



Cracow University of  
Technology



Research project

# DEVELOPMENT OF BIODIESEL FROM RAW MATERIALS WITH A HIGH CONTENT OF FREE FATTY ACIDS

CARLOS MONSERRAT AGUILAR

Supervisor – dr Elżbieta Skrzyńska

Cracow 2019

# INDEX

1. ABSTRACT.....	3
2. INTRODUCTION.....	3
2.1 BIOFUELS.....	3
2.1.1 DEFINITION.....	3
2.1.2 CLASSIFICATION .....	3
2.1.3 TYPES .....	4
2.1.4 ADVANTAGES AND DISADVANTAGES.....	5
2.2 BIODIESEL.....	6
2.2.1 DEFINITION.....	6
2.2.2 BIODIESEL ENGINE.....	6
2.2.3 RAW MATERIALS.....	7
2.2.4 TRANSESTERIFICATION REACTION.....	8
2.2.5 BIODIESEL OBTAINING PROCESS.....	9
2.2.6 PROPERTIES.....	11
3. EXPERIMENTAL SESSION.....	13
3.1 PART 1: OBTAINING BIODIESEL.....	13
3.1.1 OBJECTIVE .....	13
3.1.2 INTRODUCTION.....	13
3.1.3 MATERIALS.....	14
3.1.4 EXPERIMENTAL PROCEDURE.....	15
3.1.5 RESULTS DISCUSSION.....	25
3.1.6 EXPERIEMENT COMPARISON.....	34
3.2 PART 2: PROPETIES OF BIODIESEL.....	41
3.2.1 DENSITY.....	41
3.2.2 VISCOSITY.....	43
3.2.3 CLOUD AND FREEZING POINT.....	44
3.2.4 SMOKE AND IGNITION POINT.....	45
3.2.5 CONCLUSION.....	46
4. FINAL CONCLUSION.....	47
5. LITERATURE REVIEW.....	48

# 1. ABSTRACT

In this research project biodiesel will be developed from an oil with a high content of free fatty acids (98.16%) by transesterification, under different reaction conditions, varying both the temperature, the volume of alcohol and the catalyst used. , to know which is more favorable for the raw material used. After this study, a study will be made of the most significant properties (density, viscosity, freezing point, cloud point, acid number, smoke point and ignition point) of the biodiesel obtained to know if it is suitable or not for its use according to the current regulation.

# 2. INTRODUCTION

One of the main objectives of today to cope with climate change is based on finding substitutes for petroleum-based fuels. A feasible and quality alternative is found in biofuels. In this research project, the properties of a biodiesel obtained from fatty raw materials with a high content of fatty acids will be analyzed, but first it is very important to know the different types of biofuels that are currently used and above all, the whole process of obtaining biodiesel, starting with the raw materials to the properties of the final product

## 2.1 BIOFUELS

### 2.1.1 DEFINITION [4]

Biofuels are mixtures of substances of organic origin that are used as fuels to obtain energy. Biofuel is derived from biomass—that is, plant or algae material or animal waste.

The advantage of biofuels is that, in addition to being able to replace part of the consumption of fossil fuels, they reduce the impact produced by them, such as the levels of CO<sub>2</sub> that are emitted into the atmosphere through combustion. Actually, the emission of CO<sub>2</sub> is the same in both, the difference is that in the process of production and development the materials that will produce the biomass destined for biofuels absorb this CO<sub>2</sub> produced.

### 2.1.2 CLASSIFICATION [12]

Biofuels can be classified into three large groups depending on the raw material used and the production process: first, second and third generation biofuels.

- **First generation biofuels:** those that have their origin in agricultural crops used in obtaining products for human consumption such as sugar, starch, vegetable oil such as palm oil or animal fats. The production systems are simpler and cheaper, however, it has serious limitations as they could endanger the food supply, as well as biodiversity.

- **Second generation biofuels:** they arise from the great demand for biofuels and are obtained from biomass of lignocellulosic nature, that is, woody or fibrous in nature. For this reason, although they involve savings in emissions, their production is more expensive and complicated than the first generation. This group of biofuels is produced with crops that are not used for food or that are considered waste such as used oil, stems, fruit shells, sheaths or wood chips.
- **Third generation biofuels:** they also come from the biomass of inedible products or waste, but in this category, microalgae are also included. In this case, molecular biology techniques are used for its production.

### 2.1.3 TYPES OF BIOFUELS<sup>[3]</sup>

Although it is only going to study biodiesel, it is very important to know that other biofuels exist. They are the following type:

- **Biodiesel:** It is made on the basis of vegetable oils, such as soybean oil, palm oil, raps and marigold, both new and used. It also incorporates animal oils, animal fats and fish oil.
- **Bioethanol:** It is manufactured on the basis of alcohol product of the fermentation of sugars, mainly sugar cane and beet. You also get *decerealescomo* wheat, barley and corn, thanks to the starch they contain.
- **Biopropanol or biobutanol:** these two are less popular but the research aims to get their development for use, along with bioethanol and biodiesel, compared to fossil fuels.

Another explanation focused on vehicles.

