RESEARCH PROJECT

CHEMICAL ENGINEERING

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SYNTHESIS AND PROPERTIES OF BIODIESEL OBTAINED FROM FATTY WASTE MATERIALS

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INTRODUCTION

I.1. Introduction to Biodiesel

Biodiesel is defined as the mixture of monoalkyl ester of fatty acid obtained from vegetable oils or animal fats. The major components of vegetable oils and animal fats are Triacylglycerols (TAG), it typically contains several different fatty acids (FA) conditioning the properties and behaviour of the final biodiesel.

To obtain biodiesel the FA is subjected to a classic chemical reaction termed *transestirification* (Figure I.1). In that reaction, the vegetable oil or animal fat is reacted in the presence of a catalyst (usually a base) with an alcohol (usually methanol) to give the corresponding alkyl esters (or for methanol, the methyl esters) of the FA mixture that is found in the parent vegetable oil or animal fat. (Knothe et al., 2005).

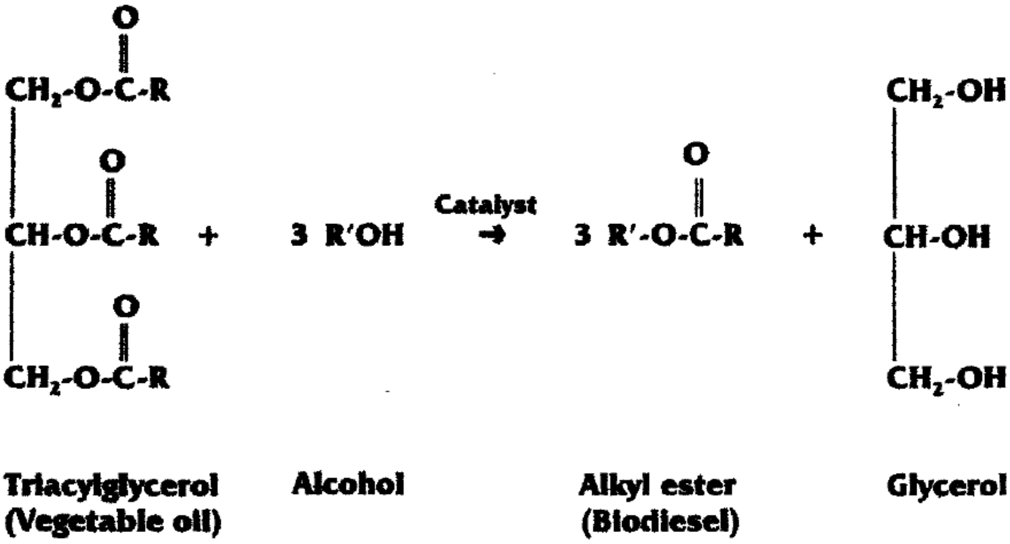


Figure I.1. The transesterification reaction. R is a mixture of various fatty acid chains. The alcohol used for producing biodiesel is usually methanol (R′ = CH3). (Knothe et al., 2005).

To determinate the quality of the biodiesel after the transesterification the result is divide in two groups: the first includes density, viscosity, flash point, sulfur content, carbonaceous residue, sulphated ash, cetane number and acid number, similar to those made to diesel; the second group corresponds basically to determinations of methanol glycerol. (Monteiro, et al., 2008)

Biodiesel constitutes an alternative fuel more eco-friendly respect to diesel because:

- Biodegradability,

- Renewable product derivate from domestic resources, it can decrease the dependence on petroleum.
- Does not produce greenhouse effects because the balance between the amount of CO_2 emitted and absorbed by the plants producing the vegetable oil is equal.
- Biodiesel contains no sulfur. (Amit, S., 2012).
- Non-toxic reducing of most exhaust emissions except nitrogen oxides NO_X.
- The oils used to manufacture biodiesel can be edible or inedible turning it into a very versatile fuel.
- Higher flash point, leading to safer handling and storage.
- Excellent lubricity. (Ordoñez et al., 2013)

Some problems associated with biodiesel are the higher price, which in many countries is offset by legislative and regulatory incentives or subsidies. Against the expensive raw materials, it can be use of less expensive feedstocks as waste oils (e.g., used frying oils). (Knothe et al., 2005)

A variety of biodiesel fuel feedstocks are available currently some of the most important are:

- Virgin oil: Most commonly rapeseed and soybean.
- Waste vegetable oil.
- Animal fats: Tallow, lard, yellow grease, fatty acids and chicken fat are some examples.
- Algae.
- Oil from halophytes: Halophytessuch and Salicornia bigelovii. (Knothe et al., 2005)

Biodiesel can be used in most diesel engines, it is made from either agricultural or recycled resources, the table I.1 contrast alternative fuels for transportation qualitatively.

Table I.1. Contrast between modern available alternative fuels for transportation. (Amit, S., 2012).

FUEL	AVAILABILITY	FUTURE AVAILABILITY
COMPRESSED NATURAL GAS	Excellent	Moderate

GASOLINE	Excellent	Moderate-poor
BIODIESEL	Moderate	Excellent
HYDROGEN FUEL CELL	Poor	Excellent

The principal obstacle for commercialization of biodiesel as product is the cost to refine it but, currently the possibility of a continuous transesterification process and the recovery of high quality glycerol as a biodiesel by product should be considered to decrease the cost of manufacturing. (Demirbas, A., 2009)

I.2. Situation of Biodiesel

I.2.1. Mundial situation

Currently the production of biodiesel has grown exponentially principally because the increase of the petroleum price, the environmental care and politics that promote the development of biodiesel as a fuel. The figure I.2 represents that growth in 19 years.

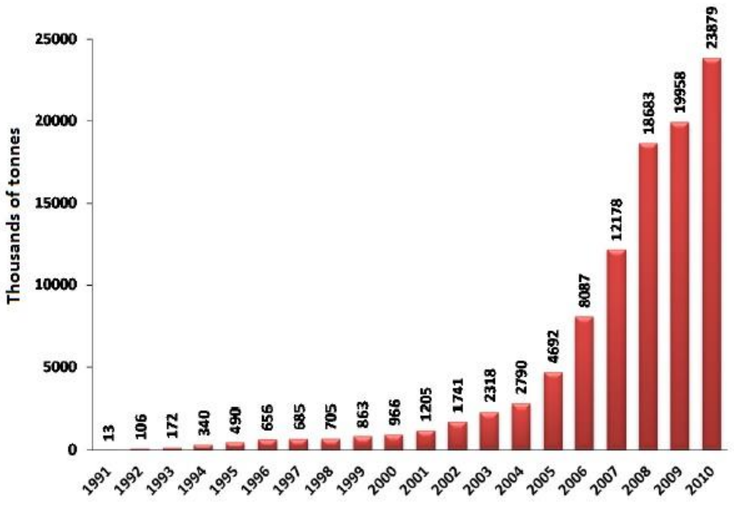


Figure I.2. Evolution of biodiesel production per year between 1991-2010 (Earth Policy Institute and F.O. Licht.)

Nowadays the most important biofuels are biodiesel and bioethanol, both are the best alternative of the fossil fuels because are renewable and reduce the atmosphere emissions. The European Union concentrate the higher percentage of biodiesel production meanwhile United States of America has the bigger production of bioethanol. In 2009 Europe produced the 50% of the global production of biodiesel and

USA the 33%, the following figure shows the global production in 2009. The five principal's producers of biodiesel are: Germany, USA, France, Brazil and Argentina, they produced the 68% percentage of the global production. (Eurobserver 2009).

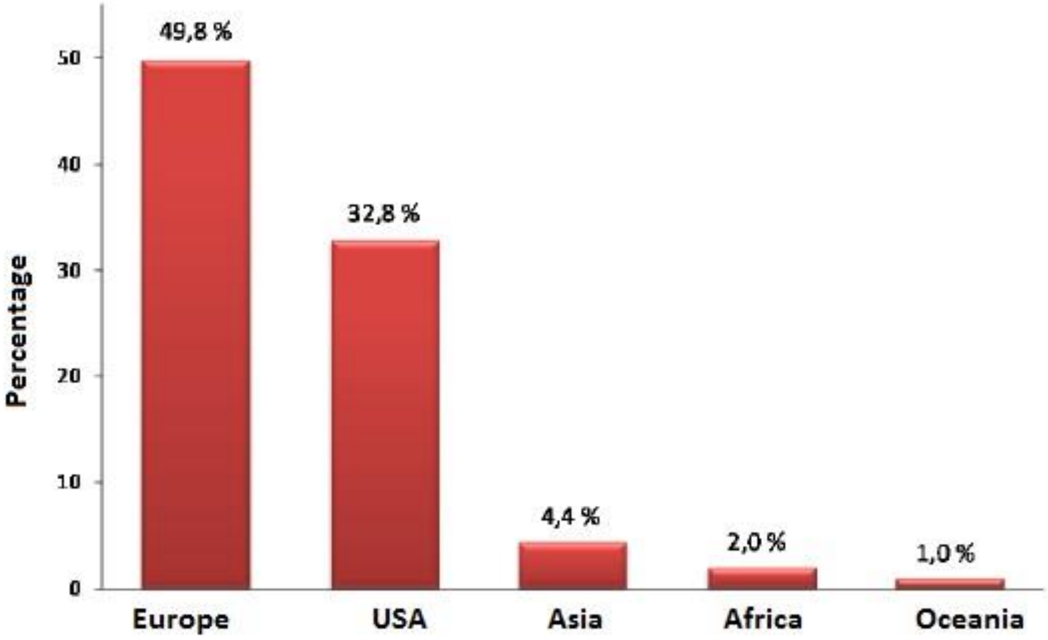


Figure I.3. Percentage of global production in 2009 by continents. (Eurobserver 2009).

The use of biodiesel as a new fuel allow us to substitute or decrease the importance of petroleum but, currently is impossible to eliminate totally the dependence of the petroleum with biodiesel, that's why most of the arable lands of the world should be used to produce biodiesel and in the current agricultural context that's impossible. But some other alternatives that don't compete with food for example:

- Oils produced from non-edible oilseeds, it would allow the use of lands in disuse.
- Oils from frying processes as raw material, it would allow the elimination of this waste.
- Microalgae because the ease of reproduction and the high amount of oil that you can extract. (Knothe et al., 2005).

I.2.2. Europe situation

To have an idea about the importance and the industrial dimension of the biofuels production in Europe, specifically the biodiesel production the figure I.4 shows the variation between the production in 2008 and 2009 in some of European countries.

