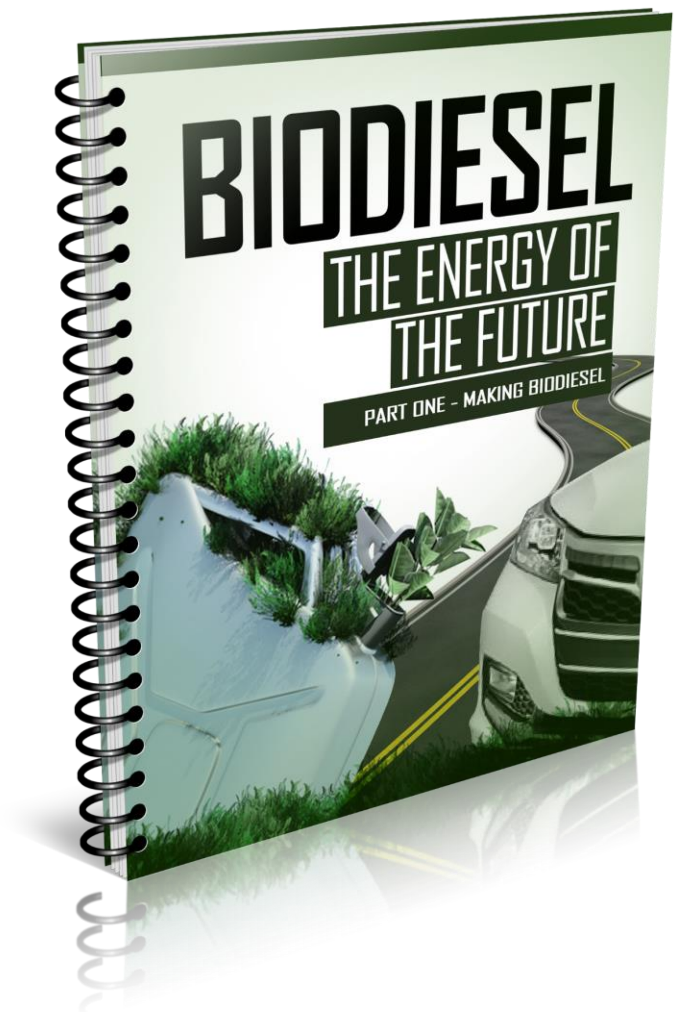
BIODIESEL – THE ENERGY OF THE FUTURE – MAKING BIODIESEL



Why Biodiesel?

What is biodiesel? Simply put, it is diesel fuel that is made from vegetable oil. It will run in any unmodified diesel engine. It has many advantages over petroleum diesel fuel such as:

1) It burns cleaner
2) It has a higher cetane rating (less knocking)
3) It has better lubricity
4) You can make it yourself from used vegetable oil (a waste product) often for less than the cost of petroleum diesel.

The energy yield of biodiesel is tremendous. Biodiesel can actually return more than three times the amount of energy required to produce it. That leaves petroleum and other biofuels in the dust, some of which require more energy to make them than can be gained by burning them.

Do you need any more reasons to make biodiesel TODAY?
Then go ahead! We are providing all the information necessary for this process, so read on and start your project.

Some general things to know

Biodiesel is a liquid fuel produced from vegetable oils and animal fats. The properties of biodiesel are virtually the same as for diesel fuel in terms of density and cetane number.1 It does, however, present a higher flashpoint and can be used in blends with fossil diesel, and individually if engines are suitably adapted. Thus,

biodiesel is an alternative to diesel for both the automotive and industrial sector.
With respect to its nomenclature, the letter B is typically used followed by the percentage of mixture (so, for pure biodiesel it is B100, and B20 for a diesel with a 20% addition of biodiesel).

At first, the term biodiesel is used as a generic name that brings together various products used as an alternative to diesel fuel in diesel engines: vegetable oils, mixtures of diesel and vegetable oils, ethyl or methyl esters of oils and/or vegetable or animal fats and its blends with diesel, and so on.

