

## Biodiesel technology

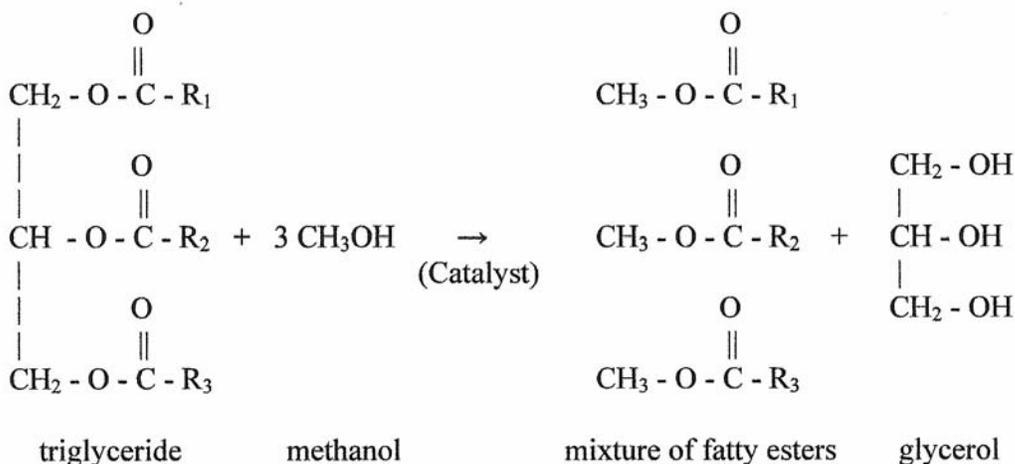
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**Key words:** biodiesel, installation, transesterification;

**Abstract:** In this paper we present the main technology for biodiesel, the principal issues regarding the production in Romania, the behavior of biodiesel in engine with ignition through compression as well as an experimental installation of biodiesel which we build in Craiova at laboratory of Thermodynamics. Thought this we wish to show the benefices of biodiesel in the rural communities and to promote a healthy life.

### 1. BASICS OF BIODIESEL PRODUCTION

Biodiesel is an alternative fuel for diesel engines that is gaining attention in the Romania after reaching a considerable level of success in Europe (especially in Germany). Its primary advantages are that it is one of the most renewable fuels currently available and it is also non-toxic and biodegradable. It can also be used directly in most diesel engines without requiring extensive engine modifications. The purpose of this paper is to describe and explain the processes and issues involved in producing this new fuel. Vegetable oil is transformed into biodiesel through a process called transesterification (Fig.1) in which we reduce his viscosity.



**Fig.1. The process of transesterification**

Were R1, R2 and R3 are long chains of carbon and hydrogen atoms, sometimes called fatty acid chains. There are five types of chains that are common in vegetable oil and animal fats (others are present in small amounts):

Palmitic: R=-(CH<sub>2</sub>)<sub>14</sub>-CH<sub>3</sub> 16 carbons (including the one that R is attached) (16:0)

Stearic: R=-(CH<sub>2</sub>)<sub>16</sub>-CH<sub>3</sub> 18 carbons, 0 double bonds (18:0)

Oleic: R=-(CH<sub>2</sub>)<sub>7</sub>CH=CH(CH<sub>2</sub>)<sub>7</sub>CH<sub>3</sub> 18 carbons, 1 double bonds (18:1)

Linoleic: R=-(CH<sub>2</sub>)<sub>7</sub>CH=CH-CH<sub>2</sub>-CH=CH(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub> 18 carbons, 2 double bonds (18:2)

Linolenic: R=-(CH<sub>2</sub>)<sub>7</sub>CH=CH-CH<sub>2</sub>-CH=CH-CH<sub>2</sub>-CH=CH-CH<sub>2</sub>-CH 18 carbons, 3 double bonds (18:3)

These chains are designated by two numbers separated by a colon. The first number designates the number of carbon atoms in the chain and the second number designates the number of double bonds. Note that the number of carbon atoms includes the carbon that is double bonded to the oxygen atom at one end of the fatty acid (called the carboxylic carbon). This is the end that the methanol attaches to when methyl esters are produced. Table 1 shows the percentages of each fatty acid chain present in common oils and fats.