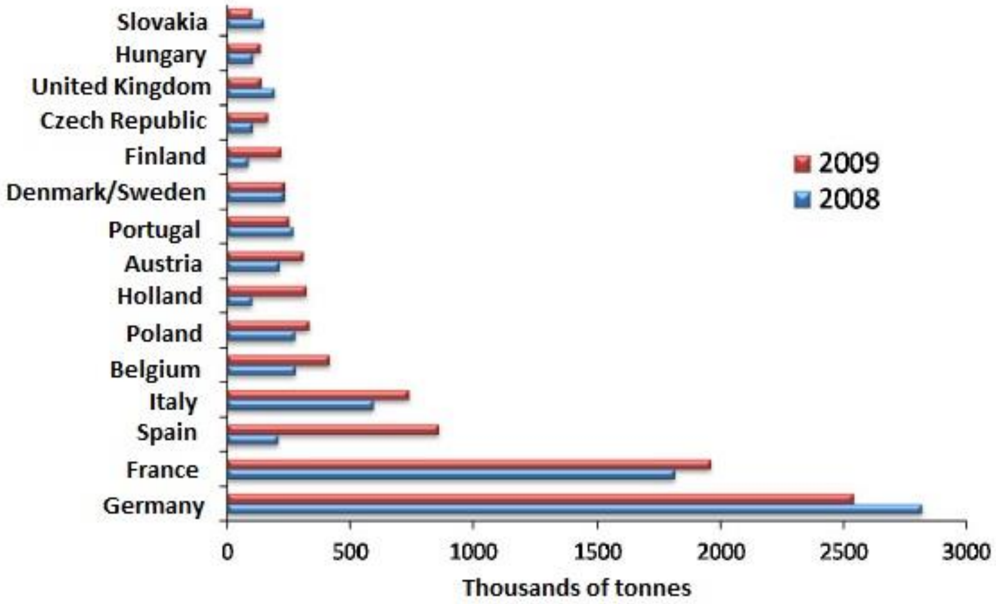


Figure I.4. Growth of the production between 2008/2009. (Eurobserver 2009).

In Europe in 2010 there was a 13% decrease of the number of biodiesel plants compared with 2009 but, capacity of production increase in 38% to reach 24 million of tonnes. This variation is because the experience and investment in R+D+I that increase the capacity and efficiency of the installations.

CHAPTER II

PROPERTIES OF BIODIESEL

To use biodiesel as a fuel is necessary to know basic information about it. The properties can teach us how to manipulate and synthesize the raw materials and the final product as we wish.

II.1. Standard specifications

The development of provisional specifications of biodiesel started in 1999 in USA with the American Society for Testing and Materials (ASTM), currently the US and EU standards have international significance, they are usually the starting point for biodiesel specifications developed in other countries.

The ASTM most important regulation is:

- ASTM D6751 defines biodiesel as *"mono-alkyl esters of long chain fatty acids derived from vegetable oils and animal fats"* these mono-alkyl could be produce with any alcohol

  the standard specifications of two grades of biodiesel: grade 2B and grade 1B (with tighter controls on monoglycerides).

In Europe, the most important diesel fuel specifications are:

- EN 14213 define the heating fuels requirements and test methods for fatty acid methyl esters (FAME).
- EN 14214 is more restrictive and establishes specifications for fatty acid methyl esters for diesel engines that can be only made with methanol (FAME), and the minimum ester content s specified at 96.5%. These regulations not allow the addition of components that are not fatty acid methyl esters. It was update in 2013 and now it covers heating oil applications and one set of climatic classes based on monoglycerides content.
- EN 590:2009 allowed blends up to 7% of fatty acid methyl ester in diesel fuel.

All the properties with their limits described mainly by the EN and ISO standards regulations are described in the table II.1.

Table II.1. Standard specifications of biodiesel according to EN and ISO regulations. (István, B., 2011).

PROPERTY	TEST METHOD	LIMITS		UNITS
		MIN	MAX	
ESTER CONTENT	EN 14103	96.5	-	% (m/m)
DENSITY (15 ^{O}C)	ISO 3675, ISO 12185	860	900	Kg/m^3
KINEMATIC VISCOSITY (40 ^{O}C)	ISO 3104	3.5	5.0	mm^2/s
FLASH POINT	ISO 3679	120	-	^{o}C
SULFUR CONTENT	ISO 20846, ISO 20884	-	10.0	mg/kg
CARBON RESIDUE (ON 10% DISTILLATION RESIDUE)	ISO 10370	-	0.3	% (m/m)
CETANE NUMBER	ISO 5165	51.0	-	-
SULFATED ASH CONTENT	ISO 3987	-	0.02	% (m/m)
WATER CONTENT	ISO 12937	-	0.05	% (m/m)
TOTAL CONTAMINATION	ISO 12662	-	24	mg/kg
COPPER STRIP CORROSIÓN (3 HOURS AT 50 ^{O}C)	ISO 2160	-	No. 1	rating
OXIDATION STABILITY (110 ^{O}C)	EN 14112	6	-	hours
ACID VALUE	EN 14104	-	0.5	mg KOH
IODINE VALUE	EN 14111	-	140	g I/100 g
LINOLENIC ACID METHYL ESTER	EN 14103	-	12	% (m/m)

METHANOL CONTENT	EN 14110	-	0.2	% (m/m)
COLD FILTER PLUGGING POINT (CFPP) WINTER/SUMMER	EN 116	-	-4/+3	°C
GROUP I METALS (NA + K)	EN 14108; EN 14106	-	5.0	mg/kg
GROUP II METALS (CA + MG)	EN 14538	-	5.0	mg/kg
PHOSPHORUS CONTENT	EN 14107	-	10.0	mg/kg
MONOGLYCERIDE CONTENT	EN 14105	-	0.8	% (m/m)
DIGLYCERIDE CONTENT	EN 14105	-	0.2	% (m/m)
TRIGLYCERIDE CONTENT	EN 14105	-	0.2	% (m/m)
TOTAL GLICEROL	EN 14105	-	0.25	% (m/m)
FREE GLYCEROL	EN 14105; EN 14106	-	0.02	% (m/m)

The most notable differences between the regulations in Europe and USA are:

- Limiting blends to B5 maximum.
- The oxidation stability of B100.
- The EU Introduce an oxidation stability requirement for blends that limits the increase in TAN to less than 0.12 mg KOH/g.
- The ash limits.
- The ferrous corrosion limits.
- Addition of free water and sediment limit.

- The ASTM has Loose the limits for: kinematic viscosity, iodine number and flash point.
- Labelling pumps dispensing any blend—including B5 or less. (ACEA 2009)

II.2. Operation properties

In order for biodiesel to be synthesized is necessary to learn the operation properties of the biodiesel because the goal of the process is to manufacture and amount of fuel with the highest quality possible.
All the standard bounds were described previously in the table 2.

II.2.1. Oxidation stability

Biodiesel oxidation is a complex process affected for the composition of the fuel and the conditions of storage. This fuel is more sensitive to oxidative degradation than fossil diesel fuels. Due to their chemical composition biodiesels with a high content of di- and higher unsaturated esters, as the methylene groups adjacent to double bonds are particularly susceptible to radical attacks as the first step of fuel oxidation. The figure II.2 describe the oxidation process of biodiesel. (Amit, S., 2012).

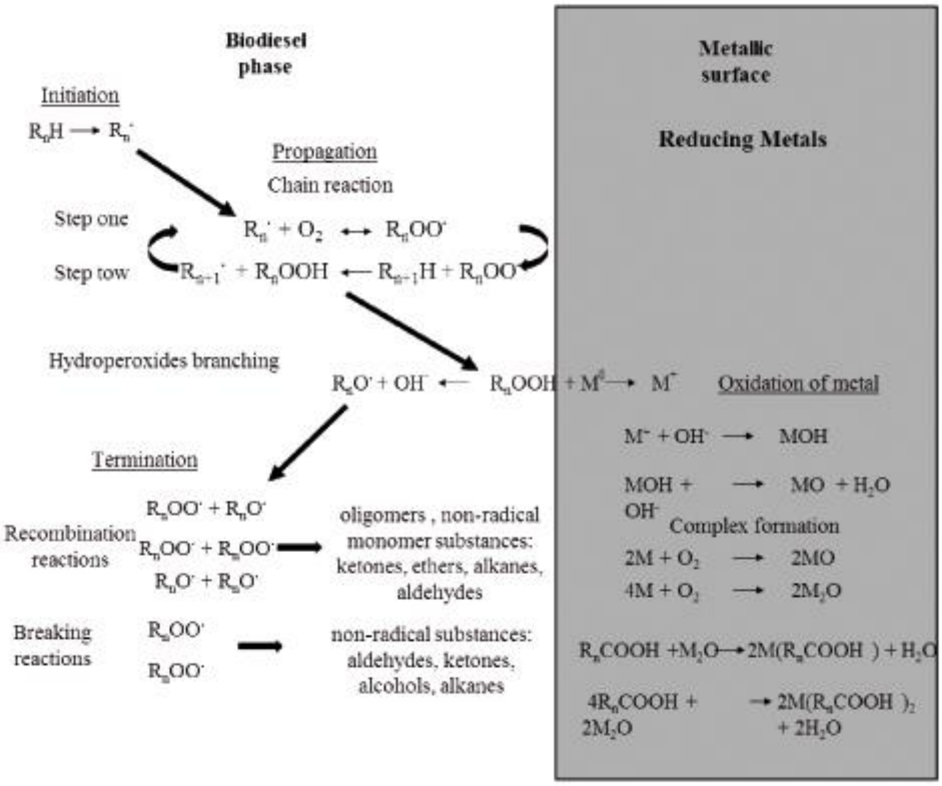


Figure II.1. Stages involved in lipid oxidation. (Ernesto C. Zyleta et al., 2012).

Is impossible to prevent completely the oxidation process but with appropriate precautions it can be delayed because the resistance to oxidative degradation is an important issue for the correct development and viability of alternate fuels. (Amit, S., 2012).

II.2.2. Low-Temperature Flow properties

Low temperature performance is one of the most important properties for users of biodiesel, reflects the behaviour of the fuel and it depends on the cloud point (CP), pour point (PP) and cold filter plugging point (CFPP) of the fuel.

- Cloud Point (CP): Is the temperature at which sample of fuel starts to appear cloudy, indicating that wax crystals have begun; it can clog the fuel lines and filters. (Amit, S., 2012).

  The figure II.2 compare the different cloud points between the raw materials.

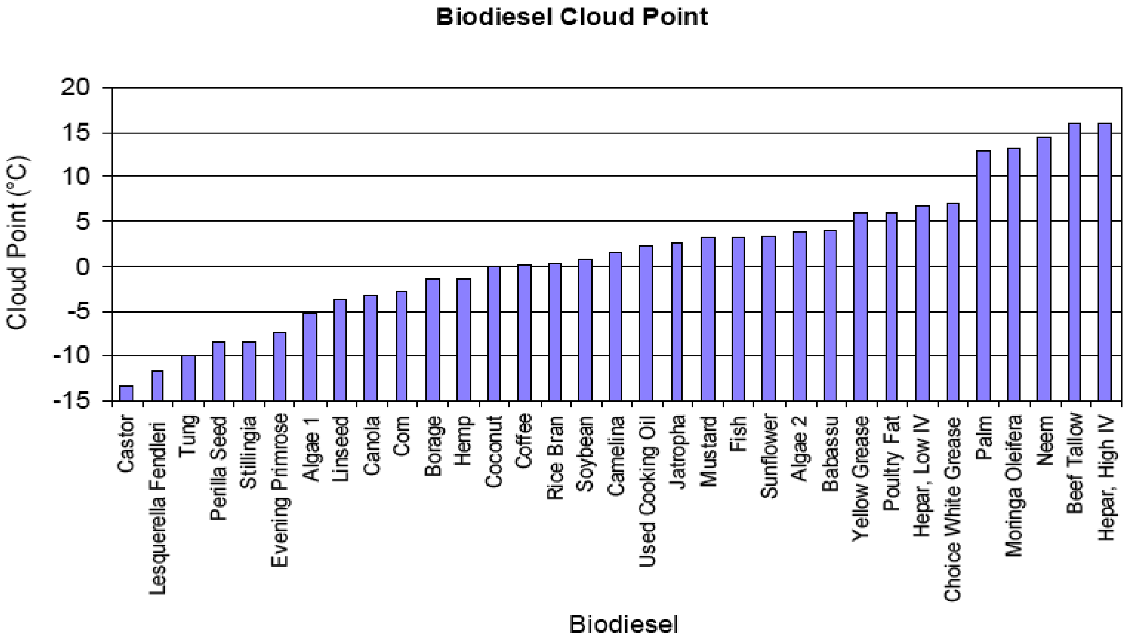


Figure II.2. Biodiesel cloud point (CP). (Renewable energy group, 1995)

- Pour Point (PP): Represent the lowest temperature at which oil can still be moved the next table shows the values of different PP in function of the feedstock. (Mushtaq, et al., 2013).