The definition of biodiesel specifications proposed by the ASTM (American Society for Testing and Materials Standard) describes it as mono alkyl esters from long chain fatty acids derived from renewable lipids such as vegetable oils or animal fats, and used in compression spark ignition engines.

The conversion of oil to methyl or ethyl ester can be carried out by means of different processes, including transesterification, pyrolysis and emulsification. The process for ester formation from any oils or animal fats is transesterification, and esterification if it is based on fatty acids.

The methyl esters derived from vegetable oils have some physical characteristics and properties similar to diesel, which allows them to be mixed in any proportion and used in conventional diesel vehicles, without making major changes to the basic design of the engine. However, in proportions of more than 5% it is necessary to replace the material used in the fuel circuit by another more resistant one, as the solvent power of biodiesel can cause its deterioration.

Biodiesel as a renewable resource

Fuels derived from crops and other organic matter, called biofuels, have a number of advantages. Firstly, they can help to reduce the growth in CO_2 emissions, making it possible to fulfil Kyoto Protocol commitments. The CO_2 balance of biofuels is low (it is not zero as the energy consumed in the production process has to be taken into account). On the other hand, they reduce dependence on oil by diversifying and improving security in the supply of fuel. Also, these fuels can be alternative sources of income for rural areas.

The production of vegetable oils is possible from more than 300 different species.
Although crops like olive, coconut, etc. have the highest yields of oil, the complexity of their harvesting operations makes them less interesting than arable crops. In this case, the soil and climatic conditions, the agricultural yields, the oil content of seeds and the mechanization possibilities limit the species to a few profitable oilseeds.

The raw materials currently used for obtaining vegetable oils in biodiesel production are the seeds of conventional oleaginous plants. These are followed, in terms of volume, by palm and coconut oils, animal fats and used oils.

As biofuel production is based on vegetable products, the characteristics of agricultural markets should be taken into account.

At the same time, the energy market will exert a definitive influence on the viability of the product. In this sense, it is noteworthy that the biofuels industry depends not only on the local availability of raw material, but also on the existence of sufficient demand.

The development of the biofuel market can help to promote other agriculture policies, fostering job creation in the primary sector, establishing population in rural areas, developing agricultural and industrial activities, and, at the same time, reducing the effects of desertification by planting energy crops.

Reactions in biodiesel production

The production of biodiesel is a well known chemical process. Although based on the free fatty acid content of raw material there can be different production processes.
Although the esterification process is possible, the method used commercially to obtain biodiesel is transesterification. This consists of the reaction, in the presence of a suitable catalyst, of the oil or fat with a low molecular weight alcohol, typically methanol or ethanol.

In this process, depending on the alcohol used, ethyl or methyl esters of fatty acids (biodiesel) are obtained, with glycerine as a subproduct.

Transesterification reactions of triglycerides

This is based on the reaction of triglyceride molecules, which are the primary component of vegetable oil or animal fat, with low

molecular weight alcohols (methanol, ethanol, propanol, butanol) to produce esters and glycerine.
Depending on the raw material, the basic process of biodiesel production can undergo differences:

• From conventional vegetable oils: the crude vegetable oil must undergo a refining process to remove free fatty acids, waxes and gums that can interfere with the process. This supplies the raw material that will power the transesterification unit.

• From frying oils: frying oils should be, first, degummed, dried and cleaned of impurities by centrifugation and filtration processes. This stage is critical to ensure the smooth operation of the post-process. Depending on the free acids, a pre-esterification with methanol is required (in the presence of an acid, usually sulfuric), which can improve the transesterification yield by reducing acidity and minimizing the formation of soaps.

From here on the processes are similar, although the stages of purification and decoloration of both biodiesel and glycerine tend to be more complex in the case of used oils, since, despite the pre-cleaning, there are always impurities left.

The process requires the preparation of the mixture of catalyst and alcohol (methanol in this case) before the reaction.

• The transesterification reaction is brought about by raising the temperature (typically to between 60–70◦ C). The analysis of the matter transfer in this process is of great importance due to the inmiscibility of triglycerides with methanol and to the inmiscibility of methyl esters with glycerine, so that there are phase separations through in the process.

