

THE PROCESS OF TRANSESTERIFICATION



Clean
POWER 

The logo for Clean Power features a stylized flame or arrow shape pointing upwards and to the right. The shape is composed of three curved segments in blue, yellow, and green, with a red arrowhead at the top.

DEFINITION

Transesterification is the process of reacting a triglyceride molecule (oil extracted from seed) with an excess of alcohol in the presence of a catalyst to produce glycerol and fatty esters. It reduces the high viscosity of triglyceride oils. In this process, the long fatty acid chains are removed from the glyceride molecule by reacting with alcohol and a catalyst. Common catalysts are potassium hydroxide KOH, sodium hydroxide NaOH, and sodium methoxide NaOCH₃. The reaction produces fatty monoesters and free glycerin. Any remaining unreacted monoglycerides, diglycerides, or triglycerides make up the bonded portion of the remaining glycerol in the fuel. Together, the free and bonded glycerol make up the total glycerol percentage remaining. This total glycerol percentage is used to determine the completion of the reaction.

- **TRIGLYCERIDES**

Molecules having three fatty acid chains are referred to as triglycerides.

- **DIGLYCERIDES**

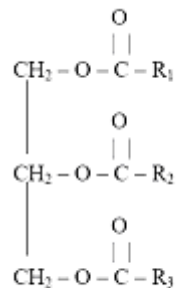
Those molecules which have two fatty acid chains are called diglycerides.

- **MONOGLYCERIDES**

Molecules with one fatty acid chain are called monoglycerides.

- **METHYL ESTERS**

The monoesters commonly known as Bio-diesel are usually produced through the transesterification of vegetable oils or animal fats. Both oils and fats are triglycerides or fatty esters of glycerin. Fat usually refers to the triglycerides which are solid at room temperature while oils are liquid at room temperature. The triglyceride molecule has the chemical structure shown in figure given below, where R₁, R₂, and R₃ represent long chain fatty acids.



Triglyceride Chemical Structure.

Figure I: Chemical structure of the triglyceride molecule

The final product after reaction with methanol is methyl esters. Other alcohols may be used, such as ethanol or butanol, resulting in ethyl esters and butyl esters, accordingly.

CHEMICAL REACTION

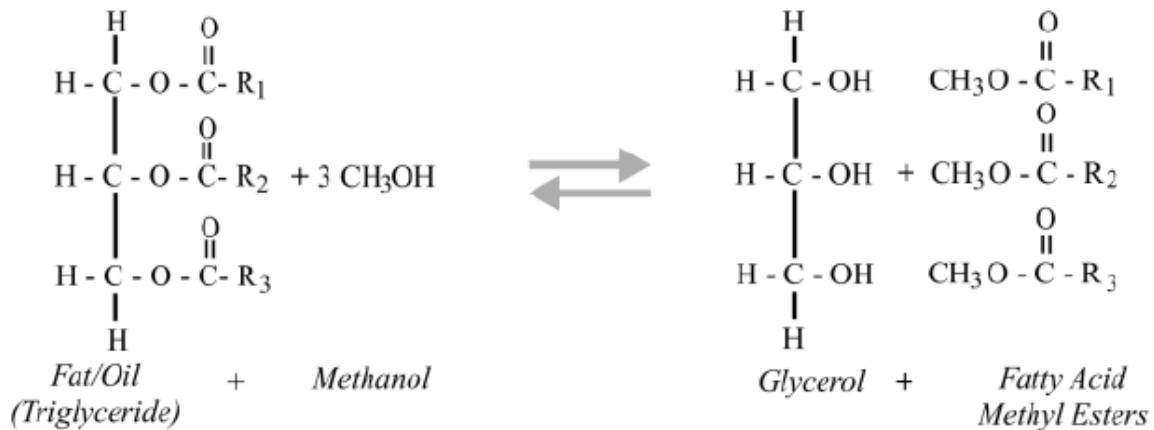


Figure II: Chemical Reaction of Bio-Diesel Production

PRODUCTION PROCESS

Bio-diesel can be produced from Straight Vegetable Oil (SVO), animal oil / fats, tallow and Waste Vegetable Oils (WVO). For this purpose base catalyzed transesterification of the oil is performed.

1. INGREDIENTS REQUIRED

(a) For Mixture

- (i) Vegetable oil used cooking oil, fryer grease, animal fats, lard, plants oil
- (ii) Methanol (CH₃OH) 99% + pure
- (iii) Sodium hydroxide (NaOH, also known as caustic soda or lye) must be dry

(b) For Titration

- (i) Isopropyl alcohol (rubbing alcohol) 99%+ pure
- (ii) Distilled water
- (iii) Phenolphthalein solution (not more than a year old, kept protected from strong light).

(c) For Washing

- (i) Vinegar
- (ii) Water

2. FILTRATION AND PRE HEATING

Filtration is carried out to remove unnecessary particles or contaminations present in the oil. Filtration of oil is carried out through an oil filter or by using cotton cloth placed on a funnel; oil is poured through this cloth into a beaker. Heat the oil after filtration up to 120°C to remove water contents present in the oil. After heating, the oil is allowed to cool down to 60°C.