Table II.2 Different values of PP. (Mittelbach, M., 2005)

BIODIESEL FEEDSTOCK	POUR POINT (PP) ^{O}C
SOYBEAN OIL	0
PALM OIL	-15
JATROPHA OIL	-6
CANOLA OIL	-9
TALLOW	-6

- Cold Filter Plugging Point(CFPP): Reflects its cold weather performance. At low operating temperatures, fuel may thicken and might not flow properly. It defines the fuel's limit of filterability. Fatty acid chains, particularly, the saturated fatty acid chains, play an important role in determining the cold flow properties of biodiesel fuel, the figure II.3 describes the variation of the CFPP value in function of the raw materials; that means the content of saturated fatty acids. (Mushtaq, et al., 2013).

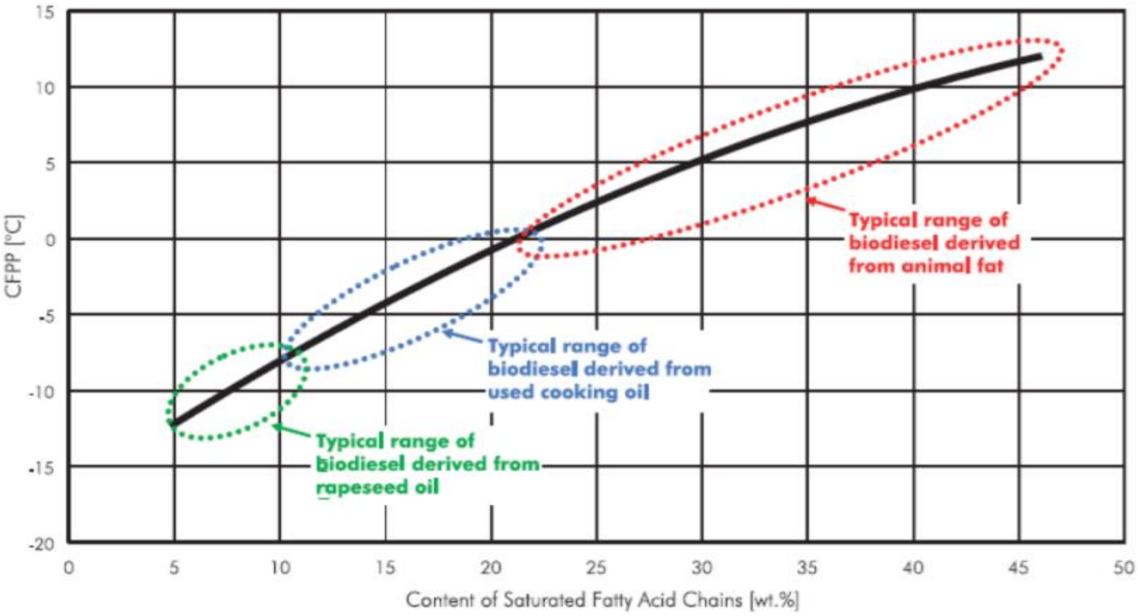


Figure II.3 Relation between saturated fatty acid chain in biodiesel and its CFPP value. (Chhetri, et al., 2008).

II.3. Quality properties

Quality is a prerequisite for the long-term success of a biofuel. It depends on several factors that reflect the chemical and physical characteristics of the biodiesel.

There is a series of regulations that determinate the acceptable ranges of values of the parameters and compounds that the biodiesel must have to be commercialized, also exist some factors that influenced in the quality as: the production process, the raw materials, the postproduction. (István, B., 2011).

II.3.1. Cetane number

Cetane number (CN) is a diesel fuel quality parameter related to the ignition delay time and combustion quality, higher value of the CN means better ignition properties of the fuel and it increase with bigger length of the fatty acid chains and ester groups. (Amit, S., 2012), If we compare diesel and biodiesel the value of the CN in biodiesel is higher, so the biodiesel has higher combustion efficiency. (Mushtaq, et al., 2013).

Differences situations according to the value of the CN:

- High value: good cold-start properties and lessening the formation of white smoke.
- Low value: deterioration and higher exhaust emissions (particulates and hydrocarbons. (L.C. Meher 2009).

CN affects many engine performance parameters like combustion, stability, driveability, white smoke, noise, and emissions of CO and HC. (Mushtaq, et al., 2013).

II3.2. Copper strip corrosion

Basing us in the EN-ISO 2160, to have the highest quality possible a measure of possible difficulties with copper, zinc, brass or bronze parts of the fuel system must be made with the objective of determinate the corrosiveness. The presence of acids or sulfur compounds might induce the corrosion so, this parameter is related with the acid number.

To determinate the grade of corrosiveness of the fuel on copper a test is performed: a polished copper strip is immersed in a specific volume of the sample; is heated under conditions of temperature and time that are specific of the material. At the end, the copper strip is removed and washed, the colour and tarnish level are assessed against the standards. The equipment is described in the figure II.4 and figure II.5.

Figure II.4 Copper corrosion tester. (Yung et al., 2009).

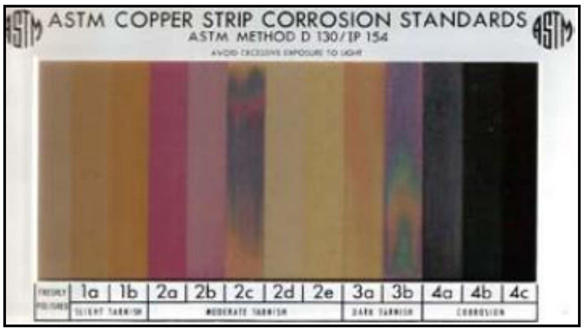


Figure II.5 Copper strip corrosion standards. (Yung et al., 2009).

II.3.3. Phosphorus content

The amount of phosphorus in the biodiesel proceed from animal and vegetables (phospholipids), and inorganic salts (used frying oil). (Tripartite task force 2007)

The point of the phosphorus presence in the diesel fuels is that it can damage the catalytic converters used in emission. To have a good quality of fuel the phosphorous content should be as low as it could. (Amit, S., 2012).

II.3.4. Conradson Carbon residue

The term carbon residue is used to measure the tendency of carbonaceous residue formed during evaporation and pyrolysis that is deposited in the fuel oil**.** (Amit, S., 2012). The Conradson indicator shows the quality of the biodiesel because it has a strong relationship with the triglycerides that don’t reaction in the transesterification step and also with the content of soaps, polymers, catalytic residues and impurities. (Molina, C., 2012).

There are many tests for carbon residue that provides the value of carbon residue in specific conditions and some indication of relative coke forming propensity, these tests are: Conradson (D 189), Ramsbottom (D 524) and Micro method (D 4530).

II.3.5. Storage stability

The degree of unsaturation makes the vegetable oil derivates susceptible to be deteriorate by thermal/oxidative polymerization, these reactions favour the formation of insoluble products that cause problems in the fuel system.

Several properties during the storage demonstrated changes related with the raw material, like viscosity, peroxide value and Rancimat induction period. (Mushtaq, et al., 2013).

The figure II.6 represents one diesel/biodiesel storage tank typical from fuel stations.

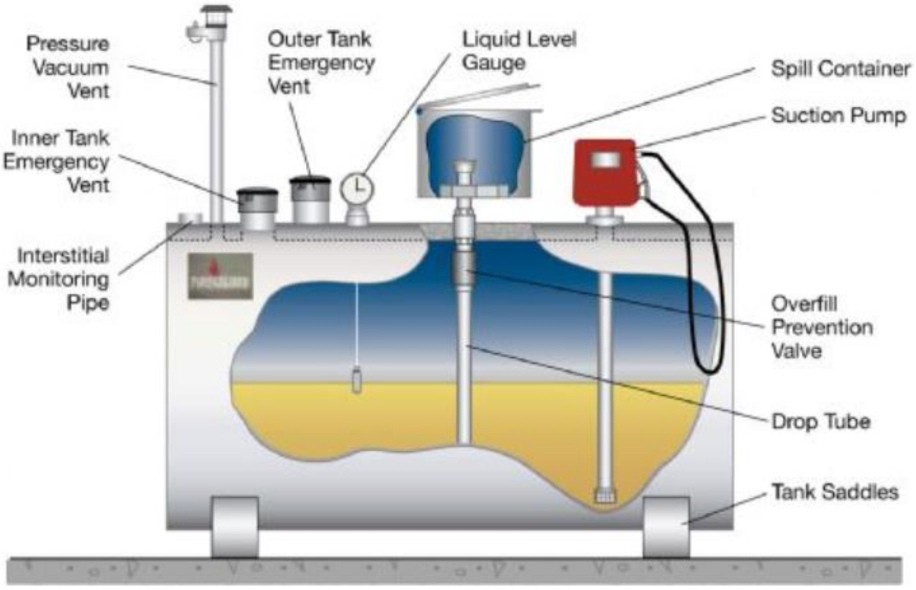


Figure II.6 Storage system of diesel/biodiesel in a fuel station. (Mashoshin 2017)

II.4. Contaminates

Biodiesel production is very susceptible to contain some contaminates that obstruct to reach the optimal values of the product characteristics, that's why is due to control some limits of compounds quantities. The following sections describe the most important compounds that must be controlled.

II.4.1. Sulfated Ash

The formation of Sulfated ash proceeds from the oxidation of the compounds such as abrasive solids, soluble metallic soaps and catalyst residues during the combustion; It contributes to injector, fuel pump, ring wear and piston and to engine deposits.
The primary forming materials that appears in the biodiesel are calcium, magnesium, sodium and potassium. (Mittelbach, M., 2005)

II.4.2. Sulfur content

The presence of sulphur on the engine and deposits depends principally on the operation conditions and affect in the limits of environmental emissions, that’s why is due to have a strong control system. (Mittelbach, M., 2005)

II.4.3. Alkali and alkaline Earth metals

These compounds are partially limited by the sulfated ash, however is necessary a tighter control for vehicles with particulate traps. The formation of this metals in the fuel is because: (Amit, S., 2012).