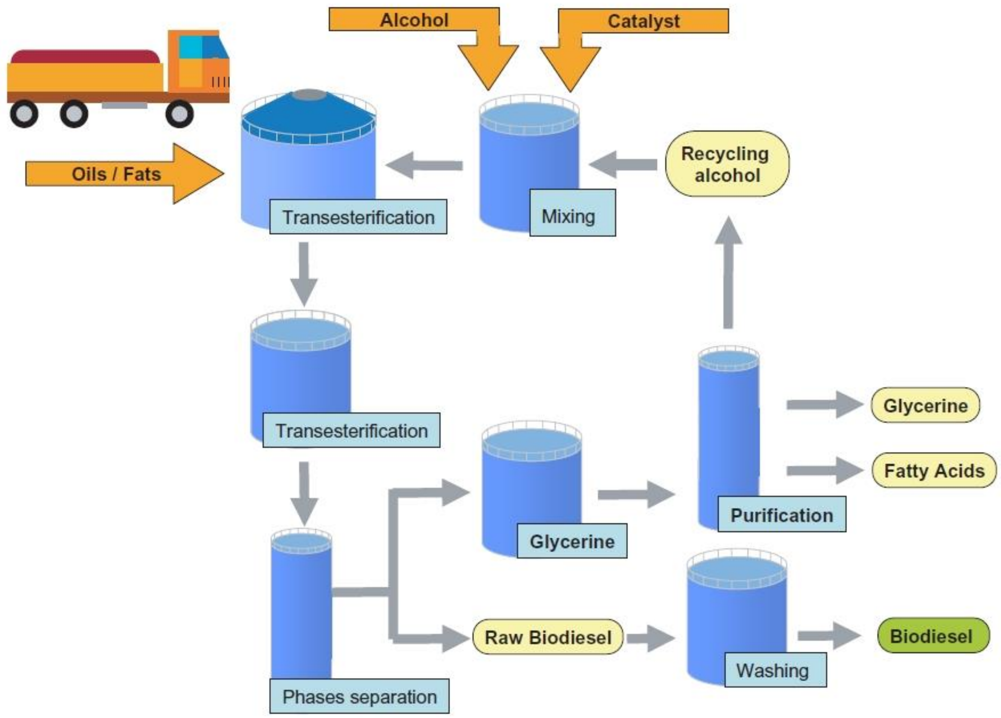
• In a first decantation, the crude biodiesel is separated from the glycerin. Crude biodiesel is subjected to a washing process to separate one part of the non-reacting alcohol and to remove impurities. Subsequent drying makes it possible to obtain biodiesel. Other operations of purification, such as discoloration, can be necessary to ensure compliance with marketing standards. The recovered methanol is reused in the process.

• The transesterification process produces as a subproduct about 10% glycerin. This crude glycerin contains impurities from crude oil, fractions of the catalyst, mono and diglycerides and traces of methanol. In order to sell it on the market it must be purified.

• The methanol recovered at this stage is reused in the process.

• In the glycerine purification fatty acids are separated. Those can be esterified once again to produce more biodiesel, or be used as raw material for soap production or for animal feed.

• The glycerine obtained after the washing process has technical quality. If, later on, it is distilled, the glycerine obtained is of pharmaceutical grade (99.8%). The glycerine can be channeled into traditional uses (cosmetics, pharmaceutical, food) or modern ones (animal feed, plastics industry, etc.).



Apart from the general scheme for diesel production, on the market there are different types of technologies that propose industrial processes with several variants: continuous or batch, with recovery of fatty acids or not, with recovery of the catalyst in the form of salts that can be reused as fertilizer; with previous esterification phases to minimize the free acidity of the oils, etc.

Plants between 500–10000 t/year usually work with batch systems in two stages.
The advantage of this type of process is its low investment cost and flexibility.
In contrast, they have trouble in achieving consistency in product quality and the process is not very reliable.

For over 10000 t/year, continuous reactors are normally used, which provide greater consistency, greater security and better design options for the reactor and subprocesses such as separation and glycerine purification.

In addition to this processing type, alternative optimization is being developed, such as the use of heterogeneous catalysts that facilitate the refining of the glycerine obtained or the use of enzymatic pathways for the production of biodiesel.