- **E5:** The biofuel E5 is a mixture of 5 percent bioethanol and 95 percent gasoline. This is the usual mixture and the maximum currently authorized by European regulation. Since different studies confirm that current vehicles tolerate blends up to 10 percent of bioethanol without problems and the benefits for the environment are significant.
- **E10:** The E10 biofuel means a combination of 10 percent bioethanol and 90 percent gasoline. This mixture is the most used in the United States, because up to this mixing ratio the engines of the vehicles do not require any modification and, even, it produces the elevation of an octane in the gasoline improving its result and obtaining a remarkable reduction in the Emission of polluting gases.
- **E85:** It is a mixture of 85 percent bioethanol and 15 percent gasoline, used in vehicles with special engines. In the United States, the best known brands offer vehicles adapted to these mixtures. Also they are commercialized, in some countries (the USA, Brazil, Sweden ...) the calls vehicles FFV (Flexible Fuel Vehicles) or Vehicles of Flexible Fuels with adapted motors that allow a variety of mixtures.
- **E95 and E100:** Mixtures up to 95 percent and 100 percent bioethanol are used in some countries like Brazil with special engines.

- **E-Diesel:** Bioethanol allows its mixture with diesel oil using a solvent additive and producing a diesel biofuel, E-Diesel, with very good characteristics in terms of combustion and pollution reduction. E-Diesel is already successfully marketed in the US and Brazil and will soon appear in Spain and Europe.
- **ETBE:** It is not marketed as a biofuel, but used as a gasoline additive. ETBE (ethyl tertiary butyl ether) is obtained by synthesis of bioethanol with isobutylene, a by-product of petroleum distillation. ETBE has the advantages of being less volatile and more miscible with gasoline than ethanol itself and, like ethanol, it is additive to gasoline in proportions of 10-15 percent. The addition of ETBE or ethanol serves to increase the rate of octane of gasoline, avoiding the addition of lead salts, before MTBE was used.

## 2.1.4 ADVANTAGES AND DISADVANTAGES [2][9]

It is very important to know what are the advantages and disadvantages of the use of biofuels. Below are the most important

### ADVANTAGES

- The cost of biofuels will be lower than that of gasoline or diesel once the technology with which it is generated is available to a greater extent. In addition, the cost of raw materials will be virtually zero when it comes to waste.
- The production processes are more efficient; consume and pollute less.
- It is a source that is much less limited than fossil fuels, which take thousands of years to generate.
- It allows the closing of the carbon cycle (CO<sub>2</sub>), which contributes to the stabilization of the concentration of this gas in the atmosphere (this helps to slow global warming).
- Sometimes a large area for growing plants can be used for the production of biofuels.
- Generation of employment and income in the field (this prevents collapse in urban centers).
- Less financial investment in research (oil prospecting research is very expensive).
- Biodiesel replaces diesel gasoline without the need for adjustments in the engine.
- Reduction of garbage on the planet (can be used for the production of biofuels).
- Handling and storage safer than fossil fuels.

### DISADVANTAGES

- It consumes large amounts of energy to produce itself.
- Increase in water consumption (for crop irrigation).
- Reduction of biodiversity.
- The cultures for the production of biofuels consume many nitrogen fertilizers, with the release of oxides of nitrogen, which also contribute to the greenhouse effect.
- Devastation of forest areas (large consumers of CO<sub>2</sub>) for planting the crops involved in the production of biofuels.
- Possibility of reducing food production at the expense of growing biofuel production, which can contribute to increasing hunger in the world and the rising cost of food.
- Pollution of groundwater by nitrites and nitrates of fertilizers.
- Biofuels provide less energy than fossil fuels at equal amounts, so much more raw material is needed to match these energy levels.

## 2.2 BIODIESEL [12]

Once exposed the characteristics, types, advantages and disadvantages of biofuels, the work will focus on analyzing in depth the biodiesel.

### 2.2.1 DEFINITION

Biodiesel is a liquid obtained from natural lipids such as vegetable oils or animal fats, with or without prior use, through industrial processes of esterification and transesterification and which is applied in the preparation of total or partial substitutes of petrodiesel or gas oil obtained from petroleum. Biodiesel can be mixed with diesel.

Next, the raw materials used for the production of biodiesel will be explained, as well as the production process and the most significant properties to analyze of biodiesel

### 2.2.2 BIODIESEL ENGINE

The properties of biodiesel greatly influence its proper functioning. Therefore, it is important to know how a diesel engine works. Operation that is very well explained in the following image:

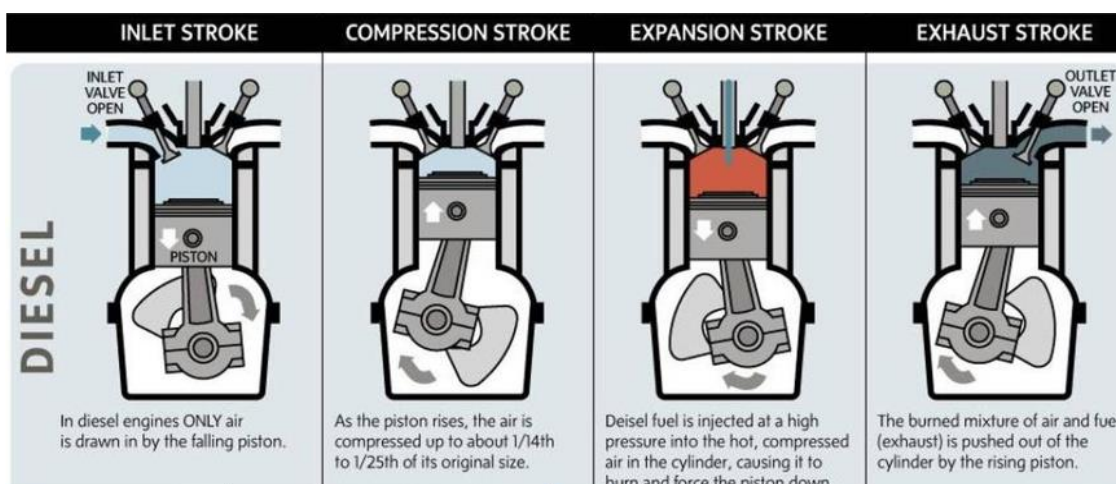


Figure 1. Operation of a diesel engine<sup>[12]</sup>

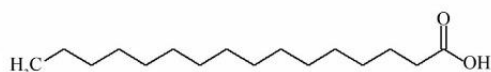
## 2.2.3 RAW MATERIALS [7][8][11][14]

Various raw materials can be used in the production of biodiesel, and each has a characteristic profile of fatty acids. Fatty acids influence biodiesel properties in different ways.

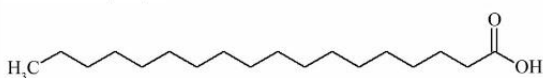
The differences in the fatty acid profiles of the raw materials, and therefore the properties of the biodiesel, serves as a parameter to help in the choice of materials for the production of biodiesel fuel quality, and other important possibilities.

Vegetable oils, as well as animal fats, are composed mainly of triglycerides. Chemically, triglycerides are esters of fatty acids connected to a glycerol molecule. The triglyceride molecule normally contains different fatty acids in its structure. The main fatty acids present in vegetable oils have 16 and 18 carbon atoms, the most common are: palmitic, stearic, oleic, linoleic and linolenic.

Palmitic acid (16:0)



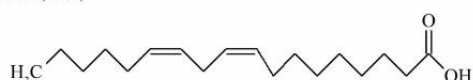
Stearic acid (18:0)



Oleic acid (18:1)



Linoleic acid (18:2)



Linolenic acid (18:3)

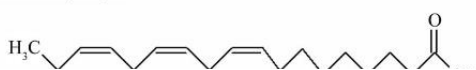


Figure 2 Most common types of fatty acids

These various fatty acids and their respective concentrations make up the vegetable oil profile. Fatty acids have different physical and chemical characteristics due to their structure, which in turn influence the properties of the corresponding oil. In general, unsaturated fatty acids have a low melting point, while saturated ones have a high melting point. Thus, oils that contain a large number of unsaturated compounds are liquid, while those that are high in saturated fatty acids are solid at room temperature.

Vegetable oils or animal fats can be transesterified to obtain biodiesel. For this reason, different sources of vegetable oils are used in the production of biodiesel. The properties of biodiesel are determined by the amount of each fatty acid present in the triglyceride molecule (chain length and

number of double bonds), and these have a direct implication in the physical properties of biodiesel. The transesterification process does not alter the fatty acid composition of the raw material used in the production of biodiesel, the esters formed have the same source profile of vegetable oil fatty acids or animal fat from the source. Thus, the composition and concentration are critical parameters in determining the properties of the fuel.

The vegetable oil used in the production of biodiesel can be obtained from various oilseeds. These oilseeds differ in their species for their agronomic characteristics, and in relation to the oil content in the grain composition and fatty acid profile.

#### OIL CONTENT

The oil content is an important feature that can influence the choice and use of a raw material to produce biodiesel. In this sense, sunflower, rapeseed, jatropha, ricin and peanuts are the sources that have a higher content of oil in grain, a variation of between 40 and 64% of oil. With a lower level around 15 to 25% oil, are soy, palm and cotton.

Soy, despite having a low oil content compared to most raw materials, is widely cultivated in several countries, being the characteristics of the raw materials used in the production of biodiesel main producers, US (33%), Brazil (27%), Argentina (21%) and China (7%).

In Brazil, more than 70% of biodiesel is soybean oil. In Argentina, the percentage is 100% in the United States around 74% and the European Union only 16% of biodiesel is produced with soy

Palm oil and soybean oil are the most commercialized vegetable oils in the world, and the production of both is practically the same. Although the content of palm oil and soybean is similar, the productivity of palm oil per hectare is much higher. In Malaysia, a leading producer and exporter of palm oil, palm biodiesel is the main biofuel added to petroleum diesel

Jatropha, in turn, has a good oil production per hectare, due to its high oil content in the seed. Widely used in the production of biodiesel in India, exploration and cultivation of this plant have been strengthened to increase the demand for biodiesel production from non-edible oils. The insertion of non-edible raw materials in the production of biodiesel is seen as an important ally but does not compete with the raw materials used in food.