Figure III: Filtration

3. MIXING OF ALCOHOL AND CATALYST

The catalyst (KOH, NaOH or NaOCH₃) is dissolved in alcohol (methanol) using a standard agitator or mixer producing Sodium Methoxide. The agitation time is almost 01 hour. Generally the amount of methanol needed is 20% of the oil by mass. The densities of these two liquids are fairly close, so measuring 20% of methanol by volume should be just about right.

CAUTION

Do not inhale any vapors. If any sodium methoxide gets splashed on your skin (it causes burning without feeling it because it kills the nerves), wash immediately with lots of water. Always have a hose running when working with sodium methoxide. Sodium methoxide is also very corrosive to paints.

4. REACTION

The alcohol / catalyst mix is charged into a closed reaction vessel and the oil or fat is added. The system from this point onwards should preferably be closed to the atmosphere to prevent loss of alcohol. The reaction mix is kept just above the boiling point of the alcohol (around 160°F) to speed up the reaction. Recommended reaction time is about 01 hour. Excess alcohol is normally used to ensure total conversion of the fat or oil to its esters. Care must be taken to monitor the amount of water and free fatty acids in the incoming oil or fat. If the free fatty acid level or water level is too high it may cause problems with soap formation and the separation of the glycerin by-product downstream.

5. SETTLING & SEPARATION

The solution is allowed to stay and cool for at least 08 hours. The methyl esters Bio-diesel floats on top while the denser glycerin congeals on the bottom of the container forming a hard gelatinous mass.



Figure IV: Glycerin Settled Down

An alternative method is to allow the reactants to sit for at least 01 hour after mixing while keeping the brew above 100°F (38°C), which keeps the glycerin semi-liquid (it solidifies below 100°F). Then the Bio-diesel is carefully decanted.

This can be done by draining the reactants out of the bottom of the container through a transparent hose. The semi-liquid glycerin has a dark brown color; the Bio-diesel is honey-colored. There has to be a close watch on what flows through the sight tube. When the lighter-colored Bio-diesel appears, it is diverted to a separate container. If any Bio-diesel stays with the glycerin, it is easy to retrieve it later once the glycerin has solidified.

In case mixture is left in the tank until the glycerin gells, reheating is required to liquefy the glycerin again. It is then decanted out as above without stirring.

Once the reaction is complete, two major products exist: glycerin and Bio-diesel. Each has a substantial amount of the excess methanol that was used in the reaction. The reacted mixture is sometimes neutralized at this step if needed. The glycerin phase is much denser than Bio-diesel phase and the two can be gravity-separated with glycerin simply drawn off the bottom of the settling vessel. In some cases, a centrifuge can be used to separate the two materials faster.

6. ALCOHOL REMOVAL

Once the glycerin and Bio-diesel phases have been separated, the excess alcohol in each phase is removed with a flash evaporation process or by distillation. In others systems, the alcohol is removed and the mixture neutralized before the glycerin and esters have been separated. In either case, the alcohol is recovered using distillation equipment and is re-used. Care must be taken to ensure no water accumulates in the recovered alcohol stream.

7. GLYCERIN NEUTRALIZATION

The glycerin by-product contains unused catalyst and soaps that are neutralized with an acid and sent to storage as crude glycerin. In some cases, the salt formed during this phase is recovered for use as a fertilizer. In most cases the salt is left in the glycerin. Water and alcohol are removed to produce 80-88% pure glycerin that is ready to be sold as crude glycerin. In more sophisticated operations, the glycerin is distilled to 99% or higher purity and sold to the cosmetic and pharmaceutical markets.

8. WASHING & DRYING

Once separated from the glycerine, the Bio-diesel is sometimes purified by washing gently with warm water to remove residual catalyst or soaps, dried, and sent to storage. This is normally the end of the production process resulting in a clear amber-yellow liquid with a viscosity similar to that of petro-diesel. In some systems the Bio-diesel is distilled in an additional step to remove small amounts of colored bodies to produce a colorless Bio-diesel. Washing is typically repeated thrice for best quality. Each time, water of equal volume to that of Bio-diesel, and vinegar in minute quantity is added and left for 2-3 hours. Water, due to its higher density, settles down at the bottom and recovered. Thus the Bio-diesel is separated after washing as shown in the figure given below.



Figure V: Pure Bio-diesel after Washing

PRODUCT QUALITY

Prior to use as a commercial fuel, the finished Bio-diesel must be analyzed using sophisticated analytical equipment to ensure it meets the required specifications. The most important aspects of Bio-diesel production to ensure trouble free operation in diesel engines are:

- Complete Reaction
- Removal of Glycerin
- Removal of Catalyst
- Removal of Alcohol
- Absence of Free Fatty Acids

TITRATION

To determine the correct amount of lye (NaOH) required, a titration is advised on the oil being transesterified.