Variables affecting the transesterification reaction

Among the most important variables affecting the transesterification reaction are the following ones:

• *Fatty acids and moisture content*. The complete reaction requires a value of free fatty acids (FFA) of less than 3%. The higher the oil's acidity is, the lower the conversion is. Moreover, both catalytic excess and catalytic deficiency can cause the formation of soap,18 and in addition, as noted, the presence of moisture decreases the yield of the reaction, since water reacts with the catalyst to form soaps.

• *Type and concentration of catalyst*. The bases, in particular sodium and potassium hydroxides, are the most widely used, especially if the oil has a high degree of fatty acids and high moisture.

• Although the process of transesterification with alkaline catalysts has a very high conversion in a shorter period of time, it presents some drawbacks: the catalyst must be removed from the final product, recovery of glycerol may be hard, alkaline water resulting from the process should be treated, and, fatty acids andwater affect the reaction.

• Enzyme catalysts can obtain relevant results in both aqueous and non-aqueous systems. In this way, the glycerol can be separated easily, and the fatty acids contained in the reused oil can be completely converted into alkyl esters. However, the use of these catalysts has a higher cost than the alkaline ones.

Alcohol/oil molar ratio and alcohol type. The stoichiometric relation requires three moles of alcohol and one mole of triglyceride to produce three moles of esters and one mole of glycerol. Transesterification requires an excess of alcohol to drive the reaction to the right side. For maximum conversion a 6:1 molar ratio should be used. However, a high value of the alcohol molar ratio affects the separation of glycerine because of increased solubility.

When glycerine is retained in the solution, the reverse reaction goes to the left, lowering the ester yield.

• The formation of ethyl ester is more difficult than that of methyl ester. Ethanol and methanol do not dissolve with triglycerides at room temperature and the mixture should be agitated mechanically to allow mass transfer. During the reaction, an emulsion is usually formed, which quickly drops in the metanolysis forming a layer rich in glycerol, while another area rich in methyl ester stays on top.

In contrast, in the etanolysis this emulsion is not stable and the separation and purification of the ethyl esters is much more complicated.

• *Effect of reaction time and temperature*. Increasing these parameters increases the conversion.

The transesterification process

It is the most common process for producing biodiesel, and presents different variants. Many of these technologies can be combined in different ways by varying process conditions and feeding. The choice of technology should be made depending on the desired capacity of production, supply, quality and recovery of alcohol and catalyst.

The *batch process* is the simplest method for the production of biodiesel, and is used in the plants of lower capacity and different quality of feeding.

The alcohol/triglyceride ratio commonly used is 4 to 1. The most common catalyst is NaOH, although KOH is also used, ranging from 0.3% to 1.5% (depending on whether the catalyst used is KOH or NaOH). If acid catalysts are used, it is necessary to increase the temperatures and reaction times.

These reactors are sealed or fitted with a reflux condenser. To achieve a proper mixture of oil, catalyst and alcohol, a rapid agitation is required.

Towards the end of the reaction, and to allow the separation of glycerol from the ester phase, the agitation should be reduced. The reaction usually lasts between 20 minutes and 1 hour at temperatures around 65.C, although it can range between 25 and 85.C.

Results of between 85% and 94% are obtained. Higher temperatures and higher ratios of alcohol/oil can increase the yield of the reaction.
Some operating plants use two-step reactions, the glycerol being removed between them, which increase the final yield to greater percentages, as high as 95%.

The continuous process is the most suitable for large capacity plants, which require more staff since more uniform feeding is required. Continuous Stirred Tank Reactors (CSTR) are used and these can vary in volume to allow greater residence time and to improve the outcome of the reaction.

Thus, after the decantation of glycerol, the reaction in a second CSTR is much faster, with 98% of reaction product.

An essential element in the operation of the CSTR reactors is the assurance that the composition in the reactor is virtually constant, so the mix must be controlled at all times. This has a growing effect on glycerol dispersion in the ester phase, the result of which is that the time required for the separation of phases increases.