Castor oil, even with a high oil content in the seed and a good oil yield per hectare, still has some disadvantages with respect to the use of its oil for biodiesel because its viscosity is about 7 times higher than the one of other vegetable oils. For sunflower, rapeseed and peanut crops, the content of oil in grain and the yield of oil per hectare are similar. The lowest yield of oil per hectare occurs for the cultivation of cotton.

### 2.2.4 TRANSESTERIFICATION REACTION <sup>[5]</sup>

The most used process for the production of biodiesel is transesterification, which refers to the reaction between an oil or fat and an alcohol in a catalyzed medium, to produce alkyl esters of fatty acids (*i.e.* biodiesel) and glycerol, known also as glycerin. Figure 3 shows the reaction that transforms the molecules of triglycerides, large and branched, in alkyl ester molecules, linear, not branched, smaller and very similar to those of petrodiesel.

The alcohols used must be lightweight molecular; Among these, the most used is the methanol due to its low cost, followed by ethanol.



The reaction can be catalyzed with homogeneous catalysts (acid or base) or heterogeneous (acid, base, or an enzyme). An example of acid catalyst may be the sulfuric acid, and one of the basic catalysts, sodium hydroxide.

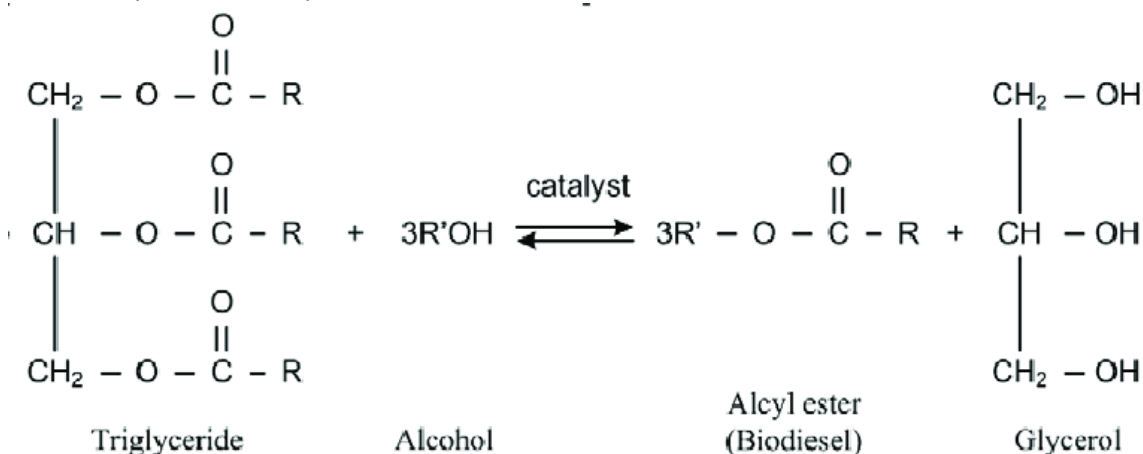


Figure 3. Transesterification reaction [5]

## 2.2.5 BIODIESEL OBTAINING PROCESS [16]

Depending on the catalyst used, the reaction is carried out under different conditions:

- For a basic catalyst, the reaction is carried out at a temperature between 40 and 60°C, at atmospheric pressure, with a proportion of methanol:oil greater than 4 mol/mol. If it is a homogeneous catalyst, the reaction time ranges between 30 and 60 minutes, while for a heterogeneous one, between 6 and 24 hours.
- For an acid catalyst, the reaction temperature is above 100°C, a pressure between 0.2 and 0.4 Mpa and a proportion of methanol: oil greater than 6 mol/mol. The reaction times are similar for any acid catalyst.
- Both for an enzymatic catalyst and for ionic liquids, the reaction temperature ranges between 30 and 40°C, with a large excess of methanol. These catalysts carry a high cost.
- Finally, for reactions not catalysed, a temperature higher than 200°C, a pressure between 3.9 and 4.9 MPa and a considerable excess of alcohol are needed.

The fact of fatty raw material purity affects the process conditions and the choice of the catalyst. For pure materials basic catalyst are preferred. In case of a high content of FFA, acid catalysts are better. The advantages of these catalysts are that they are less vulnerable than the basic ones, you can use a raw material with a high content of FFA

One of the main disadvantages is that higher pressures and temperatures will be needed, since they are slower. The amount of catalyst affects the synthesis of biodiesel and it is known that with an excessive amount of catalyst you can promote ether formation with dehydration of alcohol.

On the other hand, there are catalysed homogeneous acids, such as sulfuric acid, and heterogeneous acids, like sulfonic acid resins. The homogeneous acid catalysts give serious problems of pollution, since at the end of the reactions, the catalyst has to be separate by purifying the biodiesel, making the production cost increase. With the intention of solving this problem that increases the production cost of biodiesel, they are studying how assets are the heterogeneous acid catalysts in the reactions of transesterification and esterification.

