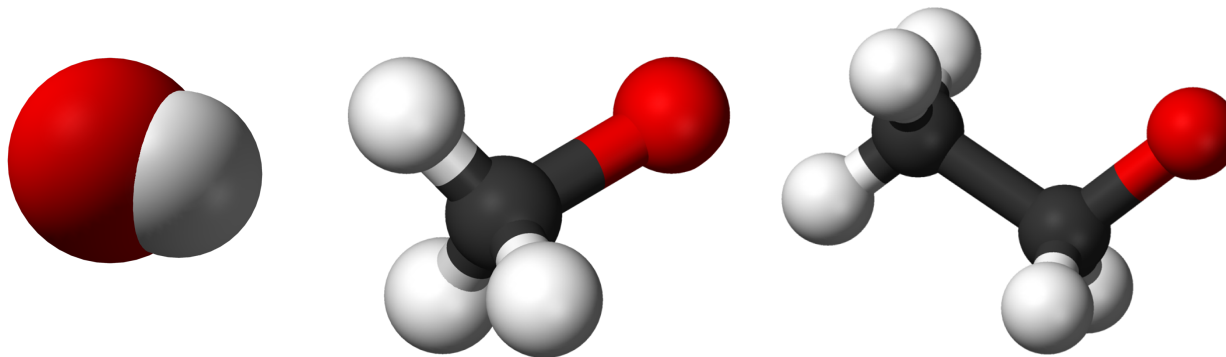


It's all about equilibrium...sort of

- Transesterification and saponification are reversible, so both are driven by equilibrium.
- Both hydroxide and methoxide will be formed with the addition of catalysts NaOH or KOH.
 - Hydroxide > Saponification
 - Methoxide > Transesterification
- Methyl ester does not does not take up the alkali metals to form soap.
 - Hydroxide > FFA > Soap
 - Methoxide > Methyl Ester

It's also about competition

- Hydroxide is smaller and easily outcompetes methoxide in attacking the carbonyl groups of the esters.
 - A very small amount of water ($>1\%$) can lead to excessive soap formation.
 - Ethoxide is even less competitive than methoxide, making biodiesel production from ethanol even more sensitive to water content.



Water, water, everywhere

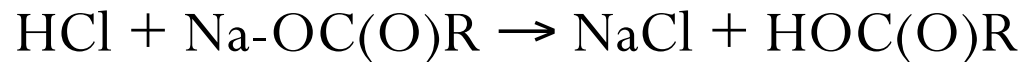
- Used fryer oil can contain a lot of water due to food, which then hydrolyzes the oil to make FFAs
- Adding more catalyst to neutralize the FFAs creates more water.

A few notes on post-processing

- Glycerol is very dense and quite polar, and tends to carry catalyst, excess methanol, water, and soaps with it during the separation process.
- A little bit of all of these remain in the biodiesel, especially if there is a lot of soap.
- Water washing can be used to remove them, but can be problematic due to emulsion formation.

Water washing

- Soap makes it more difficult to water wash without emulsification.
- Softened water helps, as can the addition of a strong acid
 - Soap is just a salt, so if you create a different salt it can release the FFA.



- Note that this will leave FFAs behind in the fuel.

Summary

- Understanding the chemistry behind biodiesel production can add insight into how to make a better fuel.
- There is no substitute for high quality, low water, low FFA oil.