There are various processes to facilitate the esterification reaction using an intense mixture. They use tubular reactors, where the mix moves longitudinally, with little mixing in the axial direction. This Plug Flow Reactor (PFR), behaves like small CSTR reactors working one after the other.

The result is a continuous system that requires lower residence times, between 6 and 10 minutes, the reactors needed being smaller.

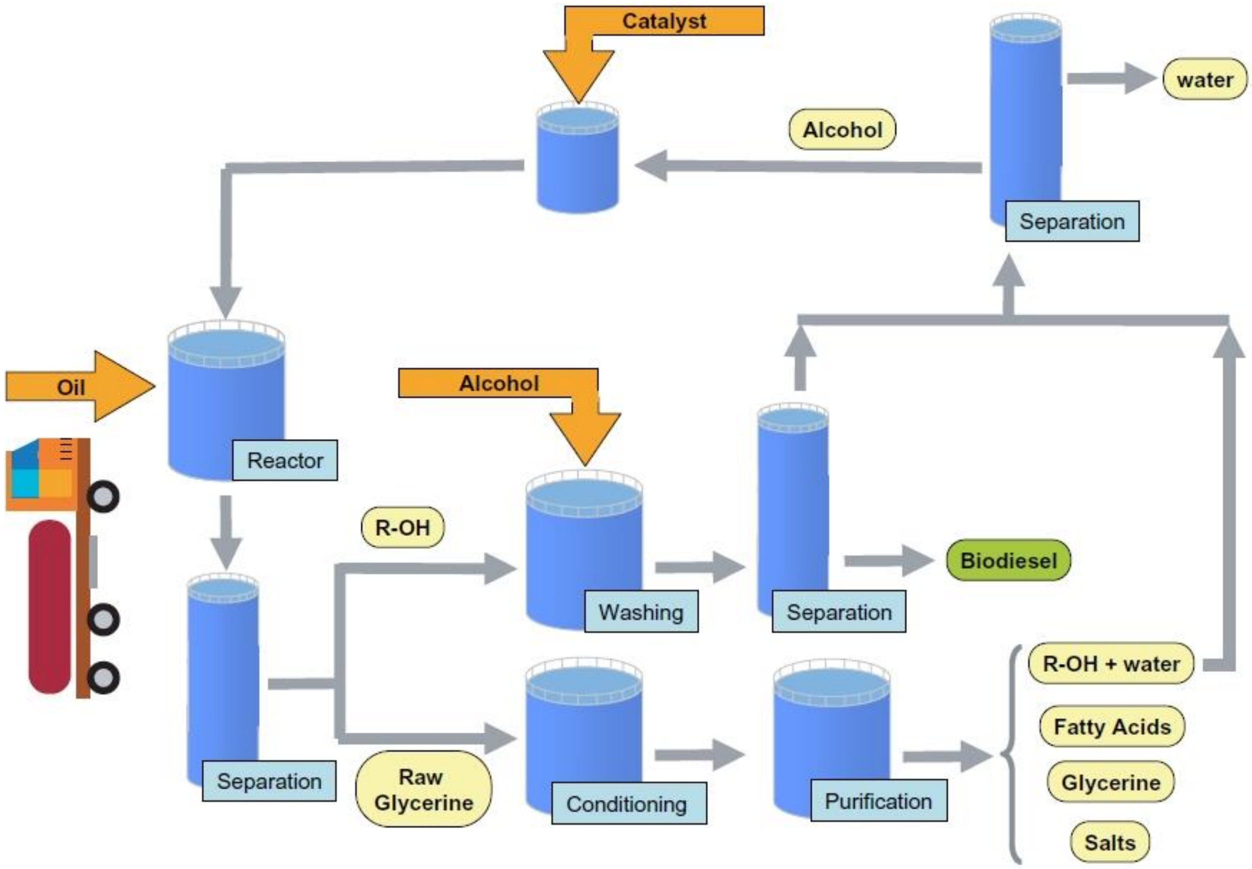
This type of reactor can operate at high temperature and pressure, which increases the conversion rate.

The most common Esterification Process involves heating a mixture of alcohol and acid catalyst, typically sulfuric acid, using the cheaper reagent in excess to increase performance and shift the balance towards the right.