The use of heterogeneous insoluble catalysts in MeOH would reduce the problems derived from the use of homogeneous catalysts, since it would avoid the washing stage of the products. This causes a reduction in the environmental and economic costs. Another advantage of this type of catalysts is that they catalyse simultaneously transesterification and esterification and there is no need to combine it with the basic catalyst, in this way, the costs of production decrease.

The process of obtaining biodiesel works in the following way:

First, the oil is mixed with the alcohol and the catalyst in the reactor: in this the transesterification reaction takes place where biodiesel and glycerol are obtained as a product. Once the reaction is finished, the products are sent to the separator, where the biodiesel is separated from the glycerol and the alcohol that may have remained unreacted.

The biodiesel is sent to a washing column where it is mixed with water to eliminate the possible remains of glycerol and alcohol that may have remained in the biodiesel. Once all the alcohol and glycerol have been removed, the biodiesel is sent to a dryer and then stored.

On the other hand, the glycerol and alcohol stream from the separator, together with the glycerol water stream and alcohol from the washing column, are sent to an alcohol recovery column, where the alcohol is separated from the water by distillation and the glycerol. Alcohol is recirculated to the reactor, while glycerol and water are sent to another column, but this time glycerol recovery. Once the water is separated from the glycerol, the water is recirculated to the washing column while the glycerol is stored.

The biodiesel production processes can be batch or continuous.

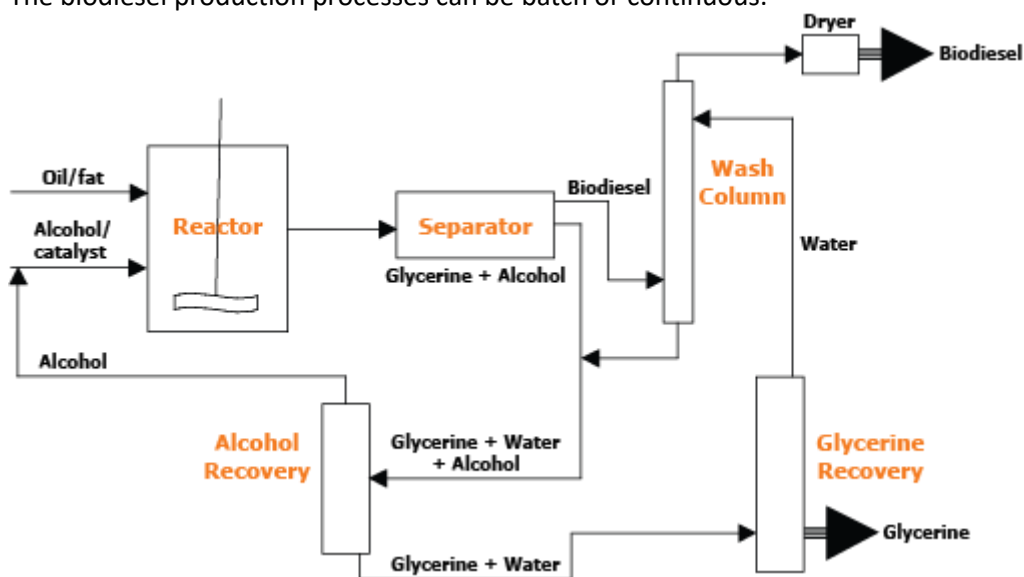


Figure 4. Biodiesel obtention process <sup>[1]</sup>

## 2.2.6 BIODIESEL PROPERTIES [6][10][14]

Once the biodiesel is obtained, its properties must be analyzed in order to verify if that biodiesel is suitable or not for its use and commercialization. These properties are kinematic viscosity, density, flash point, cetane number, cloud point

- **The kinematic viscosity:** is defined as the resistance of the liquid to flow and is the most important feature of the fuel. It affects the operation of fuel injection, formation of mixtures and combustion processes.  
The high viscosity interferes with the injection process and induces insufficient atomization of the fuel. The structure present in the composition of the fatty acids such as long chains, degrees of unsaturation, orientation of the double bonds and type of functional group of the ester can influence the kinematic viscosity of the biodiesel. The viscosity increases with the increase in the length of the chain and decreases with the number of double bonds.  
In biodiesel, according to the standards ASTM D6751 and EN14214, the viscosity could be between 1.9-6.0 mm<sup>2</sup>/s and 3.5-5.0 mm<sup>2</sup>/s respectively
- **Density** is another important property of biodiesel. It also influences the efficiency of fuel atomization due to poor ventilation of the combustion system. It has many effects on the disintegration of the fuel injected into the cylinder. In addition, more fuel is injected if the fuel density is increased. All independent biodiesel fuels produced from vegetable oils or fats are dense and less compressible than diesel fuel. According to ASTM D6751 and EN14214 standards, the density can be between 860 kg/m<sup>3</sup>-900 kg/m<sup>3</sup> for standard biodiesel
- **Ignite point** is the temperature at which the fuel will start to burn when it comes into contact with fire. This is an important parameter from the point of view of safety such as safety for transportation, handling, storage and general safety of any fuel. According to the ASTM D6751 and EN14214 standards, biodiesel has a flash point of not less than 120 °C. This is greater than that of petroleum diesel which has a flash point of 71 °C.
- **The smoke point** is the temperature at which, under specific and defined conditions, it begins to produce a continuous bluish smoke that becomes clearly visible.<sup>[1]</sup> Smoke point values can vary greatly, depending on factors such as the volume of oil utilized, the size of the container, the presence of air currents, the type and source of light as well as the quality of the oil and its acidity content, otherwise known as free fatty acid (FFA) content. The more FFA an oil contains, the quicker it will break down and start smoking. The higher in quality and the lower in FFA, the higher the smoke point.
- **The cetane number** is related to the time that elapses between the injection of the fuel and the start of its combustion, called "Ignition Interval". Quality combustion occurs when a rapid ignition occurs followed by a total and uniform burning of the fuel. The higher the cetane number, the lower the ignition delay and the better the combustion quality. On the contrary, those fuels with a low cetane number require a longer time for ignition to occur and then burn very quickly, producing high pressure rise rates.  
If the cetane number is too low, combustion is inadequate and gives rise to excessive noise, increased emissions, reduced vehicle performance and increased engine fatigue.