- Alkali metals from catalyst residues and alkaline earth metals originate from the washing step with hard water.
- Metal ions introduces during the production process or storage.
- Sodium and Potassium from the sulphated ash in the engine.
- Calcium soaps from the ash that cause the injection pump sticking. (Tripartite task force 2007)

II.4.4. Methanol or Ethanol content

The presence of these two alcohols are negatives to the biodiesel product because:

- Material level: Are harmful to some materials in fuel distribution and vehicle fuel system.
- Chemical level: Can cause corrosion, low lubricity, changes the flash point of esters and generate adverse effects on injectors due to their high volatilities. (Tripartite task force 2007).

II.4.5. Ester content

In terms of quality this parameter provides the information of our fuel that defines it as a biodiesel or not in the legal limits. We distinguish between two situations:

- High ester content as unsaponifiable matter (residual alcohols, partial glycerides and sterols) can lead to values below the limit.
- Low ester content originates inappropriate reaction conditions. (Tripartite task force 2007)

II.4.6. Water and sediments

The water in the biodiesel can be found in two forms: dissolved or as small drops floating. The second case can produce important problems in the injection system generating corrosion in the engine. The main problems

Biodiesel with considerable water content shows bad behaviour in cold situations because when the temperature is around 0 ^{o}C it triggers the formation of ice crystal that advantage the solidification of the fuel. (Yuan Lin et al., 2007; Leung et al., 2010; Lin et al., 2010).

During the storage, the water is acidified and it attacks to the vessels and favours the formation of microorganism such as bacteria, fungi, etc, that originate sludges and sediments that obstruct the fuel filters and/or can transform the content of sulfur to sulfuric acid and it derivates in the corrosion of pipes, vessels, engine, etc. Definitely is necessary to be careful in the storage conditions and the microbial contamination that affects to the stability of the biodiesel. (Predojevic, 2008; Demirbas, 2009; Azócar et al., 2010).

The figure II.7 represents three samples of biodiesel with different percentage of water content, being at left the optimum biodiesel with the lowest water content, in the middle a hygroscopic glycerides sample and at right a cloudy biodiesel with the highest percentage of water

Figure II.7 Different samples of biodiesel. (Make biodiesel 2017)

II.4.7. Glycerol

The free glycerol content is an indicator of the quality of the production process. High values of glycerol may come from insufficient separation or washing of the ester product. The limits of the glycerol values are specified because free glycerol can attract other polar components such as monoglycerides, water and soap. These can lodge in the vehicle fuel filter and cause damage in the fuel injection system and can also cause injector coking. (Tripartite task force 2007)

The figure II.8 shows how easy is to see the difference between the biodiesel and the glycerol.

Figure II.8 Mixture biodiesel and glycerol.

II.4.8. Glycerine

To measure the level of glycerine in the fuel is used the total glycerine method that includes free glycerine and the glycerine portion of any unreacted or partially reacted oil or fat. Principal situations:

- High levels of mono-, di- and triglycerides can cause injector deposits and negatives effects with cold weather such as filter plugging.
- Low levels of glycerine ensure the conversion of the fat and oil into monoalkyl esters. (Amit, S., 2012).

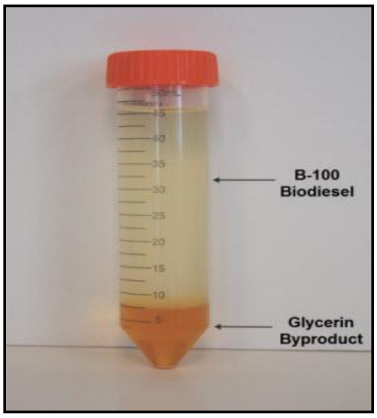


Figure II.9 Mixture of biodiesel and glycerine.

II.4.9. Mono-, Di- and Tri-glycerides

The amount of glyceride depends on the production process. Higher value of glyceride contents is prone to deposit formation on pistons, injection nozzles and valves. (Amit, S., 2012).

II.4.10. Linolenic acid Methyl ester and Polyunsaturation content

Some experts have suggested limiting the content of linolenic acid methyl ester and polyunsaturated biodiesel to have a stricter control in the polymerization of glycerides that can derivate to deposit formation or deterioration of lubrication properties is necessary to limit the unsaturated fatty acids, because of this many types of seeds oil have been discarded. (Mittelbach, M., 2005)

II.4.11. Total contamination

Total contamination is defined as "the amount of insoluble material retained after filtration of a fuel sample under standardized conditions" (Tripartite task force 2007). This parameter allows us to have a criterion of the amount of insoluble impurities that can cause blockage of injection pumps and fuel filters. (Amit, S., 2012).

II.5. Chemical properties

In general, the oils can't be used directly as fuels without a previous transformation into biofuels through the transesterification reaction. In order to realize this reaction is due to have the knowledge of the principal chemical and physic properties of the biofuels because with that we can foresee the minimum requirements of the transformation operation.

II.5.1. Kinematic viscosity

The viscosity is a fluid property that measure the resistance to gradual deformation by shear stress. The shear resistance in a fluid is caused by inter molecular frictions exerted when layers of fluid attempt to slide by one another; is the measure of a fluids resistance to flow, and the term kinematics refers to the quantitative description of fluid motion or deformation. (R.H., Perry, 1997).

This chemical property is one of the most important inconvenient that the oils have because, it generates: increase the CO emissions, incomplete combustion, obstruction of the injectors, etc. These problems exist because the scarce use of oil as biofuel during the injection, a cause of its high viscosity. (Molina, C., 2012).

Besides, the oils can’t be use directly in cold weather because the viscosity rise when the temperature is lower. To solve the viscosity problem the oil must be chemical modified through pyrolysis, emulsion or transesterification, the last one is which is more clean and respectful with the environment. (Alptekin et al., 2008).

The figure II.10 shows the changes of the kinematic viscosity of samples of biodiesel with different percentages of biodiesel content, as it was told the value of temperature and the biodiesel composition change the kinematic viscosity, and its directly proportional.

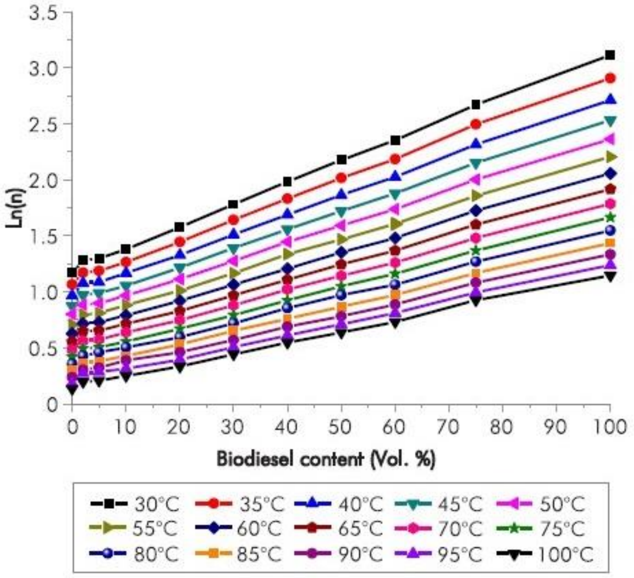


Figure II.10 Experimental results of the kinematic viscosity. (Knothe, 2005).

II.5.2. Flash point

The flash point is defined as *"the lowest temperature at which vapours above a volatile combustible substance ignite in air when exposed to flame"* (R.H., Perry, 1997). Is an important chemical property that must be determinate for legal requirements and safety precautions involved in fuel handling and storage.
This property is used as the mechanism to limit the level of unreacted alcohol remaining in the finished fuel and as an indicator of the presence of methanol. To manipulate the value of the flash point can be use the quantity of residual alcohol because both are strictly correlated. (Amit, S., 2012).

II.5.3. Volatility and distillation temperature

The volatility represents the tendency of the biodiesel to change to a vapour phase in specific conditions, it affects to the start of the engine, that is why the value of the volatility is regulated and it must be between some limits. Higher volatility means bigger capacity of vaporization outside the injector.
The distillation temperature allows us to determinate the presence of esters in the fuel, the behaviour of the biodiesel during the storage, the relationship between the fuel and the engine and provide us the legal definition of biodiesel.

With the distillation curve, it can evaluate the chemical stability of the FAME because it can decompound into rubber and residues in the injector or the surface of the deposit, it can derivate in bad behaviour of the engine, corrosion and the formation of exhaust gas. That is why this parameter must be analysed with the objective of not damage the diesel engine, because the biodiesel is an oxygen fuel and it has different behaviour as the regular diesel. (Phan et al.,2008).

II.5.4. Acid number

Acid number or neutralization number is an indicator of the stability of the biodiesel, it measures the amount of free fatty acids contained and the value increase with the time, so, lower value of acid number means better transesterification reaction. (Predojevic (2008) and Knothe et al. (2009))

The systems that works at elevate temperatures accelerate the degradation and that's why the acid number increase. (Tang et al., 2008). It is expressed in mg KOH required to neutralize 1 gram of FAME.

The increase of the acid number also increases the possibilities of: corrosion, oxidation, decrease the stability of the biodiesel, etc.

II.5.5. Density

The density of biodiesel is usually higher than the diesel, whose levels should be between 820 and 845 kg/m^3 (UNE-EN 590:2009). In the case of biodiesel, the value of the density is higher and depends on the length of the fatty acid chains, so shorter chains and more instaurations generate higher density, and the purity of the biodiesel. (Molina, C., 2012).

II.5.6. Iodine

The iodine value is a measure of the total unsaturation within a mixture of fatty acids, and is expressed as the grams of iodine which will react with 100 grams of biodiesel. (Amit, S., 2012). Must distinguish between to principal situations:

- High iodine number: It presents a higher quantity of unsaturated acids and it improves the operativity of biodiesel with low temperatures but also favours the oxidation and polymerization in the storage, this situation favours the formation of heavy compounds that can clog the engine deposit and the injection system.
- Low iodine number: It improves the stability against oxidation and prevent the generation of polymers avoiding the previous problems. (Vicente et al., 1998, 2004; Abdullah et al., 2007).

II.5.7. Lubricity

Lubricity refers to the reduction of friction between solid surfaces in relative motion decreasing the engine wear. Two mechanisms contribute to overall lubricity:

- Boundary lubrication: Compounds that adhere to the metallic surface generate a protective surface that avoid the wear.
- Hydrodynamic lubrication: Liquid layer prevents contact between opposite surfaces. (National Renewable energy lab., 2009).

CHAPTER III

PRODUCTION OF BIODIESEL

III.1. Oil extraction

Depending on the production scale we have different equipment, but the most practical and economical way to extract oil from seeds is with commercial hydraulic presses (Figure III.1). Currently exists three types of commercial processing systems:

- Solvent extraction: a portion of the oil is removed by expellers and the rest can be extracted with organic solvent.
- Expeller pressing: mechanically extraction of the oil from the seed.
- Direct solvent extraction: The oil is removed directly from the seed with an organic solvent.

Figure III.1 Electrical hydraulic presses (Mushtaq, et al., 2013).

The objectives of the extraction steps are:

- Produce components without undesirable impurities.
- Minimize the damage to the fat or oil in the solid extraction.
- Produce a residual oil cake of the greatest possible value.
- Maximize the yield of fat or oil from the oil-bearing material. (Mushtaq, et al., 2013).