The sulfuric acid, in addition to being a catalyst, serves as a hygroscopic substance which absorbs water formed in the reaction. Sometimes it is replaced by concentrated phosphoric acid.

The Combined Esterification-Transesterification Process refines fatty acids coming from the supply system or through a different treatment in the esterification unit. Caustic catalysts are added and the reaction product is separated by centrifugation (a process called Caustic Stripping).

Refined oils are dried and sent to the transesterification unit for subsequent processing. In this way, fatty acids can be transformed into methyl esters using an acid esterification process.



The processes of acid catalysis can be used for direct esterification of free fatty acids (FFA). An alternative would be to use a base catalyst to deliberately form soap in the FFA. The soap is recovered, the oil dried and subsequently used in a conventional system using base catalysts.

In the esterification-transesterification reaction, the fatty acids, subproducts of the reaction, can be used to later feed the esterification reactor.

How to make Biodiesel

You will need the following things to make your first batch:

1) At least 1 Litre (1.1 Quart) vegetable oil. Canola oil, corn oil, soybean oil, etc will suffice.

2) A variable speed blender with a slow speed option. Use one with a glass pitcher only. The methanol that is used in this process will "eat" a plastic pitcher. Make sure that this blender will never be used for food products again.

3) A scale that will accurately measure 3.5 grams (.12 oz). Search Ebay for "digital scale". A good one should cost about $20.

4) 1 bottle Red Devil Lye Drain Cleaner (Sodium Hydroxide) available from you local hardware store. Make sure the label says "contains sodium hydroxide".

Most other drain cleaners are chlorine (Calcium Hypochlorite) based and will NOT work! Notice: Lye is poisonous! Take all necessary safety precautions!!

5) At least 200 milliliters (6.8 fl. oz) of methanol (Methyl Alcohol or "Wood" Alcohol). Methanol is widely available in 12 oz. quantities as "gas tank antifreeze" in auto parts stores, hardware stores and even some grocery stores. Popular brands include "Heet" and "Pyroil".

Read the label carefully and make sure it says "contains methanol"! Many gas line antifreeze products contain isopropyl alcohol or "isopropanol" and will NOT work!

Methanol is available in larger quantities as racing fuel through some racetracks that cater to drag racers and some "high performance" auto parts stores. Keep in mind that Methanol is both poisonous and flammable. Take all necessary safety precautions!!

6) A glass container that is marked for 200 milliliters (6.8 fl. oz). We like to use a beaker.

7) A glass or plastic container that is marked for 1 liter (1.1 Quart)

8) A wide mouth glass or plastic container that will hold at least 1.5 litres

9) A common spoon (preferably plastic or stainless steel).

10) Safety Glasses and Rubber Gloves! Methanol and Lye are extremely poisonous and must not come into contact with skin or eyes!

Methanol is a poison that attacks the eyes (ocular nerves) even if it comes into contact with your hands. Use extreme care when blending the methanol and lye, as the blender can spash the chemicals around.

Put on your glasses and gloves BEFORE opening the chemicals! Do your work close to a sink or hose, or have a bucket of water handy to wash any part of your body immediately if it comes in contact with these chemicals.

Step 1: Get organized in a well lit, well ventilated area! This process is best done at or above room temperature (70 degrees F or 21 Degrees C). Temperatures lower than 60 F or 15 C may cause an incomplete reaction. Plan for spills by spreading paper or plastic on your work surface. Put your safety glasses and gloves on before opening any chemicals!

"Heet" is a popular brand of "gas line antifreeze" in the US. It is widely available in auto parts stores, hardware stores and even some grocery stores.
Make sure that the label says "Contains Methanol"

Step 2: Measure 200 milliliters (6.8 fl. oz) of methanol

Step 3: Pour the methanol into the blender. Notice the glass pitcher on the blender.

Step 4: Weigh out 3.5 grams of lye on your scale. Notice that we use a white piece of plastic to hold the lye. The weight of the plastic is 4 grams, so we set the scale to 7.5 grams.