**Table 1 Composition of various oils and fats**

| Oil or fat                    | 14:0     | 16:0                   | 18:0  | 18:1  | 18:2  | 18:3  | 20:0 | 22:1 |
|-------------------------------|----------|------------------------|-------|-------|-------|-------|------|------|
| Soybean                       |          | 6-10                   | 2-5   | 20-30 | 50-60 | 5-11  |      |      |
| Corn                          | 1-2      | 8-12                   | 2-5   | 19-49 | 34-62 | trace |      |      |
| Peanut                        |          | 8-9                    | 2-3   | 50-65 | 20-30 |       |      |      |
| Olive                         |          | 9-10                   | 2-3   | 73-84 | 10-12 | trace |      |      |
| Cottonseed                    | 0-2      | 20-25                  | 1-2   | 23-35 | 40-50 | trace |      |      |
| Hi linoleic<br>Safflower      |          | 5.9                    | 1.5   | 8.8   | 83.8  |       |      |      |
| Hi Oleic Safflower            |          | 4.8                    | 1.4   | 74.1  | 19.7  |       |      |      |
| Hi Oleic Rapeseed             |          | 4.3                    | 1.3   | 59.9  | 21.1  | 13.2  |      |      |
| Hi Erucic<br>Rapeseed         |          | 3.0                    | 0.8   | 13.1  | 14.1  | 9.7   | 7.4  | 50.7 |
| Butter                        | 7-10     | 24-26                  | 10-13 | 28-31 | 1-2.5 | .2-.5 |      |      |
| Lard                          | 1-2      | 28-30                  | 12-18 | 40-50 | 7-13  | 0-1   |      |      |
| Tallow                        | 3-6      | 24-32                  | 20-25 | 37-43 | 2-3   |       |      |      |
| Linseed Oil                   |          | 4-7                    | 2-4   | 25-40 | 35-40 | 25-60 |      |      |
| Yellow<br>grease<br>(Typical) | 2.4<br>3 | 23.24<br>16:1=3<br>.79 | 12.96 | 44.32 | 6.97  | 0.67  |      |      |

Data derived from *Organic Chemistry*, W.W. Linstromberg, D.C. Heath and Co., Lexington, MA, 1970

## 2. PRODUCTION

The primary raw materials used in the production of biodiesel are vegetable oils, animal fats, and recycled greases. These materials contain triglycerides, free fatty acids, and other contaminants depending on the degree of pretreatment they have received prior to delivery. Since biodiesel is a mono-alkyl fatty acid ester, the primary alcohol used to form the ester is the other major feedstock. Most processes for making biodiesel use a catalyst to initiate the esterification reaction. The catalyst is required because the alcohol is sparingly soluble in the oil phase. The catalyst promotes an increase in solubility to allow the reaction to proceed at a reasonable rate. The most common catalysts used are strong mineral bases such as sodium hydroxide and potassium hydroxide. After the reaction, the base catalyst must be neutralized with a strong mineral acid.

### 2.1 Fats and oils

Choice of the fats or oils to be used in producing biodiesel is both a process chemistry decision and an economic decision. With respect to process chemistry, the greatest difference among the choices of fats and oils is the amount of free fatty acids that are associated with the triglycerides. Other contaminants, such as color and odor bodies can reduce the value of the glycerin produced, and reduce the public acceptance of the fuel if the color and odor persist in the fuel. Most vegetable oils have a low percentage of associated free fatty acids. Crude vegetable oils contain some free fatty acids and phospholipids. The phospholipids are removed in a "degumming" step and the free fatty acids are removed in a "refining" step. Oil can be purchased as crude, degummed, or refined. The selection of the type of oil affects the production technology that is required. Animal tallow's and recycled (yellow) grease have much higher levels of free fatty acids. Yellow grease is limited to 15% free fatty acids and is a traded commodity that is typically processed into animal and pet food. Trap greases come from traps under kitchen drains and these greases can contain between 50 and 100% free fatty acids. There is no market for these greases at this time and most are land filled. Trap grease is not yet used for biodiesel production and may have some technical challenges that have not be fully resolved such as difficult to break emulsifications (gels), fine silt that will cause equipment wear, high water contents, and very strong color and odor bodies that affect biodiesel and glycerin products. There are also unresolved questions about small quantities of other contaminants such as pesticides that might be present in the fuel. The options for the triglyceride choice are many. Among the vegetable oils sources are soybean, canola, palm, and rape. Animal fats are products of rendering operations. They include beef tallow, lard, poultry fat, and fish oils. Yellow greases can be mixtures of vegetable and animal sources. There is other less desirable, but also less expensive triglyceride sources such as brown grease and soap stock. The free fatty acid content affects the type of biodiesel process used, and the yield of fuel from that process. The other contaminants present can affect the extent of feedstock preparation necessary to use a given reaction chemistry.

