

## **BIODIESEL**

Biodiesel is a vegetable oil-based fuel that can be used to replace diesel oil. The main argument for its usage in internal combustion engines is that it causes less pollution than diesel.

All fossil fuels pollute the environment with the gases released from the exhaust. Diesel oil is no exception.

1. One of the most important pollutants is sulphur. Sulphur is released by the exhaust line as sulphur oxide (SO<sub>x</sub>), which is converted into sulphuric acid when combined with the moisture in the air, leading to the creation of acid rain. Global trends have gone towards reducing the content of sulphur allowed in fuels.

Low-sulphur diesel oil loses lubrication properties, so additives must be used to make up for this loss. Biodiesel has good lubricity (5,000 grammes according to the ASTM D 6078 standard), greater than diesel oil (3,000 to 4,000 grammes with another additive), meaning that it can be considered as an additive to improve lubricity.

2. Another pollutant is nitrogen. However, it should be recognised that the level of nitrous oxide in the exhaust gases is slightly higher when using biodiesel than in diesel oil. Nitrous oxides also give rise to acid rain (generating nitric acid). In general, however, biodiesel causes less contamination when the effects of SO<sub>x</sub> and NO<sub>x</sub> of 100% pure biodiesel (B100) with 100% pure diesel oil are compared.

3. Nevertheless, as regards other pollutants, biodiesel has clearly fewer contaminating effects. It does not contain polynuclear aromatic hydrocarbons. The content of unburnt fuel and carbon monoxide, as well as the level of fumes, particles and aldehydes present in exhaust gases is less.

It should be said that there is no absolute comparison of whether biodiesel is better than conventional diesel. It will depend on the types of biodiesel and diesel oil compared

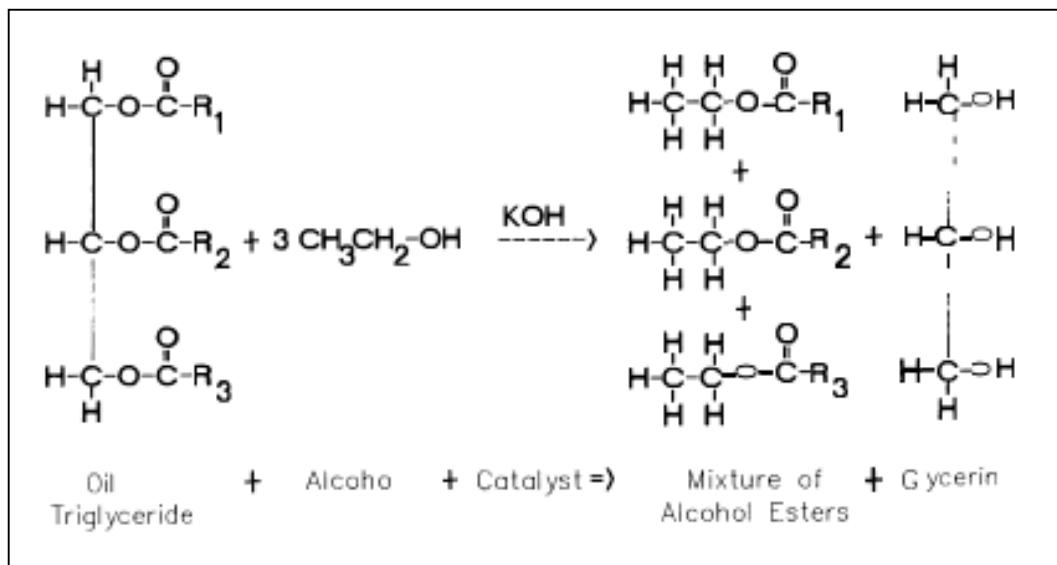
The quality of biodiesel depends on two important factors:

- Source oil type
- Manufacture quality

## 2. BIODIESEL PRODUCTION PROCESS. TRANSESTERIFICATION

Vegetable oils are mainly comprised of esters called triglycerides, which are a combination of saturated and unsaturated fatty acids of different molecular weights with glycerol. When triglycerides react with an alcohol (methanol) in the presence of an alkaline catalyst (Sodium hydroxide or Potassium hydroxide), they produce a mixture of methyl esters and glycerol. Figure 1 shows the transesterification process.