In cold weather the oil might congeal. Therefore, titration may be required to be carried out in a heated room.

1. PROCEDURE

A solution of 01 gram of lye to 01 liter of distilled water is prepared, ensuring that the lye dissolves completely. This sample is then used as a reference tester for the titration process. It is important not to let the sample get contaminated; it can be used for many titrations. 10 milliliters of isopropyl alcohol is mixed, in a small container, with a 1 milliliter sample of oil. The oil titration sample is taken from the reaction vessel after it has been warmed up and stirred. To this solution, 2 drops of phenolphthalein are added; phenolphthalein is an acid-base indicator that is colorless in acid and red in base.

Using a graduated eye dropper (with increments marked in tenths of milliliters) or some other calibrated instrument (from medical supply outlets), while carefully keeping track of the amounts, measured amounts (a couple of tenths of milliliters at a time) of the lye/water solution are dropped into the oil/isopropyl/phenolphthalein solution. Vigorous stirring of the solution is required after every drop. If conditions are right, eventually the solution turns pink (magenta) and stays pink for 10 seconds. This is the indicator color for a pH range of 8-9. It is important to find the exact amount to reach this pH without dropping in too much.

It is advisable to conduct this entire process more than once to ensure that the pH number is correct. Depending upon the type of the oil, what was cooked in it and how long it was used, the amount of lye/water solution needed to titrate it is usually 1.5 to 3 milliliters. Litmus paper or a digital pH tester instead of the phenolphthalein can also be used.

NOTES

- 1- The lye (NaOH or KOH) must be dry keep it away from water, store it in an airtight container.
- 2- Phenolphthalein has a shelf life of about a year; it is very sensitive to degradation by light so after a while it will start giving erroneous readings.

2. THE CALCULATION

The next step is to determine the amount of lye needed for the reaction. The number of milliliters derived from the titration is multiplied with the number of liters of vegetable oil to be transesterified.

Every liter of neat vegetable oil (fresh; never been burned) needs 3.5 grams of lye for the reaction. Hence for every liter of vegetable oil to be transesterified, an additional 3.5 grams of lye must be added. If the titration result was 1.8 milliliters to reach pH 8-9, the final amount of lye needed for the reaction would be 795 grams. The number of grams of lye needed per liter of vegetable oil is generally between 6 and 7.

BY PRODUCTS OF BIO-DIESEL PRODUCTION PROCESS

There are two by-products of the transesterification process: Glycerine and Soap.

1. GLYCERIN



Figure VI: Glycerine

The glycerin from used vegetable oil is brown and usually turns to a solid below about 100°F (38°C). Glycerin from fresh oil often stays a liquid at lower temperatures.

Reclaimed glycerine can be composted after being vented for 03 weeks to allow residual methanol to evaporate off or after heating it to 150°F (66°C) to boil off any methanol content (the boiling point of methanol is 148.5°F, 64.7°C). The excess methanol can be recovered for re-use when boiled off by running the vapors through a condenser.

Another way of disposing of the glycerine, though more complicated, would be to separate its components, mostly methanol, pure glycerine (a valuable product for medicines, tinctures, hand lotions, and many other uses) and wax. This is often accomplished by distilling it, but glycerin has a high boiling point even under high vacuum so this method is difficult.

The glycerine by-product makes an excellent industrial-type degreaser/soap. One way to purify it is to heat it up to 150°F (65.5°C) to boil off excess methanol, making it safe for skin contact (while taking precautions with fumes). Once the glycerin is back to a liquid form the impurities sink to the bottom and the color will become a more uniform dark brown. This can be cut with water leaving it a tan color, less concentrated, and softer and easier to handle when washing hands. Produced this way the degreaser could be sold in squeeze or pump dispensers.

Other ideas for disposing of the glycerine are breaking it down to usable methane gas, with a methane digester or, for a much wilder idea; it could be broken down with pyrolysis (Pyrolysis was used extensively to run cars on firewood in oil-scarce Europe and elsewhere during World War 2). The processor has a heat source that heats the fuel

(wood or glycerine) in an airtight box without oxygen. This allows the fuel to release its methane while not allowing it to burn. The methane is trapped in an inflatable storage container or compressed into a tank. This is an area of Bio-diesel development that warrants further work.

2. SOAP RESIDUE



Figure VII: Soap

Suspended in the Bio-diesel will also be some soapy residues. These are the result of Na^+ ions from the sodium hydroxide (NaOH) reacting with water created when the methanol bonds with the ester chains along with any other water that was suspended in the oil.

If the reaction produces more than the usual amount of soap, this happens when lye comes into contact with water before it has a chance to react with the oil. In this case, the excess water should have been boiled off first.

The part of the process where it is vital to keep all water out of the reaction is when making the sodium methoxide. The blender and all utensils the lye comes in contact with must be kept as dry as possible. The chances of a good clean splitting of esters from glycerine with little soap by-product are much better on a warm dry summer day than on a damp winter day.