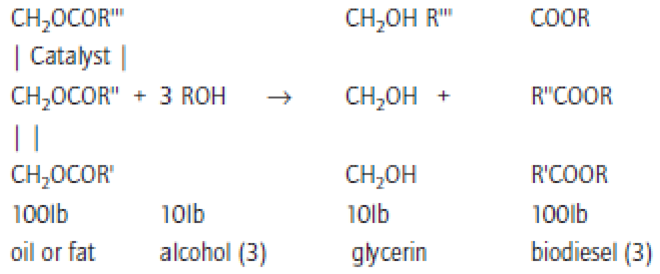
III.2. Biodiesel synthesis

Biodiesel standards ensure that the following critical factors must be controlled: Complete reaction, absence of free fatty acids, low sulphur content, removal of glycerine, removal of alcohol and removal of catalyst.

In terms of production and processes there are different routes of synthesized, the most common is the base-catalysed transesterification of the oil because:

- It is a direct conversion to biodiesel.
- It is a process which works at low temperature and pressure.
- Yields high conversion (98%).
- No exotic or complex construction materials are needed. (Simon Ford 2007)

The biodiesel chemical reaction that is realized in this process is described in the figure III.2 in pounds, the alcohol that is used is usually methanol but, sometimes is ethanol, is charged in excess to assist in a rapid conversion. The catalyst is usually potassium or sodium hydroxide that has already been mixed with the alcohol.



$$\begin{array}{lllll} CH_2OCOR''' & & & CH_2OH\ R''' & COOR \\ |\ \text{Catalyst}\ | & & & & \\ CH_2OCOR'' + & 3\ ROH & \rightarrow & CH_2OH\ + & R''COOR \\ |\ | & & & & \\ CH_2OCOR' & & & CH_2OH & R'COOR \\ 100lb & 10lb & & 10lb & 100lb \\ \text{oil or fat} & \text{alcohol (3)} & & \text{glycerin} & \text{biodiesel (3)} \end{array}$$

Figure III.2 Based-catalysed transesterification chemical reactions (Simon Ford 2007)

The general production process of biodiesel with base-catalysed transesterification is descried in the figure III.3 and occurs using the following steps:

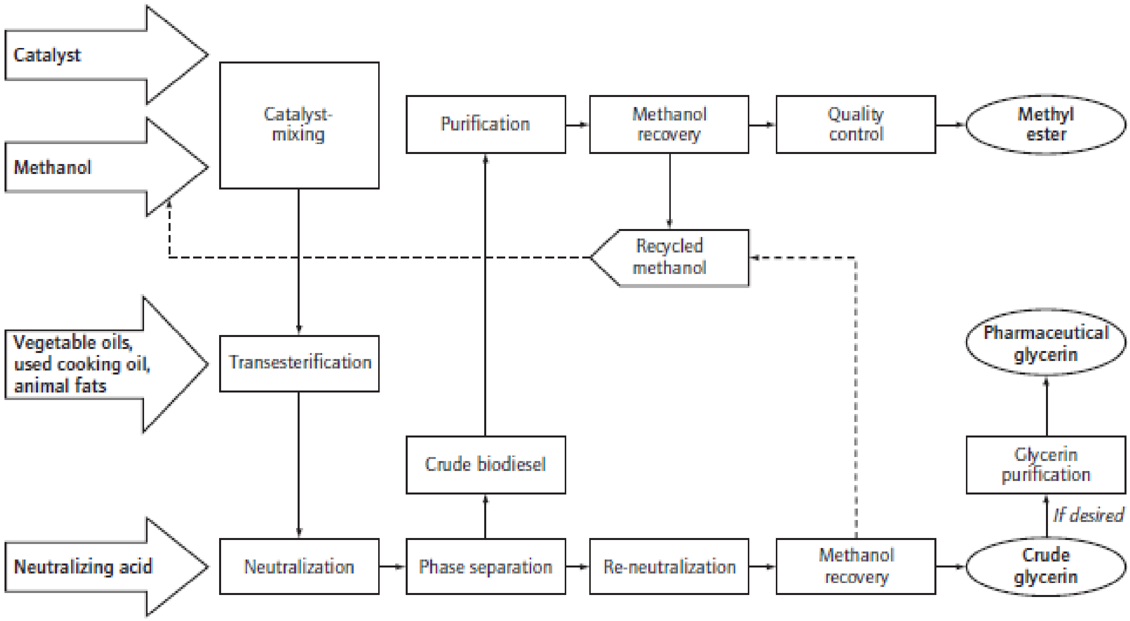


Figure III.3 Based-catalysed transesterification production scheme (Simon Ford 2007)

1. **Mixing of alcohol and catalyst**

The catalyst dissolved in the alcohol via standard agitator or mixer.

2. Transesterification

Transesterification or alcoholysis is the displacement of alcohol from an ester by another in a process similar to hydrolysis, but with alcohol instead of water, the figure 16 represent that reaction. This process has been widely used to reduce the high viscosity of triglycerides, the most common alcohol that is used is methanol because the low water content and the price.

The mix is charged into a closed vessel with the oil or the fat, the reactions is maintained above the boiling point of the alcohol (72 ^{o}C) in order to control the speed of the reaction. The time of this step varies between 1 hour and 8 hours. It is important to monitor the amount of water and free fatty acids in the incoming oil or fat because, if the free fatty acid level or water level overcome the limits it may cause soap formation. (Mushtaq, et al., 2013).

3. Separation

The reacted mixture is frequently neutralised at this stage. The glycerine is gravity separated drawing off the bottom of the settling vessel. Another alternative that can be used to separate these two materials is centrifuge. (Simon Ford 2007)

4. Alcohol removal

To remove the excess of alcohol from the mixture the separation can be realized by distillation or flash evaporation. The alcohol that was removal can be re-used in the beginning of the process. Highest yields happen when no water has accumulated in the recovered alcohol stream. (Simon Ford 2007)

5. Glycerine neutralisation

The glycerine by-product contains unused catalyst and soap that are neutralised with an acid and sent to storage as crude glycerine that will be purify to 99% and can be use in pharmaceutical and cosmetic applications. (Simon Ford 2007)

6. Methyl ester wash

The last step of biodiesel synthesis is to purify the product by washing with warm water with the objective to remove soaps or residual catalyst, dried and sent to the storage the result.

The storage product will be clear, amber, yellow liquid with similar appearance as petrodiesel. (Simon Ford 2007).

III.3. Industrial production

Biodiesel processing is related with the quality of the product. The process used to refine the feedstock determinate the fuel application and specifications. The figure III.4 represents a diagram of a biodiesel production with alkali-catalysed transesterification with feedstocks with a low level of FFA contains.

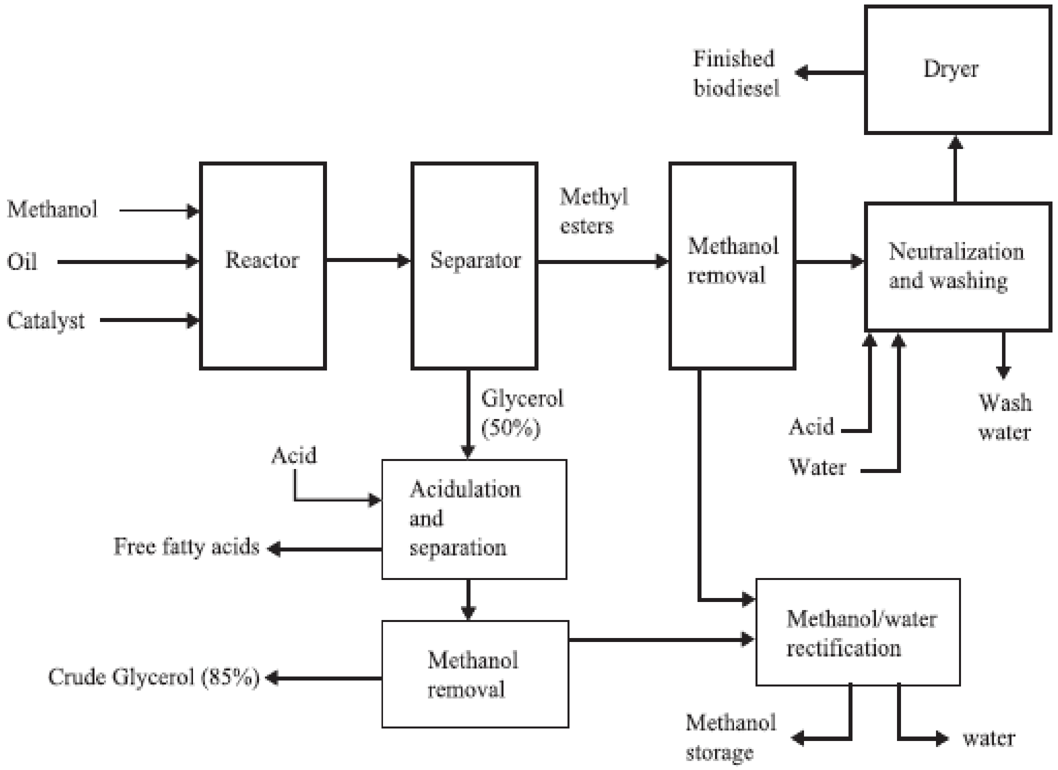


Figure III.4 Biodiesel production in industrial scale. (Jon Van Gerpen, 2015).

III.4. Different treatments

With the objective of use oil as fuel is necessary to submit it to some treatments. Those treatments have the aim to reduce the high viscosity of the oils and avoid problems in the engine deposit and in the proper performance of the engine, the most commonly treatments are: Microemulsion, pyrolysis, dilution with petroleum and transesterification.

A. Pyrolysis

Pyrolysis is a thermochemical process that converts one substance into another heating in the absence of air or oxygen. Two different routes of pyrolysis are considered currently:

- Hydrodeoxygenation (HDO) of pyrolysis oil to produce an oil refinery compatible feedstock or final biofuel.
- Syngas production from pyrolysis oil.

The figure III.5 is a scheme of these two routes.

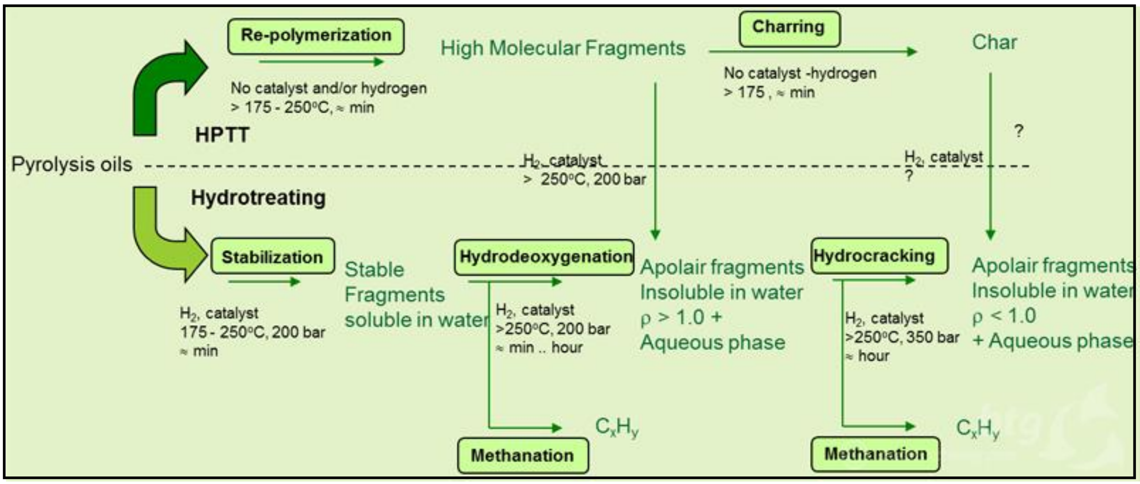


Figure III.5. Pyrolysis routes. (Biomass Tech. Group, 2017).