Figure 1. Transesterification process of an oil/fat in biodiesel production.



If the free fatty acids are not previously removed, they combine with the catalyst (KOH) and reduce the efficiency of the transesterification reaction. Furthermore, the compounds produced are soaps, which will later complicate the biodiesel and glycerine purification stage. Alkaline neutralisation can also cause sodium soap traces to be present.

All the material contained in the oils that is not fatty material (triglycerides) or free fatty acids is called an unsaponifiable substance, also known using the generic

name 'gum'. The oils contain materials such as: polypeptides, phosphatides, lecithin, proteins, mucilage, sterols, hydrocarbons etc. Since they do not participate in transesterification reactions, they will form undesired compounds in the biodiesel and can cause engine problems. Phosphatides are insoluble in fats and are usually found in colloidal suspension. In general, all gums and mucilaginous substances are treated with an acid, the most suitable being phosphoric acid. Next, the total acidity (including the acidity of free fatty acids) is neutralised with potassium hydroxide.

The colour comes from the pigments, e.g. chlorophyll and carotenes. These pigments tend to remain despite subsequent processing and at times, they are removed or changed.

The smell of predominantly unsaturated oils is unpleasant (due to terpenic hydrocarbons) and an efficient deodorisation process is required to remove them.

The presence of water is also a disadvantage, although it is not generally found in the oil, rather in the alcohol. The water tends to dilute the catalyst and form emulsions with the soaps and the biodiesel that are difficult to separate. On the other hand, the presence of moisture, high temperatures, long storage times, and enzymatic action tends to deteriorate the biodiesel, increasing free acidity.

### **3. BIODIESEL CHARACTERISTICS**

#### ***3.1. BIODIESEL PROPERTIES***

The basic components of the oils and fats are triglycerides, coming from both saturated and unsaturated fatty acids. Depending on these and other characteristics regarding the source of the triglycerides, a biodiesel with one or another quality will be obtained.

This is the main feature that differentiates biodiesel from diesel oil, as the latter is comprised paraffin compounds, aromatic naphthenic hydrocarbons. The number of carbons is fairly fixed, found to be between C<sub>10</sub> and C<sub>22</sub>.

By comparing some biodiesel properties with those of diesel, Table 1, some conclusions can be taken:

- The density and viscosity increases notably with respect to diesel oil. This could affect the injection system.
- The cetane number, which is associated with the engine operation, is greater in the methyl ester than in diesel oil. This difference is more notable in those methyl esters with higher levels of saturated fatty acids. They are good additives for improving the cetane number.
- The flash point is much higher than in diesel oil, meaning it is much safer to handle and store.
- Sulphur is not present in Biodiesel.
- Although not specified in the standards, the distillation of FAME has a very short range.
- The calorific power of diesel is approximately 10% higher than biodiesel.
- The pour point is more favourable in diesel oil than biodiesel.

Parameter	Standard	Units	EN 590 Diesel	EN 14214 Biodiesel
Density (15°C)	EN ISO 12185	g/cm <sup>3</sup>	0.820-0.880	0.860-0.900
Kinematic viscosity 40°C	EN ISO 3104	cSt	2.0-4.5	3.5-5.0
Flash point	EN 22719	°C	60 min.	120 min.
Sulphur	EN ISO 14596	ppm	2000 max	10 max.
Carbon residue (10%)	EN ISO 10370	%	0.30 max.	0.30 max.
Total contamination	EN 12662	ppm	24 max.	24 max.
Water	EN ISO 12937	ppm	200 max.	500 max.
Corrosiveness to copper	EN ISO 2160	-	Class 1	Class 1
Ashes	EN ISO 6245	%	0.01 max.	0.02 max.
Pour point*	ASTM D 97	°C	-27	-6
PCI*	ASTM D -240	Kcal/kg	10.000	8.900
Cetane number	EN ISO 5165	-	49 min.	51 min.