Excessive smoke and noise are common problems in diesel vehicles, especially under cold start conditions. Normally it stays between 40 and 45.

- **The cloud point** refers to the temperature under which the paraffin or wax contained in the biodiesel forms a turbid appearance. The presence of solidified waxes or paraffins thickens the lubricating oil and clogs the fuel filters and injectors in diesel engines. Wax deposits also accumulate on cold surfaces (*eg* pipe or heat exchanger) and form an emulsion with water. Therefore, the cloud point indicates the tendency of the oil to clog small filters or holes at cold operating temperatures.
- **Freezing point** is the temperature when a substance change from liquid to solid state. It is very important when operating at low temperatures
- **The acid number** is expressed as the amount of KOH in mg required to neutralize 1 g of fatty acids of methyl ethers. This is the presence of free fatty acids or acids used in the configuration of biodiesel and also the degradation of biodiesel due to thermal effects. High acidity index can cause severe corrosion in systems that supply fuel to an engine. The limit specified by ASTM D6751 and EN14214 standards for the acidity index in biodiesel is below 0.5 mg KOH/g biodiesel.

## 3. EXPERIMENTAL SESSION

### 3.1 PART 1: OBTAINING BIODIESEL

#### 3.1.1 OBJECTIVE

The objective of this study is based on knowing the optimal conditions to obtain biodiesel by transesterification from a raw material with a high content of free fatty acids, since the content of this affects the performance of the reaction and does not have the same behavior than a raw material with different content of free fatty acids.

#### 3.1.2 INTRODUCTION

The main method of obtaining biodiesel is by transesterification, where the fatty acid (triglyceride) reacts with an alcohol, in our case methanol, to obtain as glycerol and biodiesel products (methyl esters of fatty acids).

For our experiment, an oil with a content of 98% fatty acids will be used.

This raw material has been obtained by mixing different types of free fatty acids with rapeseed oil:

*Table 1 : composition of the raw material used to obtain biodiesel*

FATTY ACID	PERCENTAGE (%)	COMPOSITION (number of carbons : number of double bonds)
Lauric acid	2.12	12:0
Myristic acid	2.3	14:0
Palmitic acid	1.51	16:0
Oleic acid	94.08	18:1

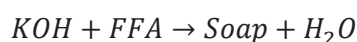
For this, transesterification will be carried out under different conditions, varying the amount of methanol used, the type of catalyst and the temperature. There will be a total of 8 different conditions:

- Experiment 1: H<sub>2</sub>SO<sub>4</sub> as a catalyst, 60°C and 25% in mass of methanol
- Experiment 2: PTSA as a catalyst, 60°C and 25% in mass of methanol
- Experiment 3: H<sub>2</sub>SO<sub>4</sub> as a catalyst, 70°C and 25% in mass of methanol
- Experiment 4: PTSA as a catalyst, 70°C and 25% in mass of methanol

- Experiment 5: H<sub>2</sub>SO<sub>4</sub> as a catalyst, 60°C and 30% in mass of methanol
- Experiment 6: PTSA as a catalyst, 60°C and 30% in mass of methanol
- Experiment 7: H<sub>2</sub>SO<sub>4</sub> as a catalyst, 70°C and 30% in mass of methanol
- Experiment 8: PTSA as a catalyst, 70°C and 30% in mass of methanol

To know the progress of the reaction, a chemical reaction called titration will be used.