Step 5: Turn the blender on "slow" speed and slowly add the lye to the methanol.

You now have a mixture called "sodium methoxide". The methoxide must be used right away to make biodiesel.

Do not plan on making a large batch of methoxide and storing it for use later. It loses its potency over time.

Step 6: After the Lye has completly dissolved into the methanol (about 2 minutes), add 1 liter of vegetable oil to the blender. Blend on low speed for 20 to 30 minutes.

The ideal speed for this process just barely creates a vortex or "tornado" in the oil without spashing the mixture around or frothing it up.

Step 7: After the blending is complete, pour the mixture into the wide mouth jar. It is advisable to label all containers used in this project as "POISON"! And of course, keep all of this stuff away from children!

Step 8: After about 30 minutes to 1 hour, you will notice a layer of darker colored glycerin settling to the bottom of the container. The lighter layer on top is biodiesel.

Wait another few hours for complete settling. At that point, you can carefully pour off the lighter biodiesel from the top and discard the glycerin (or save the glycerin to use in soapmaking).

An alternative would be to use a pump to remove the biodiesel from the jar. You are done!

Biodiesel has a solvent effect on natural rubber hoses and seals. While newer diesel engines have polymer hoses and seals (such as Dupont's "Viton" brand), older engines may need to be outfitted with new hoses and/or seals made of viton. Since most diesel injector pumps don't have rubber parts directly in contact with the fuel, it is usually easy to replace hoses and seals without any major dissasembly. A fuel mixture of 20% biodiesel and 80% petroleum diesel (called "B20") will have no effect on older natural rubber hoses.

Biodiesel will "cloud" at temperatures below 55 degrees F (13 degrees C). While this "clouding" is easily reversible by raising the temperature of the fuel again to above 55 degrees, it may cause temporary clogging of your fuel system, thus stopping your engine. Petroleum diesel fuel (Diesel #2) can be used down to -10 degrees F (-24 degrees C).

It is advisable to use a blend of at least 50% petroleum diesel with your biodiesel if you are going to be operating in cold weather. You can experiment with different blends of biodiesel and petroleum diesel to determine what works best. Simply mix up batches of fuel with different ratios of petroleum diesel and biodiesel in glass jars and put in a freezer.

Use a thermometer to determine the temperature of the fuel. Periodically check on the fuel to determine at what temperature it gets cloudy. This temperature is the "cloud point". It is best to determine this point at home before you head out on the road and get stranded in a snowstorm because your mixture is too rich in biodiesel. Of course, if you are going to be operating during the warm months, or in a warm climate, you can use 100% biodiesel with no problems.

The use of biodiesel

The idea of using vegetable oil as fuel has been around since the invention of the diesel engine. Rudolph Diesel experimented with a wide range of fuels (from coal to peanut oil). However, at the beginning of the 20th century, diesel engines were adapted to the use of petroleum distillate, inexpensive and available. The rising cost of petroleum experienced in recent decades and the support for renewable biofuels has revived interest in biodiesel.

The main use of biodiesel is in the automotive industry, although it is perfectly valid for use as a substitute for the diesel used in heating boilers. Moreover, biodiesel dissolves hydrocarbons, which make it useful to clean up oil spills (e.g., the Erika accident on the French coast).

The ways of using vegetable oils or methyl esters in diesel engines can be:

- Diesel engine adaptation for oils.
- Use of specific engines (Elsbett).
- Using mixtures of diesel and oil.
- Use of mixtures of diesel with methyl esters.
- Use of mixtures of diesel with alcohol.

None of the options: the diesel engine adjustment, the use of a mix of biodiesel with vegetable oil and the employ of the Elsbett engine have the level of implementation and development that the mixes comprised of diesel with esters (especially methyl) and with alcohol have, which appear as the most commercially viable.

Direct use of vegetable oils

The nature of vegetable oils poses a number of disadvantages that makes its direct use in engines unadvisable, as these require a preparation consisting of a previous degumming and filtration. The seeds are pressed to separate the oil from the cake, usually by subjecting the seeds to warm up and to the action of a solvent to achieve oil extraction yields close to 100%. The cake produced as a subproduct has a high protein content so it is possible to sell it on the cattle feeding market, which lowers the costs for the extraction process.