\* Typical values

By analysing biodiesel in depth, a series of properties can be seen that may affect engine operation or may cause a series of problems over time.

These are:

#### Disadvantages of biodiesel use

##### *a) Incompatibility at low temperatures.*

One of the greatest problems found when deciding whether to use biodiesel as a fuel is due to its poor properties at low temperatures. Generally speaking, the Gel point (GP), Cloud point (CP) and the Cold Filter Plugging Point (CFPP) range from being slightly higher to much higher than a diesel oil fuel, depending on the ester source (corn oil, olive oil, etc.).

##### *b) Higher viscosity.*

Since the viscosity of biodiesel is higher than that of diesel, there may be loss of flow through filters and injectors. If the spray is altered by the fuel flow, coking of the injector or lubricant dilution may occur.

*c) Lubricant dilution.*

The distillation profile of biodiesel is very different to that of diesel, although the final boiling points are quite similar. This explains why biodiesel tends to disssolve easier in the lubricant than diesel. Engine oil is degraded much quicker if the fuel used is biodiesel rather than diesel. The miscibility of biodiesel in the oil reduces the viscosity in the first stages (fuel dilution), while it can be seen that the TAN, TBN and insoluble particles are within the specifications.

*d) Corrosion problems.*

Some problems may appear due to corrosion and wear particles in the oil that will not just affect the engine, but also the installation (storage tanks...).

\* Attacks joints (Table 2) and paint.

- The nitrile joints in contact with Biodiesel are dissolved, meaning that they should be replaced by Viton joints, which are more resistant.
- The paint in the fuel tank and other parts can be replaced for acrylic paint.

Table 2. Compatibility of different joint materials with Biodiesel.

Material	Compound	Compatibility
Viton	Biodiesel 10-100%	Compatible
Polyurethane	“	“
Tygon	Biodiesel 100%	Not compatible
Teflon	“	Compatible
Polyvinyl	“	Not compatible
Polyformaldehyde	“	Compatible
Polyamides	“	Not compatible
Nitrile gums	“	“
Ebonite	“	Compatible
Epichlorhydrin	“	“
White phenols	“	“

\* Attacks Cu and Pb.

Lead (Pb) is broken down very quickly in the presence of biodiesel. The lead sources in the engine are:

- Connecting rod small end cap 10% (coating).
- Oil pump bushing (coating).

Copper (Cu) also appears to be attacked by biodiesel. Parts containing copper are:

- Oil cooler 100%
- Connecting rod small end cap 75%
- Different parts in lower percentages.

\* Corrosive agents present in biodiesel.

- Chlorine *Cl* is an extremely corrosive agent, meaning that its presence should be limited.

\* Acids present in biodiesel. As the level of acids in the engine increase, deposits are generated in the injection systems causing problems in fuel pumping. They also attack the joints and metal parts of the injection system.

\* Presence of microbians. The presence of microbians causes system corrosion and premature clogging of filters. Some anti-microbial additives can be used. The water content accelerates the presence of microbians.

e) Other pollutants

- \* The presence of potassium (K) and sodium (Na) can cause soap precipitation, blocking filters. These are present in biodiesel due to defective washing during production.
- \* Diglycerides and triglycerides increase corrosion, forming chelates with the metals from metallic surfaces.
- \* Free and total glycerine. The levels of these two compounds must be carefully controlled as they directly affect the injection pump.
  - They clog filters.
  - They also generate coked product in the injectors.
  - They increase the viscosity and thickening.
  - They cause crystallisations at low temperatures.

*f) Filter clogging.*

- \* Since biodiesel is a good solvent, it dissolves any dirt in the fuel circuit until leaving it clean. For this reason, the filters clog very quickly at the start and must be changed after a few hours of use.
- \* The filters can clog with glycerine, meaning that the fuel pumping is reduced (lubricity problems). Part of the glycerine that has been filtered may remain in the liquid trap
- \* The glycerides cause crystallisations at low temperatures. Mono and diglycerides affect the cloud point, but not the pour point. It has been verified that the reason for the filters clogging is due to saturated glycerides, meaning that unsaturated glycerides do not contribute greatly to the cloud point.