Alcohol: The most commonly used primary alcohol used in biodiesel production is methanol, although other alcohols, such as ethanol, isopropanol, and butyl, can be used. A key quality factor for the primary alcohol is the water content. Water interferes with transesterification reactions and can result in poor yields and high levels of soap, free fatty acids, and triglycerides in the final fuel. Unfortunately, all the lower alcohols are hygroscopic and are capable of absorbing water from the air. Many alcohols have been used to make biodiesel. As long as the product esters meet the standards, it does not make any chemical difference which alcohol is used in the process. Other issues such as cost of the alcohol, the amount of alcohol needed for the reaction, the ease of recovering and recycling the alcohol, fuel tax credits, and global warming issues influence the choice of alcohol. Some alcohols also require slight technical modifications to the production process such as higher operating temperatures, longer or slower mixing times, or lower mixing speeds. Since the reaction to form the esters is on a molar basis and we purchase alcohol on a volume basis, their properties make a significant difference in raw material price. It takes three moles of alcohol to react completely with one mole of triglyceride. In addition, a base catalyzed process typically uses an operating mole ratio of 6:1 mole of alcohol rather than the 3:1 ratio required by the reaction. The reason for using extra alcohol is that it "drives" the reaction closer to the 99.7% yield we need to meet the total glycerol standard for fuel grade biodiesel. The unused alcohol must be recovered and recycled back into the process to minimize operating costs and environmental impacts. Methanol is considerably easier to recover than the ethanol. Ethanol

forms an azeotrope with water so it is expensive to purify the ethanol during recovery. If the water is not removed it will interfere with the reactions. Methanol recycles easier because it doesn't form an azeotrope. These two factors are the reason that even though methanol is more toxic, it is the preferred alcohol for producing biodiesel. Methanol has a flash point of 10 °C, while the flash point of ethanol is 8°C, so both are considered highly flammable. The alcohol quality requirements are that it be un-denatured and anhydrous. Since chemical grade ethanol is typically denatured with poisonous material to prevent its abuse, finding un-denatured ethanol is difficult. Purchase ethanol that has been denatured with methanol if possible.

## 2.2 Catalysts and neutralizers

Catalysts may either be base, acid, or enzyme materials. The most commonly used catalyst materials for converting triglycerides to biodiesel are sodium hydroxide, potassium hydroxide, and sodium methoxide. Most base catalyst systems use vegetable oils as a feedstock. If the vegetable oil is crude, it contains small amounts (<2%) of free fatty acids that will form soaps that will end up in the crude glycerin. Refined feedstocks, such as refined soy oil can also be used with base catalysts. The base catalysts are highly hygroscopic and they form chemical water when dissolved in the alcohol reactant. They also absorb water from the air during storage. If too much water has been adsorbed the catalyst will perform poorly and the biodiesel may not meet the total glycerin standard. Although acid catalysts can be used for transesterification they are generally considered to be too slow for industrial processing. Acid catalysts are more commonly used for the esterification of free fatty acids. Acid catalysts include sulfuric acid and phosphoric acid. Solid calcium carbonate is used as an acid catalyst in one experimental homogeneous catalyst process. The acid catalyst is mixed with methanol and then this mixture is added to the free fatty acids or a feedstock that contains high levels of free fatty acids. The free fatty acids convert into biodiesel. The acids will need neutralization when this process is complete, but this can be done as base catalyst is added to convert any remaining triglycerides. There is continuing interest in using lipases as enzymatic catalysts for the production of alkyl fatty acid esters. Some enzymes work on the triglyceride, converting them to methyl esters; and some work on the fatty acids. The commercial use of enzymes is currently limited to countries like Japan, where energy costs are high, or for the production of specialty chemicals from specific types of fatty acids. The commercial use of enzymes is limited because costs are high, the rate of reaction is slow, and yields to methyl esters are typically less than the 99.7% required for fuel-grade biodiesel. Enzymes are being considered for fatty acid conversion to biodiesel as a pretreatment step, but this system is not commercial at this time. Neutralizers are used to remove the base or acid catalyst from the product biodiesel and glycerol.