B. Dilution with petroleum

The vegetable oil is diluted with petroleum diesel to run the engine. The key of this process is the composition of the mixture, with a pre-combustion step with a mixture of 10% vegetable oil and 90% of petroleum to maintain total power without any alteration or adjustment to the engine. The maximum oil percentage that was successful tried was 20%. (Mushtaq, et al., 2013).

C. Microemulsion

Microemulsion is defined as a colloidal equilibrium dispersion optically isotropic fluid microstructure with two immiscible liquids and one or more ionic amphiphiles. (Schwab et al. 1988).

CHAPTER IV

OBJECTIVE

Currently, there is no doubt that the substitution of fossil fuels with biofuels presents a high interest, since it is a source of renewable energy. The use of fatty waste materials as frying oil make possible to alleviate the problem of collecting the raw materials and decrease the contamination of this type of wastes.

This thesis analysis how to manufacture biodiesel from fatty waste materials in laboratory scale and the characterization of the different kinds of biodiesel such the possibility of use the final product as biofuel in order to accomplish the limits of the law.

CHAPTER V

EXPERIMENTAL SYNTHESIS

V.1. Experimental synthesis

The objective of these research project is to synthesized biodiesel from four different types of raw materials (Figure V.1) and analysed the quality of the produce.

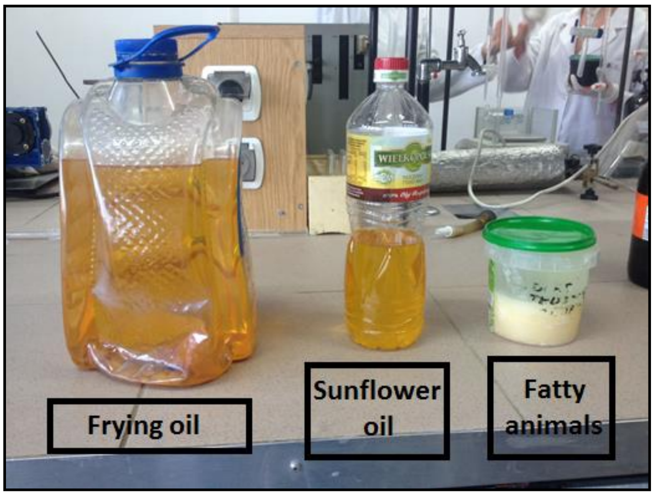


Figure V.1. Raw materials except rapeseed oil.

V.1.1. Calculation of the Acidic value of the samples.

1. Measure 4-5 grams of the oil. The quantities used to this step are described in the table V.1.

Table V.1. Samples of the different raw materials.

OIL	WEIGHT [GRAMS]
FRYING OIL	4.712
SUNFLOWER OIL	5.093
FATTY ANIMALS	4.544
RAPESEED	1.97

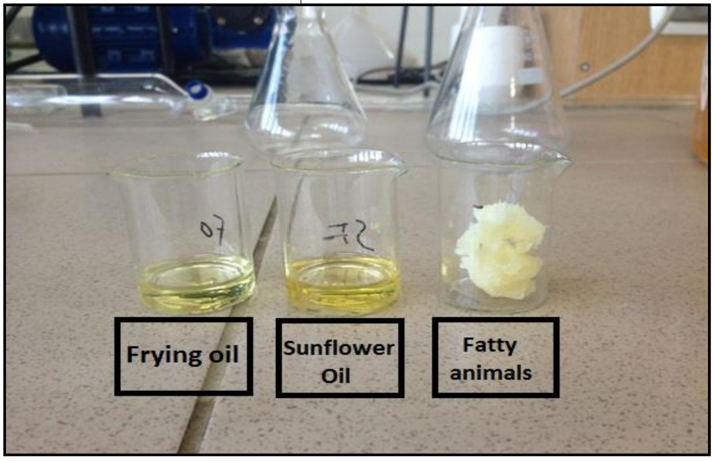


Figure V.2. Samples of the raw materials previous mixture with ethanol

2. Mix the oil with 40 mL of ethanol (in the case of rapeseed oil only with 20 ml).

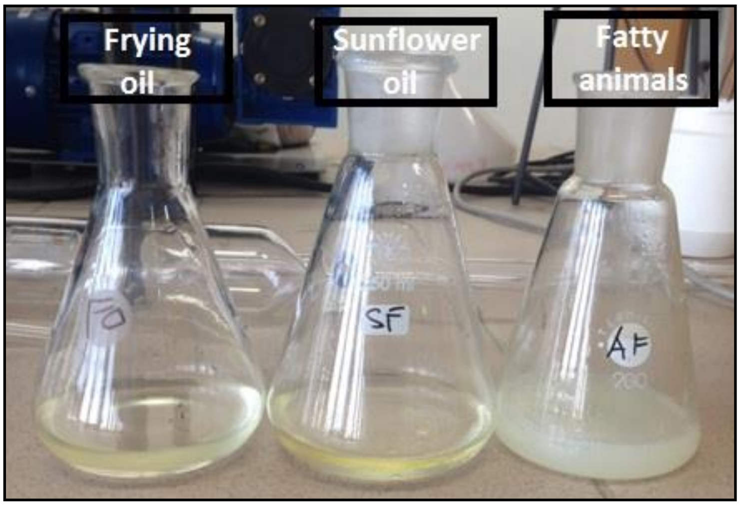


Figure V.3. Mixture between the samples and 40 ml of ethanol.

3. Add one drop of Phenolphthalein.

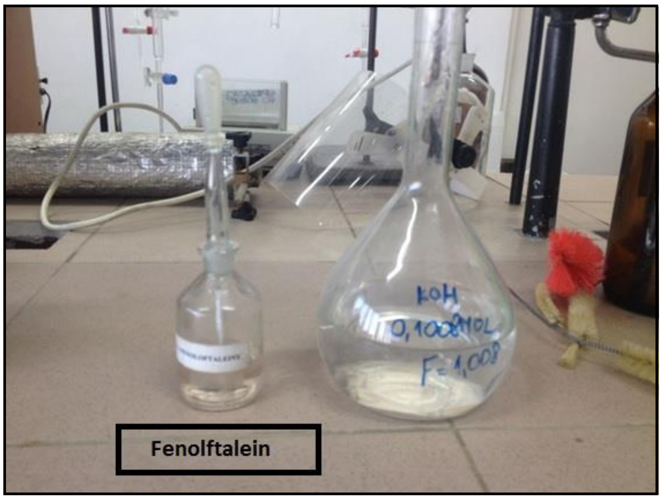


Figure V.4. Chemicals compounds necessary to do the valorisation.

4. Valorisation with KOH 0.1 mL to determinate de acidic value (LK). The results of the quantity of KOH are described in the following table V.6.

Table V.6. Values of the consumed volume of KOH.

OIL	$V\text{-}V_O$ [ML]
FRYING OIL	5.2
SUNFLOWER OIL	1.5
FATTY ANIMALS	5.4
RAPESEED	0.9

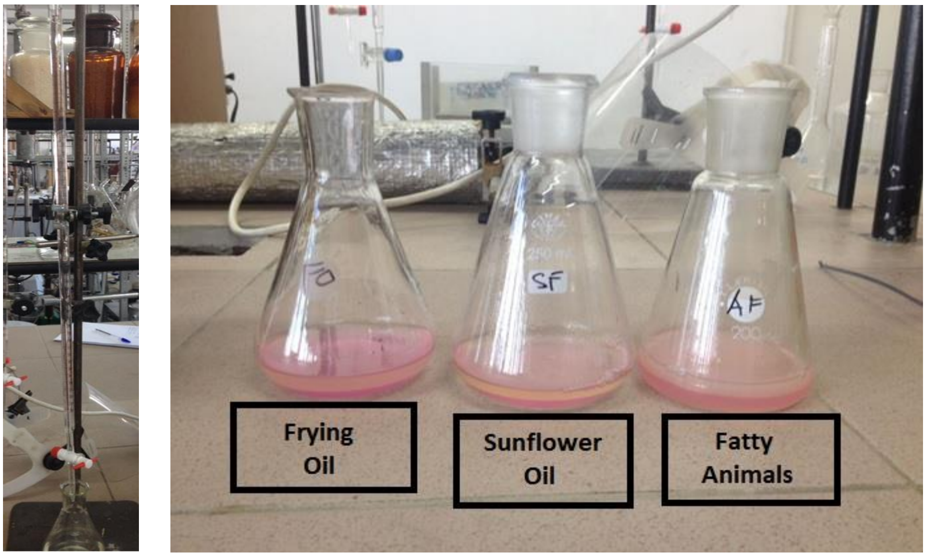


Figure V.6. At left equipment to do the valorisation and at right the results.

Calculate the value of the acidic value applying the next equation:

$$\boldsymbol{LK = \frac{56.1x(V - V_o)C_{KOH}}{m}\ [mg\frac{KOH}{g}oil]}$$

The results are:

Table V.7. Different acidic values.

OIL	LK
FRYING OIL	6.19
SUNFLOWER OIL	1.652
FATTY ANIMALS	6.67
RAPESEED	2.563

The value of the LK allows us to choose which is the best way to synthesised biodiesel. In the case of the frying oil and the fatty animals the acidic value is to high so, we will follow the Case A but, instead use methanol and KOH as catalysed it will be use Methanol with 2.5% of H_2SO_4.

V.1.2. Quantity of KOH and MeOH necessary in the process.

1. Determinate the quantity of KOH necessary for the neutralization of free fatty acids present in the raw material. This value is 1% of the quantity of oil used.

Table V.8. Quantity of KOH.

OIL	QUANTITY [GRAMS]	KOH [GRAMS]
FRYING OIL	215.4	2.154
FRYING OIL 2	124.57	1.25
SUNFLOWER OIL	215.4	2.154
SUNFLOWER OIL 2	104.7	1.047
FATTY ANIMALS	103.98	1.04
FATTY ANIMALS 2	85.93	0.86
RAPESEED OIL	198	1.98

2. Dissolve KOH in methanol assuming the molar MeOH is oil=6-12:1.

Calculations:

Molecular weight of oleic acid = 282.47 x 3-3x18+92= 884 g/mol.

Density of methanol=0.79g/cm^3.

Quantity of Oleic Acid = M_{oil} x 1/884.

Mass of MeOH = Quantity of Oleic acid x 6 x molecular Weight of MeOH.

In the case of Frying oil and fatty animals the result must be multiply by 2 because the methanol that will be use has 2.5% of sulfuric acid.

Volume of MeOH = Weight of MeOH/density of MeOH.

The results are in the following table.

Table V.9. Quantity of Methanol.