In this case, 0.0885M KOH will be used as a titrant, which will react with the free acids in the solution. As an indicator, phenolphthalein will be used, which is an indicator that changes color when the reaction is basic. Therefore, by reacting all of the free fatty acids present in the solution with the known volume of KOH, the solution will change to a pink color because it will be basic, and the amount of acid will be known from the volume of KOH used. The reaction is the following:



The formula to calculate the LK (acid number) is the following (mg KOH/g oil):

$$LK = \frac{56.1 * (V - V_0) * C_{KOH}}{m} \quad (\text{Equation 1})$$

Where:

- V - volume of KOH
- V<sub>0</sub> - volume of the blank
- C(KOH) - the concentration of KOH solution
- m - is mass of oil sample taken to titration

### 3.1.3 MATERIALS

In all the experiences, it will be used more or less the same materials:

- Pure methanol
- Oil 98%
- KOH 0.0885M
- Sulfuric acid 95%
- PTSA
- Solvent
- Phenolphthalein indicator
- Magnetic stirrer
- Round bottom flask (500mL)
- Reflux
- Dropping funnel
- Burette 50mL
- Pipette 25mL
- Separatory funnel (500mL)
- Funnel
- Dropper
- Sample tubes
- Centrifuge

- Heater
- Automatic pipette (0.1-1ml)

### 3.1.4 EXPERIMENTAL PROCEDURE

First, it is weighed approximately 50 grams of the raw material with 98.16% content of fatty acids. Then, it is heated to the desired temperature (60°C or 70°C depending of the experiment) in a bath with water, as can be seen in the Figure 5.

Once the desired temperature is reached, it is added the corresponding quantity of methanol (25% or 30% of the raw material weight depending of the experiment) and 2% of the weight of the oil used of catalyst (PTSA or H<sub>2</sub>SO<sub>4</sub> depending of the experiment). As the densities of methanol (0.78 g / ml) and sulfuric acid (1.84 g / ml) are known, it is possible to calculate the volumes that should be added to each experiment.

Is also important to be mentioned that in Experiment 7 and 8 it has been decided to install a condenser, as can be seen in Figure 6, to prevent the methanol from evaporating and affecting the reaction yield.



Figure 5. Assembly of experiment 1-6

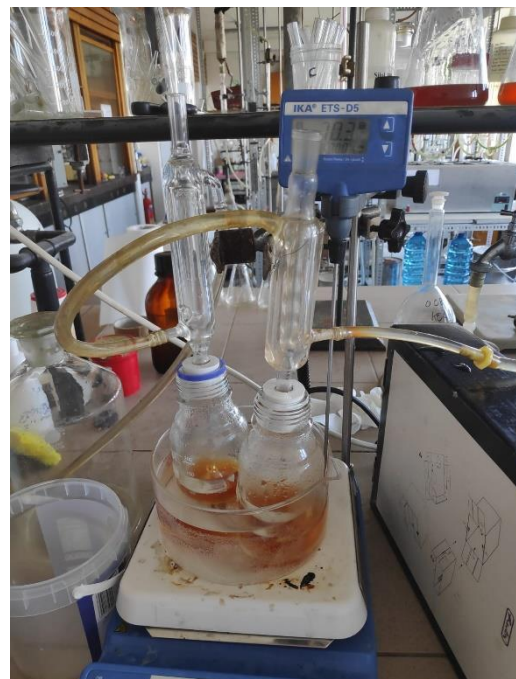


Figure 6. Assembly of experiment 7 and 8

The moment both compounds are added, a sample is taken. The procedure for obtaining the samples consists of introducing the sample into a beaker with 5 ml of distilled water inside it, covering it and shaking it strongly, so that it cools down and stops the transesterification reaction.

A total of 9 samples will be taken, at times of 0,5,15,30,45,60,90,120,180 minutes.

After taking the last sample, an extra methanol (8% or 10% of the weight of the oil depending of the experiment) and 1% of the weight of the oil of catalyst (PTSA or H<sub>2</sub>SO<sub>4</sub> depending of the experiment) are added to the reactor.

Once added, a total of 7 samples are taken again, at times of 5,15, 30, 45, 60, 90 and 120 minutes. At the end of this time, the solution is poured inside a separatory funnel. After separating the biodiesel and the glycerol, we introduce the biodiesel obtained by using sulfuric acid in one recipient and the obtained using PSTA in other recipient. At the end of each of the following experiments under different conditions, all the products obtained with sulfuric acid will be introduced together in the same container and those obtained with PTSA will be introduced together in another container. Finally, both mixtures will be analyzed to know the acid number and the lower concentration present will be used to analyze their properties and compare them with the properties of the raw material used.

All samples are centrifuged to clearly separate the two phases (oil and water). Once centrifuged, a small sample of the superficial part is taken with a pipette. This sample is weighed and diluted with 20 ml of solvent in a 250 ml Erlenmeyer flask. To this solution, 3-4 drops of indicator (phenolphthalein) are added and the solution is ready to start the titration. It is also 10 ml of water was added to the solution to see more clearly the change of color.

The titration is done with a dissolution of KOH 0.0885M. This dissolution is introduced in a 50 ml burette, and drop by drop, the dissolution is added to the solution until the color of this change to pink, as can be seen in Figure 7. In this moment, the volume of KOH used should be pointed. This process is repeated with all the samples. It is also very important to titrate a blank sample (without oil), because dissolution of solvent and water could contain acids.

