# Oil and Biodiesel Chemistry Primer

Before you embark on your backyard biodiesel journey, a basic understanding of the chemistry of fats, oils and biodiesel can be helpful. The chemistry behind fats and oils is fairly straightforward, and fortunately biodiesel chemistry is closely related.

Molecular Structure of Fats and Oils

Fats and oils are a type of material broadly defined as lipids. A lipid is any fat-soluble molecule, that is, one that will dissolve in fat. Lipids include not only animal fats and vegetable oils, but also molecules like vitamin E (tocopherol), sterols (like cholesterol), waxes (long-chain fatty acids) and gums (phosphatides).

Typically "fats" are solid at room temperature and "oils" are liquid. "Fat" is often the term used for lipids rendered from animal products, and "oils" is used for the lipids produced from vegetable products.

All fats and oils primarily consist of a molecule called a **triglyceride**, the combination of a glycerol (aka glycerin) molecule and three **fatty acid** chains. It looks like this:
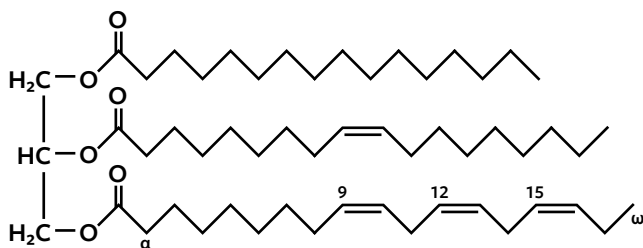
The glycerin "backbone" is to the left in this diagram, with three fatty acid chains attached off to the right. The type of fatty acid is determined by the chain length as well as the number of double bonds (aka saturation level) in the chain. In this diagram, the top chain has 16 carbon atoms with no double bonds, the middle chain has 18 carbons with 1 double bond, and the bottom one has 18 carbons with 3 double bonds. They are (in the same order) palmitic acid, oleic acid and linolenic acid. These acids can also be described numerically, with their carbon chain length and saturation level like this—16:0 (palmitic), 18:1 (oleic) and 18:3 (linolenic).

Fatty acids' molecular structure can also be expressed graphically like this:
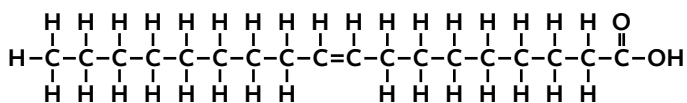
This is oleic acid again, the most common fatty acid in fats and oils. Note the single double bond in the middle of the chain, reducing the number of potential hydrogen atoms by two. Due to the presence of a single double bond, it is monounsaturated.

The saturation level of the fatty acid also affects the properties of the biodiesel produced from it. A fatty acid is considered saturated when there are no double bonds between

carbon atoms, and therefore it can hold no more hydrogen atoms. Fatty acids with one double bond are monounsaturated and those with more than one double bond are polyunsaturated. The more saturated the fat, the higher the temperature at which the fuel will gel. And the more saturated the fat, the better the oxidative stability.

Used fryer oil is typically a mix of vegetable oils—soybean, palm, canola, etc.—and usually doesn't contain too many saturated triglycerides. It's always a good idea to ask the restaurant whose grease you are collecting to show you the box that the oil came in so you know what you're dealing with.

Reactions Involving Triglycerides

Triglycerides commonly undergo a number of reactions. Understanding the nature of these reactions can help you learn to make better fuel easier. It may be a bit confusing at first, but stick with it and your increased knowledge will pay off.

Hydrolysis of fats or oils readily occurs when water is present. This reaction causes one (or more) of the fatty acids to detach from the triglyceride. The products of this reaction are one glycerin molecule and three free fatty acid molecules. If two fatty acids remain attached to the glycerin backbone, a **diglyceride** is the result. Only one fatty acid chain bound to the glycerin backbone is known as a **monoglyceride**. Hydrolysis of oil is the major contributor to the degradation of used cooking oil through the formation of free fatty acids. Water is to be avoided whenever possible.