In order to use vegetable oils in direct injection engines it is necessary to use mixtures of vegetable oil with diesel. This allows the characteristics of the fuel to be maintained, by changing the ratio of the components. In any case, these mixtures of vegetable oil and diesel continue to be part of the various problems associated with vegetable oils, which are:

• Polysaturated fatty acids have a high reactivity which makes them very susceptible to polymerization and formation of gums.

• They do not burn completely, with carbonaceous deposits resulting from this.

• Thickening of the lubricating oil.

• High viscosity, making difficult to pump it, especially in cold weather.

• A low cetane number, which means poor combustion in fast engines.

• Dirty fuel injectors with a deteriorating performance of the engine. One solution to these problems would be the following modifications to the diesel engine:

• Preheating of the fuel.
• Injection in pre-chamber. Self-cleaning injectors.
• More adiabatic engines: an indented combustion chamber, requiring less cooling.

• An auxiliary diesel starting system.

It has been demonstrated that blends of up to 1/2 (biodiesel/diesel) can be used in unmodified diesel engines, for example in the case of soybean oil. Another alternative is to use blends made of raw vegetable oil, petrol (14%) and alcohol (5%), which can be used directly as fuel for diesel engines.

Using biodiesel

Although biodiesel can be used (in pure form or mixed in different proportions with conventional diesel) in diesel engines, the following functional differences should be considered:

• A higher cetane number than conventional diesel, so it has greater autoignition ability.

• As a result of the delay time in the combustion, higher temperatures and pressures are reached, so that the emissions of nitrogen oxides generally increase.

• It is slightly denser than conventional diesel, which should be taken into account when creating blends.

• The behavior at low temperature varies depending on the fatty acids profile of the oil, but, in general, biodiesel has a higher solidification point than conventional diesel. This implies that cold temperatures (below 10◦ C) can cause problems such as starting the engine, and sealing the filter and the feeding system.

• Biodiesel provides a solvent effect for sediment accumulated in a vehicle that uses diesel. Typically, the filter system should be capable of acting as a barrier, but in severe cases, this could lead to vehicles becoming immobilized. Depending on the condition of the car, and on the use of pure biodiesel or blending in high proportions, it may be advisable to clean the tank and the piping of the feeding system to prevent filter obstruction.

• Like conventional diesel, biodiesel can corrode certain materials such as brass, bronze, copper, lead, tin and zinc. Such materials are usually replaced by aluminum or stainless steel. Additionally, biodiesel can also affect joints, seals, hoses and pipes, particularly those manufactured in natural rubber or nitrile.

• Since it is impossible to control whether or not vehicles fueling at service stations have been prepared to use 100% biodiesel, the mixture BDP-10 (10% biodiesel + 90% diesel) or BDP-5 are used, considering in this case the biofuel as an additive.

• Since the 90s, several car manufacturers (primarily German makes) have already changed the rubber hoses for others made of plastic materials which do not dissolve in biodiesel.

• Combustion engines require lubrication to prevent friction in the moving parts.
Reducing levels of sulfur and aromatics in conventional fuels has limited the traditional diesel lubrication. In this way, the addition of small amounts of biodiesel (1–2%) improves the lubricant characteristics of low sulfur diesel, making it possible to eliminate other lubricant additives. However, when using 100% biodiesel, the lubricant oil is contaminated because of the low viscosity of the ester.

Biodiesel has a calorific value slightly lower than diesel (about 11%), which implies a slight increase in consumption and a decrease in engine power. These two effects depend on the ratio of the mixture, and can reach 15% and 7% for pure biodiesel.

• The accidental loss of fuel into the environment causes a contamination of soils and water resources. For this reason, it is important to reduce the time that the environment needs to break the pollutant down into other harmless substances.
Biodiesel degrades almost completely (98.3%) in just 21 days.

• Generally, for biodiesel blends under 20% no modifications to the engines are required. For the use of pure biodiesel or blends over 20%, minor modifications such as hoses, gaskets, etc., are necessary.