*g) Stability problems..*

- \* It has lower oxidation stability than diesel as it contains double bonds and oxygen in its molecule. This is important when storing biodiesel over a long time.
- \* The products that are generated in fuel pre-reactions are usually heavier, forming deposits inside the engine and blocking the injectors.
- \* As cis double bonds are increased, it was seen that the deposits penetrate deeper into the piston ring pack. They were not seen in the cylinder, piston or injector.

*h) Performance.*

A slight increase in biodiesel consumption was seen due to:

- \* The calorific power (kcal/kg) is less than diesel oil (~90%), but since biodiesel has greater viscosity, it leaks less fuel in the injectors. By combining these two factors, the final energy loss is ~5-7% in volume.

*i) Pollutant emissions*

- \* The NO<sub>x</sub> emissions are increased slightly due to greater levels of oxygen (oxygenated fuel and greater air/fuel ratios), increasing the temperature of the combustion chamber.
- \* On starting up, the engine usually produces more fumes than a normal diesel engine, but this is minimised immediately after.

*j) Cost.* The production process of Biodiesel is approximately 2-3 times more expensive than diesel production, without taking into account premiums for using alternative fuels.

A summary of the problems occurring in an engine from using biodiesel as a fuel is shown in Table 3.

*Table 3. Summary of problems in the fuel injection equipment using biodiesel*

<b>Biodiesel property</b>	<b>Effect</b>	<b>Failure mode</b>
Fatty acid methyl ester (FAME)	Causes the nitrile joints to become soft, swell, or become hard and break.	Fuel leaks
Free methanol in FAME	- Corrodes Al and Zn -Reduces the Flash point	Corrosion of the injection system (FIE)
Reagents from the FAME process	K and Na form solid compounds	Nozzle tips blocked
Water miscible in FAME	Inverse reaction of FAME to fatty acids	Filter clogging
Free water in blends	- Corrosion - Presence of bacteria - Increase in the electrical conductivity of the fuel	- FIE corrosion - Sludge formed
Free glycerine	- Corrodes non-iron metals - Soaks the cellulose filters - Forms sediment in mobile parts - Tends to form varnishes	- Blocks the filters - Cokes the injector
Mono and Diglycerides	Similar to glycerine	
Free fatty acids	- Provides a electrolyte and accelerates Zn corrosion - Forms organic acid salts - Forms organic compounds	- FIE corrosion - Filter clogging Sediment on parts
Increases the elastic modules	Increases injector pressure	Reduces the service life
High viscosity at low temperatures	- Generates excessive local heat in rotary distribution pumps - Increases stress on the components	- Attacks the pump - Premature failures - Poor spray atomisation in the nozzle
Solid impurities	Potential lubricity problems	Reduced service life
<b>Products of Aging</b>		
Corrosive acids (formic and acetic acids)	Corrodes all metallic parts	FIE corrosion
Organic acids with higher molecular weight	Similar to fatty acids	
Products of polymerisation	Deposits, especially in <u>fuel blends</u>	- Filter clogging - Formation of varnishes in hot areas

### Advantages of biodiesel use

#### *a) Lubricity.*

Biodiesel has higher lubricity properties than diesel.

- \* Notably better results are obtained in the lubricity tests performed.
- \* Fewer wear particles (Fe) are produced than in diesel.

#### *b) Cetane number.*

In general, esters derived from fatty acids have a greater CN than diesel.

*c) Pollutant emissions.* They produce more efficient combustion due to the presence of oxygen in the ester molecules in the spray nucleus:

- \* It improves fuel performance.
- \* A significant decrease in the level of particles emitted (lower fume opacity). This is influenced by the higher CN.
- \* Lower unburnt CO and HC emissions.
- \* Biodiesel is composed of long carbon chains similar to diesel paraffins. This way, the aromatic content is diluted, reducing the particles.
- \* CO<sub>2</sub> emission balance is nil since the source is biological.