Oxidation of fats and oils is degradation resulting from the presence of oxygen. At room temperature, this is a slow reaction compared to hydrolysis, but at frying temperatures, oxidation speeds up. Auto-oxidation occurs at ambient (room) temperature and is responsible for oil turning rancid, resulting

in off smells and flavors. Exposure to light increases the rate of oxidation, so keeping your oil out of direct light will reduce its degradation.

Polymerization of fats and oils occurs when fatty acid chains are broken off the triglyceride and then recombine with other free fatty acids (**FFA**) to form longer fatty acid chains or when triglyceride molecules combine to form large molecules. Polymerization increases the thickness (viscosity) of the oil and is responsible for the unremovable "goo" that coats the outside of oil collection containers. Polymerization occurs fairly slowly, and as such, doesn't come into play much in backyard biodiesel production. If you can keep hydrolysis and oxidation at bay, polymerization won't be a problem.

Now let's turn our attention to the biodiesel side of the equation. The good news is that the reactions that degrade oil are the same ones that will ruin your biodiesel, and the way to avoid them is the same too.

Molecular Structure of Biodiesel

Biodiesel is known chemically as a methyl ester. An ester is the result of a reaction between an alcohol and an acid. Biodiesel is formed from a reaction between methanol (an alcohol) and a free fatty acid. Its molecular structure looks like this:

$$
\begin{array}{c}
\text{H–C–C–C–C–C–C–C–C–C=C–C–C–C–C–C–C–C–C–O–C–H}
\end{array}
$$
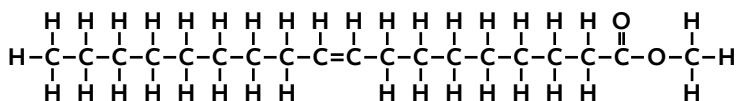
Note how similar this structure is to oleic acid. The OH group on the end has been replaced by a CH3 (methyl) group.

The type of fatty acid that comprises the fuel dictates the physical properties of the fuel produced. The more saturated

the fatty acid, the higher the gel point of the fuel, but the more shelf stable it is—just like with the original oil.

Reactions Involving Biodiesel

Remember that the same reactions that make your oil go bad will make your biodiesel go bad as well.

Hydrolysis, oxidation and polymerization can all occur in improperly made or stored methyl esters by the same mechanisms involved with your feedstock.

In addition to those reactions, a few more come into play during different phases of biodiesel production that you should be aware of and get to know.

Transesterification is the primary reaction we use to make biodiesel. It is the creation of three molecules of methyl ester from the reaction of one triglyceride molecule and three methanol molecules in the presence of a catalyst. A catalyst is a material that increases the rate of a reaction without being changed or consumed. In our backyard fuel making, we'll use potassium hydroxide (KOH) or sodium hydroxide (NaOH) as our catalyst for the transesterification reaction. Three molecules of methanol are required for each triglyceride in order to produce the three molecules of biodiesel by attaching one methyl group to the end of each of the three fatty acid chains present. The transesterification reaction looks like this:

$$(1)\,\text{triglyceride} + (3)\,\text{methanol} \underset{}{\overset{\text{catalyst}}{\rightleftarrows}} (3)\,\text{methyl ester} + (1)\,\text{glycerol}$$
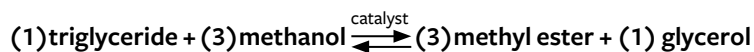
Note that the arrows point both ways, indicating that this reaction is capable of going both ways. We'll discuss this more a bit later in the Recipes section.

It is called transesterification because one ester, a triglyceride made of the alcohol glycerol and three free fatty acids, is

converted (transformed) to a different ester—biodiesel, a methyl ester comprised of the alcohol methanol and one free fatty acid chain.
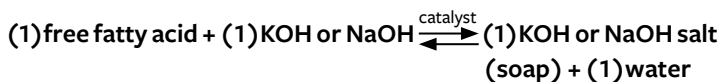
Esterification is the reaction where a free fatty acid is converted to biodiesel. It typically uses sulfuric acid as the catalyst rather than a base like KOH. In the esterification reaction, a methyl group is bonded onto the FFA, and a molecule of water is formed as a by-product. The esterification reaction looks like this:

$$(1)\,\text{free fatty acid} + (1)\,\text{methanol} \underset{}{\overset{\text{catalyst}}{\rightleftharpoons}} (1)\,\text{methyl ester} + (1)\,\text{water}$$
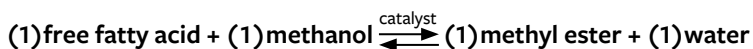
Esterification is a useful advanced technique for getting better yield from poor-quality oil, as we shall see.