OIL	QUANTITY OF OLEIC ACID [MOL]	MASS MEOH [GRAMS]	VOLUME MEOH [ML]
FRYING OIL	0.243	93.42	118.253
FRYING OIL 2	0.141	57.52	72.81
SUNFLOWER OIL	0.243	46.71	59.12
SUNFLOWER OIL 2	0.118	22.768	28.82
FATTY ANIMALS	0.117	45.22	57.42
FATTY ANIMALS 2	0.097	39.66	50.20
RAPESEED OIL	0.22	43.05	54.51

3. Mixed with the oil for 15 minutes and continue heating at 60 ºC and stirred for 1 hour.

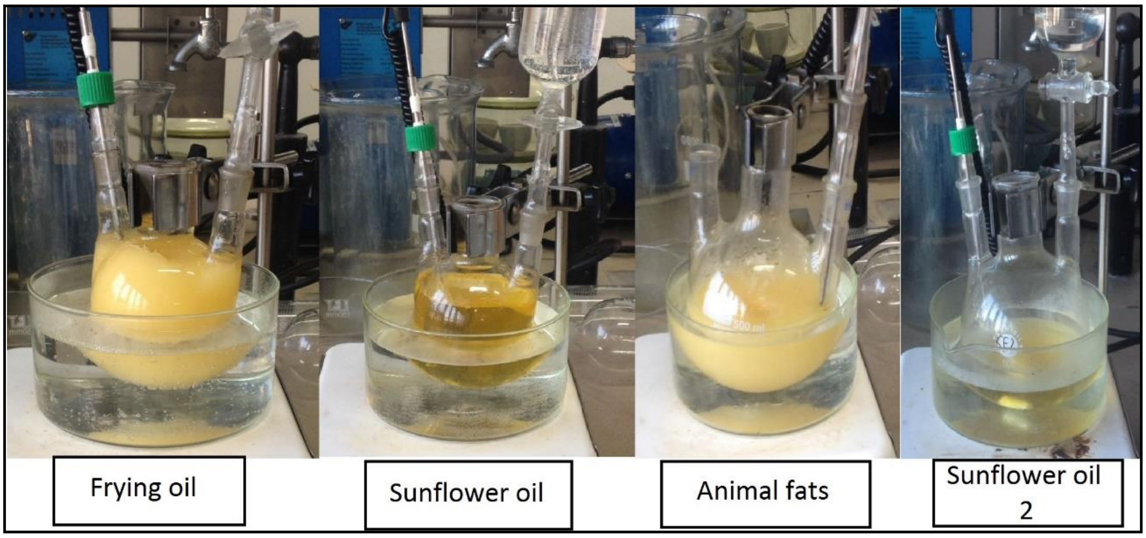


Figure V.7. Some of the samples in the synthesized step.

PROBLEMS

After one hour of heating and stirring the mixture the results are not correct in 5 of the 7 cases.

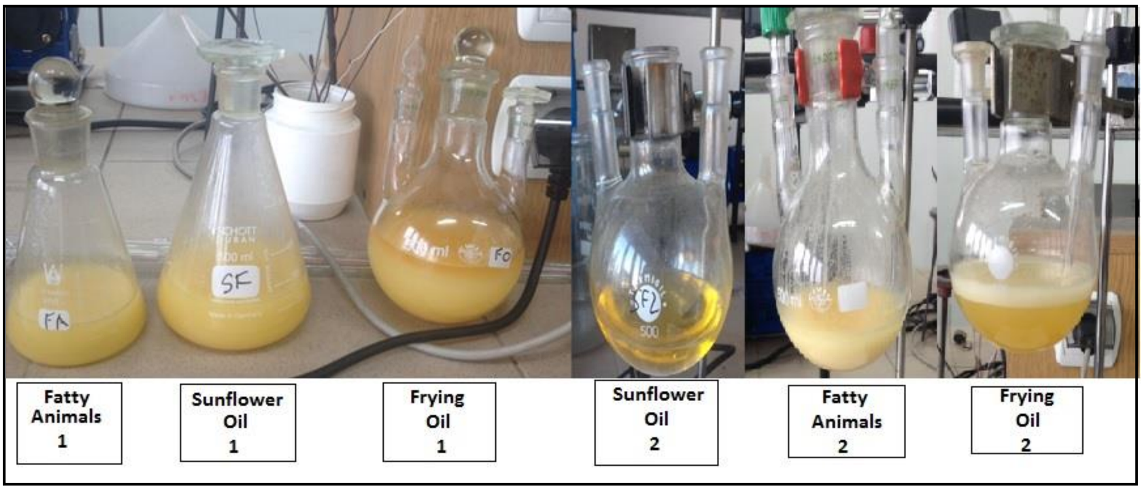


Figure V.8. Results after 2 hours of heating and stir.

- **Fatty animals 1**

The result of the biodiesel derivate from fatty animals has not the correct colour because it has a lot of water that is why is necessary to heat it until 90 ºC for 1 hour to see if the result is correct or not.

As can be seen in the figure V.9 the result is totally different that was expected.

Is necessary repeat this step with the animal fats because the result was not correct.

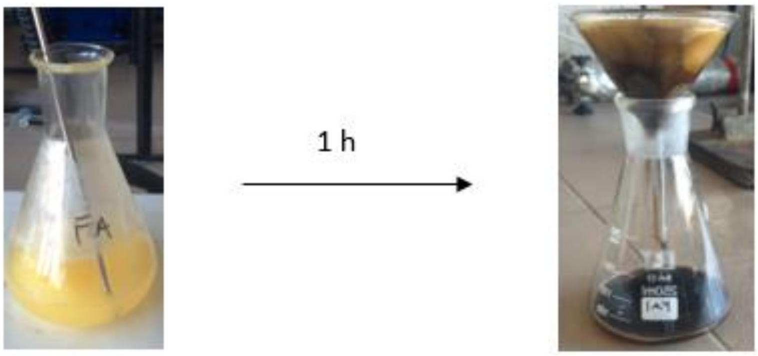


Figure V.9. Fatty animals 1 results.

- **Sunflower oil 1**

The result of sunflower oils was not good, there is not reaction inside so, is necessary to add again the amount of methanol and KOH and repeat the process.

the reaction was not finish in 3 hours and in the top of the solution there is foam. that should be remove carefully with water (not too hot or too cold) that must be drop slowly throw the wall and the result will be milky water. When the foam disappears its necessary to shake carefully the recipe, and to finish this step is necessary remove the last foam with a funnel. (Figure V.10)

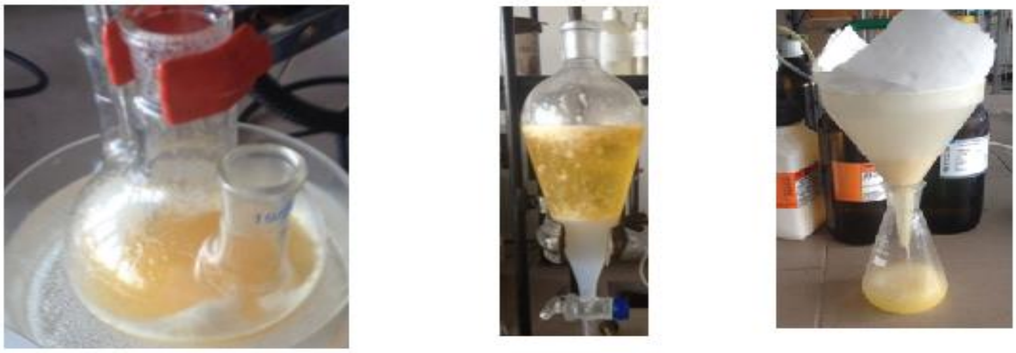


Figure V.10 Sunflower oil 1 result.

- **Frying oil 1**

After the 2 hours there was a problem, the frying oil did not react so, it is necessary to put it 1 hour or more with the reflux equipment.

The result after 2 hours is not that was expected because as the picture describe there is two different phases because the reaction did not realize 100%, and the colour of the result is too milky. (Figure V.11)

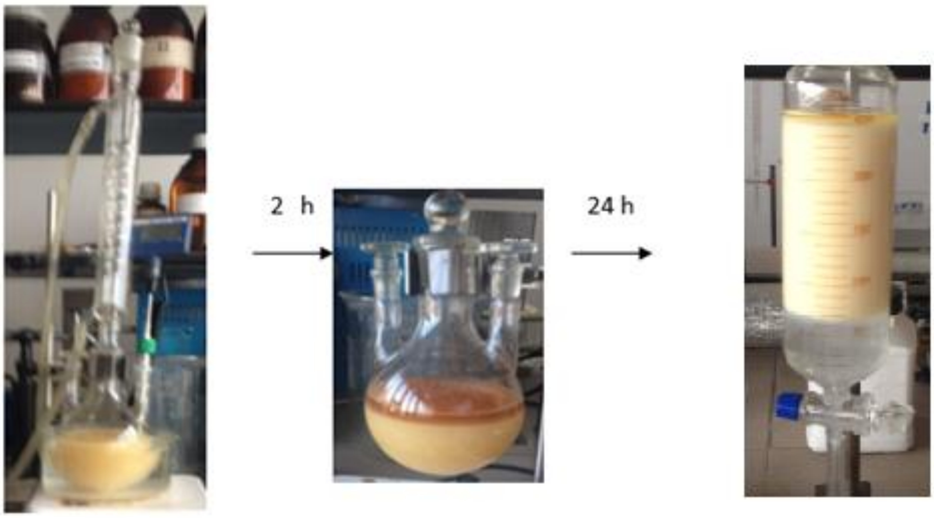


Figure V.11. Frying oil 1 result.

After the heating and stirred in the case of frying oil is necessary to try to remove the brown phase with water and leave the result for one day to separate the water from the biodiesel.

The amount of biodiesel that is obtained is not enough to do any analysis so, this synthesized fail.

- **Fatty animals 2**

The result as the figure 24 shows is too milky and is only one phase in the fluid but, it only means that the dissolution has only monoglycerides and diglycerides ad, the transesterification has not realized full.

To fix it is necessary to decrease the acidic value, the process is:

Wash the fluid with hot water very carefully to remove the sulfuric acid, to analyse the quantity of this compound that is in the dissolution is able to use pH indicator and when it is between 6.6 – 7 it will be done. Then dry the result in the oven and determinate the acidic value. (Figure V.12).

Figure V.12. Fatty animals 2 result after decrease the acidic value.

After all these steps and if the acidic value is lower than 4 is possible to do again a simple synthesis of biodiesel using methanol and KOH. (Table V.10)

- **Frying oil 2**

Same process as fatty animals 2, and the result of the biodiesel is described in the figure V.13.

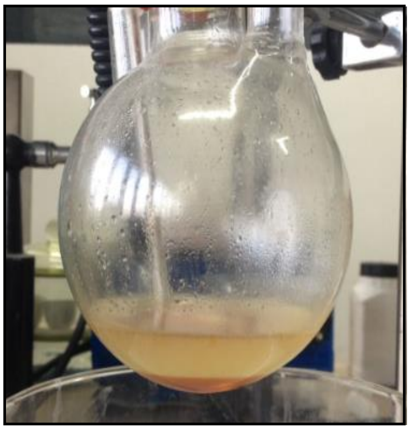


Figure V.13. Biodiesel from frying oil 2.

The table 9 shows the result of the new acidic values, all the values are decreased enough to realize the simple synthesis, the process was successfully.

Table V.10. New acidic values.