## 2.3 Catalysts selection

Base catalysts are used for essentially all vegetable oil processing plants. The initial free fatty acid content and the water content are generally low. Tallow's and greases with free fatty acid contents greater than about 1% must be pretreated to either remove the FFA or convert the FFA to esters before beginning the base catalyzed reaction. Otherwise, the base catalyst will react with the free fatty acids to form soap and water. The soap formation reaction is very fast and goes to completion before any esterification begins. Essentially all of the current

commercial biodiesel producers use base catalyzed reactions. Base catalyzed reactions are relatively fast, with residence times from about 5 minutes to about 1 hour, depending on temperature, concentration, mixing and alcohol: triglyceride ratio. Most use NaOH or KOH as catalysts, although glycerol refiners prefer NaOH. KOH has a higher cost but the potassium can be precipitated as  $K_3PO_4$ , a fertilizer, when the products are neutralized using phosphoric acid. This can make meeting water effluent standards a bit more difficult because of limits on phosphate effluents. Sodium metoxide, usually as a 25 % solution in methanol, is a more powerful catalyst on a weight basis than the mixture of NaOH and methanol. Acid catalyst systems are characterized by slow reaction rates and high alcohol's requirements (20:1 and more). Generally, acid catalyzed reactions are used to convert FFAs to esters, or soaps to esters as a pretreatment step for high FFA feedstock's. Residence times from 10 minutes to about 2 hours are reported. Counter current acid esterification systems have been used for decades to convert pure streams of fatty acids into methyl esters at yields above 99%. These systems tend to force yields to 100% and wash water out of the system at the same time because the feedstock and the sulfuric acid/methanol mix are moving in opposite directions. Acid esterification systems produce a byproduct of water. In batch systems, the water tends to accumulate in the vessel to the point where it can shut the reaction down prematurely. The sulfuric acid tends to migrate into the water, out of the methanol, rendering it unavailable for the reaction. All acid esterification systems need to have a water management strategy. Good water management can minimize the amount of methanol required for the reaction. Excess methanol (such as the 20:1 ratio) is generally necessary in batch reactors where water accumulates. Another approach is to approach the reaction in two stages: fresh methanol and sulfuric acid is reacted, removed, and replaced with fresher reactant. Much of the water is removed in the first round and the fresh reactant in the second round drives the reaction closer to completion. Acid-catalyzed esterification is discussed in more detail in the chapter on Pretreatment of High FFA Feedstock's. Lipase catalyzed reactions have the advantage reacting a room temperature without producing spent catalysts. The enzymes can be recycled for use again or immobilized onto a substrate. If immobilized, the substrate will require replacement when yields begin to decline. The enzyme reactions are highly specific. Because the alcohol can be inhibitory to some enzymes, a typical strategy is to feed the alcohol into the reactor in three steps of 1:1 mole ratio each. The reactions are very slow, with a three step sequence requiring from 4 to 40 hours, or more. The reaction conditions are modest, from 35 to 45 °C. Transesterification yields generally do not meet ASTM or EN standards, but esterification yields can occur relatively quickly and yields are good. Excess free fatty acids can be removed as soaps in a later transesterification or caustic stripping step.

### 3. EXPERIMENTAL INSTALATION

For biodiesel production we make a pilot installation to produce biodiesel in laboratory of Thermodynamics of Craiova with a small capacity of 30 L. In Fig.2 is presented the general scheme of the installation and in Fig. the command panel.

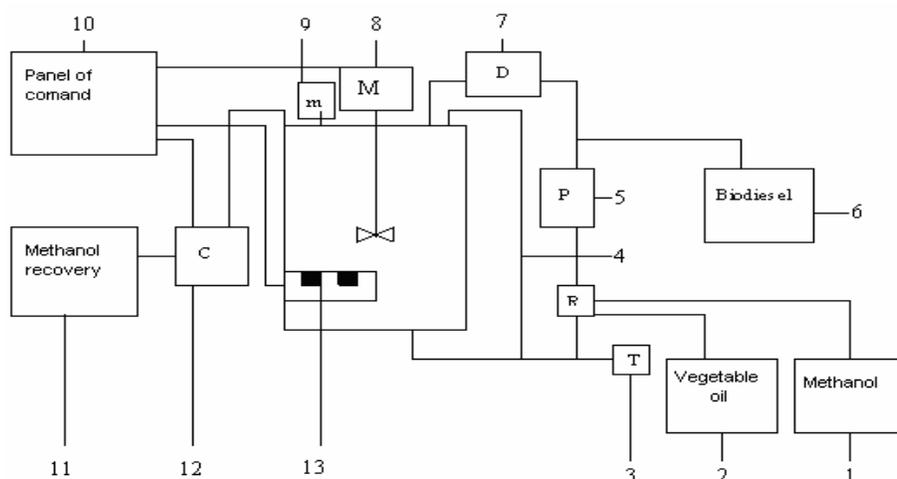


Fig.2. General Scheme of the biodiesel installation

Legend:

- |   |  |
|---|--|
| 1. Reservoir of methanol capacity 5 L       | 8. Electric blender                    |
| 2. Reservoir of vegetable oil capacity 30 L | 9. Manometer                           |
| 3. Temperature probe                        | 10. Panel of command                   |
| 4. Pipeline level                           | 11. Reservoir of methanol capacity 3 L |
| 5. Pump                                     | 12. Condenser                          |
| 6. Reservoir of biodiesel capacity 30 L     | 13. Electric resistance of 2 KW        |
| 7. Debit meter                              |  |

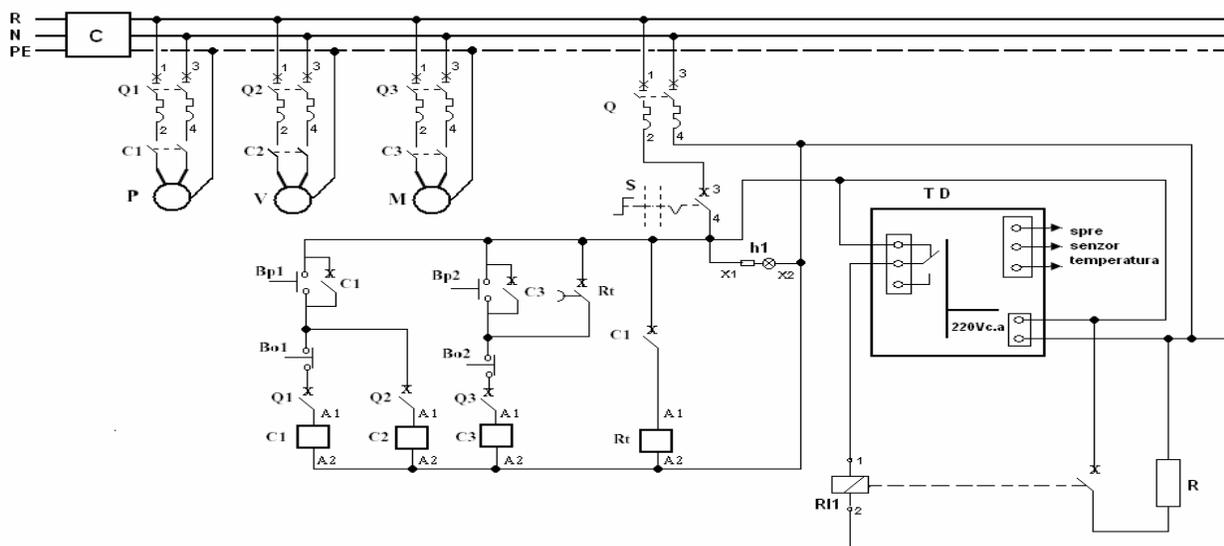


Fig.3. Electric scheme of command panel

Legend:

- |  |                                 |
|--|---------------------------------|
| Q = automatic contactor DPNa, 16 A (1P+N), curve C           | R = resistance 2000 W           |
| Q1, Q2, Q3=disjunctor monopole C60N, 4A, 230 V c.a., curve C | RT=relay with temporization     |
| C1, C2, C3= contactor CAD50M7, 220 V/50 Hz, 4A.              | Bp1, Bp2, Bo1, Bo2= push button |
| S = Knob with two positions                                  | C=electricity meter             |
| h1=lamp signal tension                                       | P=pump                          |

T D = digital thermostat  
R11 = relay

V=ventilator  
M=blender

The biodiesel installation use as raw material sunflower oil, catalyst NaOH and methanol through a process called transesterification of oil in basic catalyses because this process is more efficient and is easier to utilize.



**Fig.4. Biodiesel installation**

## CONCLUSION

There are multiple operating options available for making biodiesel. Many of these technologies can be combined under various conditions and feedstocks in an infinite number of ways. The technology choice is a function of desired capacity, feedstock type and quality, alcohol recovery, and catalyst recovery. The dominant factor in biodiesel production is the feedstock cost, with capital cost contributing only about 7 % of the final product cost. However, some reaction systems are capable of handling a variety of feedstock's and qualities, while others are not. Also, the different approaches to the esterification process result in quite different operating requirements, different water use requirements, and different operating modes. In general, smaller capacity plants and variable feedstock quality suggest use of batch systems. Continuous systems generally lead the operation on a 24/7 basis, requiring larger capacities to justify larger staffing requirements and require a more uniform feedstock quality. Our installation shows that biodiesel can be easy produce in a small capacity installation and can be utilized in engine with ignition through compression without problems as long as his quality is good.

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