We use the term **conversion** to describe the extent to which our feedstock has been turned into biodiesel, and not left as a mono-, di- or triglyceride, an FFA or turned into a soap.

Saponification is the "soap-making" reaction that biodiesel producers want to minimize, as it leads to reduced yields. It occurs when a free fatty acid meets a base catalyst and the metal (potassium or sodium) is bonded to the end of the FFA, creating a salt of the fatty acid. A salt is the product of an acid-base reaction, and in this case, we have combined a fatty acid with the base KOH or NaOH. When the salt contains a fatty acid, we call it a soap. The saponification reaction looks like this:

$$(1)\,\text{free fatty acid} + (1)\,\text{KOH or NaOH} \underset{}{\overset{\text{catalyst}}{\rightleftharpoons}} (1)\,\text{KOH or NaOH salt (soap)} + (1)\,\text{water}$$

Note that additional water is a by-product of the saponification reaction. Water contributes to the hydrolysis reaction that degrades oil or fuel. Also note that the saponification reaction proceeds much faster than transesterification; therefore,

any FFA in your feedstock will be turned into soap (and water) not biodiesel.

Soap is an **emulsifier**. An emulsifier is a molecule that is able to bond to both polar and non-polar compounds—like water (polar) and biodiesel (non-polar). This is why soap is able to get grease off your hands when washing with water. The polar water and the non-polar grease have no ability to bond until the emulsifying soap is used. The soap binds to the oil and the water, and they all go down the drain together. Emulsions are to be avoided when making biodiesel.

Polarity of molecules is a continuum, not an either-or. Materials are said to be relatively polar or relatively non-polar. A basic understanding of the polar nature of common biodiesel production materials follows.

Relatively polar materials used or created in biodiesel production include water, methanol, glycerin, base catalysts and salts (soaps).

Relatively non-polar materials used or created in biodiesel production include fats and oil, and biodiesel.

This means that when we produce our transesterification reaction, and the two liquid "phases" separate, the relatively less dense non-polar phase on top will contain the biodiesel, any unreacted oil and small amounts of glycerin, methanol, water, catalyst and soap. The heavier polar phase will contain glycerin, methanol, base catalyst, soaps, water and small amounts of biodiesel and unreacted oil.

The fact that the "contaminants" of biodiesel glycerin, water, methanol and soaps are all relatively polar accounts for the efficacy of water washing our fuel to remove them. The basic chemistry concept of "Like dissolves like" works to our advantage.

Reaction Kinetics

Reaction kinetics describe the rate with which a chemical reaction occurs and the factors that affect the rate. In the transesterification reaction, three factors that greatly affect the rate of the reaction are:

TIME — TEMPERATURE — TURBULENCE

The more you increase one factor (to a point), the more you can decrease the other two and still push the reaction forward. Since non-polar oil and polar methanol and caustic don't want to readily mix, increasing the turbulence of mixing will help ensure that methanol is available at the point when the triglyceride is being deconstructed by the catalyst. It is also for this reason that we typically use twice the amount of methanol required to "push" the reaction in the direction we want it to go, as well as to reduce soap production. Dependent on how turbulent your mixing is, you can reduce the mixing time and still get complete conversion of triglycerides into methyl esters.

The higher the temperature of your reaction, the faster it will proceed as well. Keep in mind that the boiling point of methanol (at sea level) is 148.5°F (64.7°C). This means that if your reaction gets hotter than that, you risk boiling off some of your methanol, thereby wasting it and creating additional fumes. Additionally, the transesterification reaction is slightly exothermic (generates its own heat), and so keeping your feedstock at about 131°–140°F (55°–60°C) is ideal as you begin your reaction.

Typical reaction times are 90 minutes or more, depending on what type of mixing your reactor uses.

Now that you've been armed with some basic organic chemistry, let's get on to the business of preparing our materials to make some fuel.