OIL	MASS [GRAMS]	V-V_O [ML]	LK
FATTY ANIMALS 2	4.789	3.2	3.75
FRYING OIL 2	4.918	2.2	2.51

V.1.3. Separation of the glycerol

Separation the glycerol using one decanter, because there are two phases in the biodiesel. In the bottom the glycerol and in the top the biodiesel.

Figure V.14. Glycerol + Biodiesel.

V.1.4. Clean of the biodiesel

Clean the biodiesel using one decanter and water as the cleaning element. After the water start to be crystal, is necessary wait a bit for possible leftovers of water.

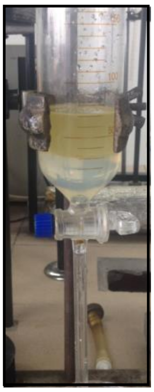


Figure V.15. Washing step.

V.1.5. Drying of the biodiesel

Dry of the biodiesel using one funnel and paper to dry.

CHAPTER VI

CHARACTERIZATION OF THE BIODIESEL

In order to determine if the biodiesel that was synthesized is able to use as regular diesel is essential to analyse some properties with the objective of check the results with the stablished limits.

VI.1. Density

1. Measure the weight of the pycnometer empty and annotate the value of the volume, in this case 25 ml and the weight is 15.46 grams.
2. Fill the pycnometer with water and put the cup, dry the outside surface of the pycnometer and measure the weight; 49.18 grams.

   Volume of pycnometer $= \frac{m_{H_2O}}{\rho_{H_2O}} = \frac{49.18g}{1^g/_{cm^3}} = 49.18\ \mathrm{cm}^3\ \&\ 45.96\mathrm{cm}^3$ in the 2^{nd} case
3. Measure the weight of the biodiesel in the pycnometer and apply:

$$\rho_{biodiesel} = \frac{m_{bio-diesel}}{V_{pycnometer}}$$

The results of the mass and the density are described in the table VI.1.

Table VI.1. Density results of the different biodiesels.

OIL	MASS [GRAMS]	DENSITY [G/CM3]
FRYING OIL 2	38.619	0.840
SUNFLOWER OIL 1	42.446	0.863
SUNFLOWER OIL 2	41.879	0.852
FATTY ANIMALS 2	43.407	0.944
RAPESEED OIL	43.40	0.880

VI.2. Cold temperature properties

To determinate the properties at cold temperature of the different biodiesel is necessary to cool one sample and:

- When the sample starts to look like crystal means that this temperature is the cloud point. (Figure VI.1)
- When the sample put in 45 degrees do not slip for 30 seconds means that is the pour point (solidification temperature). (Figure VI.1)

Figure VI.1. Cloud point at left and Pour point at right.

The results of the different biodiesels are display in the table VI.2.

Table VI.2. Characteristics at cold temperature of the different biodiesels.

OIL	CLOUD POINT [^{O}C]	POUR POINT [^{O}C]
FRYING OIL 2	-4	-14
SUNFLOWER 1	-5	-15
SUNFLOWER 2	-4	-14
FATTY ANIMALS 2	6	1
RAPESEED OIL	-7	-16

VI.3. Hot temperature properties

To determinate the heat properties of the biodiesels is necessary to heat the samples with the equipment that is described in the figure VI.2, it must be use very carefully with the presence of humidity in the samples.

Figure VI.2. Heat equipment.

The properties that will be analysed are:

- Temperature when the smoke appears for first time, Smoke point and, allow us to know the sooting tendency of the biofuel.
- Temperature when the sample start to burn, Flash point.

The results are incorporate in the table VI.3 for the biodiesel and in the table VI.4 for the raw materials.

Table VI.3. Characteristics at hot temperature of the biodiesel.

BIODIESEL	SMOKE POINT [^{O}C]	FLASH POINT [^{O}C]
FRYING OIL 2	112	185
SUNFLOWER 1	110	178
SUNFLOWER 2	114	184
FATTY ANIMALS 2	71	110
RAPESEED OIL	168	192

Table VI.4. Characteristics of the oil at hot temperature.

OIL	SMOKE POINT [^{O}C]	FLASH POINT [^{O}C]
SUNFLOWER	240	330
FRYING	260	255
FATTY ANIMALS	-	-

VI.4. Kinematic viscosity

The kinematic viscosity is determinate by measuring the time for a known volume of liquid flowing under gravity to pass through a calibrated glass capillary viscometer type Cannon Fenske (Figure VI.3).

Figure VI.3. Cannon Fenske viscometer.

The measure process is realizing at two different temperatures (figure VI.4) and the obtained time must be multiplicate for the constant value of the viscometer.

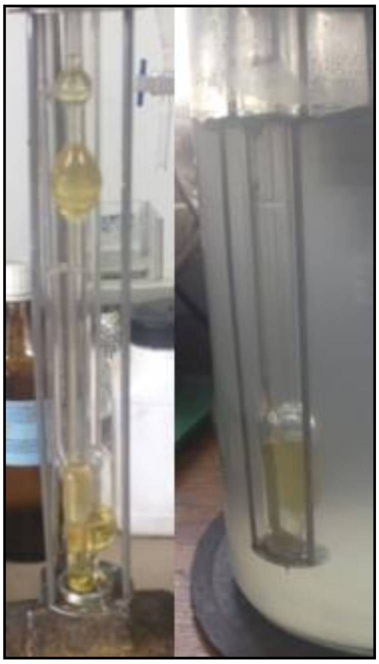


Figure VI.4. At left process at room temperature and at right at 40 °C.

The result of the biodiesel is indicated in the table VI.5 and the value of the constant in the viscometer is K = 0.02695;

Table VI.5. Kinematic viscosity of the biodiesels.

BIODIESEL	TIME 20 °C [SEC]	KINEMATIC VISCOSITY [MM^2/S]	TIME 40 °C [SEC]	KINEMATIC VISCOSITY [MM^2/S]
FRYING OIL 2	1018	27.435	578	15.577
SUNFLOWER 1	1336	36.01	633	17.06
SUNFLOWER 2	897	24.174	417	11.238
FATTY ANIMALS 2	>2100	>56.96	>1800	>48.51
RAPESEED OIL	-	-	-	-

The values for the raw materials are in the table VI.6 and the value of K is 0.0516

Table VI.6. Kinematic viscosity of the raw materials.

OIL	TIME 20 ^{O}C [SEC]	KINEMATIC VISCOSITY [MM^2/S]	TIME 40 ^{O}C [SEC]	KINEMATIC VISCOSITY [MM^2/S]
SUNFLOWER	1589	81.994	599	30.58
FRYING	1735	89.256	646	33.334
FATTY ANIMALS	-	-	-	-

CHAPTER VII

ANALYSIS OF THE RESULTS

After all the process the final result of the biodiesel is show in the figure VII.1, at first glance the result of both sunflower oil has the proper colour, in the case of frying oil is inside of the parameters but after all the process that were describe before about the synthesis from fatty animals the colour is too milky to be a good biodiesel.

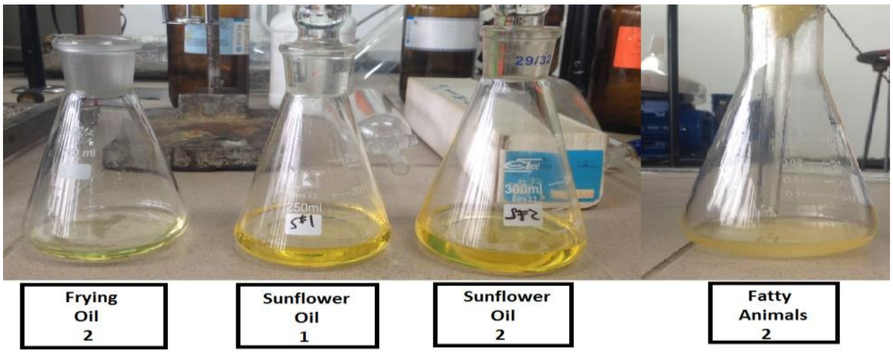


Figure VII.1. Final results of the biodiesel.

After determinate the different values of the properties of the biodiesel is necessary to compare it with the international/European limits, these limits are in the table VII.1.

Table VII.1. Range of the biodiesel properties.

PROPERTIES	NORMATIVE	MIN	MAX
DENSITY [KG/CM^3]	ISO 3675; ISO 12185	860	900
ACID VALUE [MG KOH/G]	EN 14104	-	0.5
CLOUD POINT [^{O}C]	ISO 3015:1992	-	-4.5
POUR POINT [^{O}C]	ISO 3015:1992	-	-15.2
FLASH POINT [^{O}C]	ISO 3679	120	-
KINEMATIC VISCOSITY [MM^2/S]	ISO 3104	3.5	5.0

The easiest way to detect the difference between the result and the limits is with a matrix the difference values will be:

- √ - Able
- X – Not able
- ± - Close

The results are incorporate in the table VII.2.

Table VII.2. Matrix with the results of the analysis.

BIODIESEL	DENSITY	ACID VALUE	CLOUD POINT	POUR POINT	FLASH POINT	VISCOSITY
FRYING OIL 2	√	X	√	√	√	X
SUNFLOWER OIL 1	√	X	±	√	√	X
SUNFLOWER OIL 2	√	X	√	√	√	X
FATTY ANIMALS 2	X	X	√	√	X	X
RAPESEED OIL	√	X	X	±	√	X

The conclusions that the matrix allow us to have is that any of the different biodiesel have enough quality to use is an engine or use it as a fuel because:

- Density

The value of the density is directly linked with the length of the fatty acid chains, so, higher values of density can be interpreter as higher purity of the biodiesel, but the values must be inside the range.

The value of fatty animals 2 biodiesel is outside the limits and it will affect to the kinematic viscosity properties and it can be translate as the raw material did not react with the methanol and KOH in 100%.

- Acid value

The acid number indicates the stability of the biodiesel measuring the amount of free fatty acids, it means higher value of the acidic number worst transesterification reaction. In this case every biodiesel has bigger acidic value than the limits so, the transesterification has not done 100%.

- Cloud point

This parameter is really important because it allow us to know the moment when the wax crystals start to appear and it can clog the fuel lines and filters from the engine.

Except the rapeseed oil all of them are in the range but, this biodiesel is not too far from the limits so, this characteristic is not enough conclusive to discard this biodiesel.

- Pour point

The value of the pour point represents the temperature when the biodiesel stops to slide, is a characteristic very significant because is directly related with the weather; it can affect to engine solidifying the biodiesel and clogging the engine.

All the biodiesels are in the limits.

- Flash point

The value of the flash point must be determinate for legal requirements and safety precautions, and shows the quantity of residual alcohol in the biodiesel.

In this case all the biodiesels have an amount of alcohol in the range of the legislation except the fatty animal biodiesel that has not enough.

- Kinematic viscosity

This property is linked with the CO emissions, obstruction of the injectors, incomplete combustion in the engine, that is why this property is the key of the biodiesel and in the case, that was done all the biodiesel fail, all of them have kinematic viscosity higher than the limits.

After the analysis is possible to determinate as good as the biodiesels are, in this case none of them are available to use directly as fuel because the most important characteristic (viscosity) is out of the limits.

To fix the kinematic viscosity is necessary to do again the transesterification reaction and eliminate all the traces of oil that should be mix with the biodiesel yet.

CHAPTER VIII

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