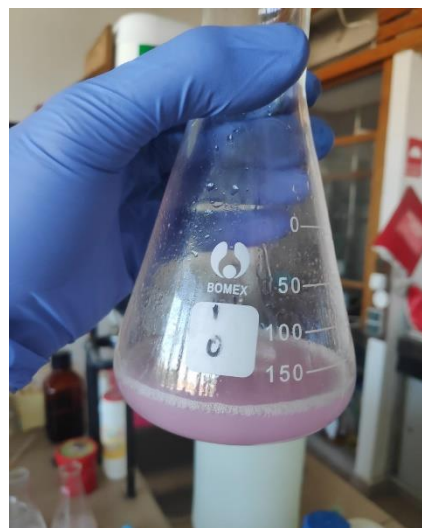


Figure 7. Phenolphthalein indicator color

Next, both the data of the added volumes of methanol and catalyst and the KOH volumes used for each of the sample titrations for each experiment made with different conditions are set forth.



## EXPERIMENT 1

H<sub>2</sub>SO<sub>4</sub> as a catalyst, 60°C and 25% and 8% in mass of methanol respectively.

Mass of raw material: 50.03 grams

First addition:

$$\text{Volume of methanol} = \frac{50.03g * 0.25}{0,79g/ml} = 15,83 \text{ ml}$$

$$\text{Volume of sulfuric acid} = \frac{50.03g * 0.02}{0.95 * 1,84g/ml} = 0,57 \text{ ml}$$

Second addition:

$$\text{Volume of methanol} = \frac{50.03g * 0.08}{0,79g/ml} = 5.06 \text{ ml}$$

$$\text{Volume of sulfuric acid} = \frac{50.03g * 0.02}{0.95 * 1,84g/ml} = 0.285 \text{ ml}$$

Table 2. Experiment 1. Titration data

Time (min)	Mass (g)	Volume KOH(ml)	Blank Volume (ml)
0	0.41	9.5	0.4
5	0.51	9	0.4
15	0.4	5	0.4
30	0.55	3.5	0.4
45	0.43	2.5	0.4
60	0.3	0.8	0.1
90	0.49	0.7	0.1
120	0.59	0.9	0.1
180	0.49	0.8	0.1
185	0.51	0.7	0.1
195	0.31	0.9	0.1
210	0.34	0.7	0.1
225	0.33	1	0.1
240	0.32	0.8	0.1
270	0.42	0.8	0.1
300	0.26	0.5	0.1

## EXPERIMENT 2

PTSA as a catalyst, 60°C and 25% and 8% in mass of methanol respectively.

Mass of raw material: 50.08 grams

First addition:

$$\text{Volume of methanol} = \frac{50.08g * 0.25}{0,79g/ml} = 15,85 \text{ ml}$$

$$\text{Mass of PTSA} = 50.08g * 0.02 = 1 \text{ g}$$

Second addition:

$$\text{Volume of methanol} = \frac{50.08g * 0.08}{0,79g/ml} = 5.07 \text{ ml}$$

$$\text{Mass of PTSA} = 50.08g * 0.01 = 0.5g$$

Only for this experiment, KOH 0.0986M was used for the titration.

*Table 3. Experiment 2. Titration data.*

Time (min)	Mass (g)	Volume KOH(ml)	Blank Volume (ml)
0	0.12	4.5	0.3
5	0.17	5	0.3
15	0.21	4.7	0.3
30	0.16	3.3	0.3
45	0.23	3.7	0.3
60	0.18	2.7	0.3
90	0.22	3.1	0.3
120	0.23	3	0.3
180	0.13	1.8	0.3
185	0.23	2.4	0.3
195	0.14	1.5	0.3
210	0.15	1.6	0.3
225	0.23	1.9	0.3
240	0.22	1.8	0.3
270	0.23	1.7	0.3
300	0.19	1.4	0.3

## EXPERIMENT 3

H<sub>2</sub>SO<sub>4</sub> as a catalyst, 70°C and 25% and 8% in mass of methanol respectively.

Mass of raw material: 49.83 grams

First addition:

$$\text{Volume of methanol} = \frac{49.83g * 0.25}{0,79g/ml} = 15,76 \text{ ml}$$

$$\text{Volume of sulfuric acid} = \frac{49.83g * 0.02}{0.95 * 1,84g/ml} = 0,57 \text{ ml}$$

Second addition:

$$\text{Volume of methanol} = \frac{49.83g * 0.08}{0,79g/ml} = 5.04 \text{ ml}$$

$$\text{Volume of sulfuric acid} = \frac{49.83g * 0.02}{0.95 * 1,84g/ml} = 0.285 \text{ ml}$$

Table 4. Experiment 3. Titration data.

Time (min)	Mass (g)	Volume KOH(ml)	Blank Volume (ml)
0	0.31	9.9	0.5
5	0.3	7.3	0.5
15	0.31	6	0.5
30	0.29	5.4	0.5
45	0.31	5	0.5
60	0.31	4.5	0.5
90	0.32	4.5	0.5
120	0.3	4	0.5
180	0.3	3.7	0.5
185	0.33	3.1	0.5
195	0.31	2.6	0.5
210	0.31	1.9	0.5
225	0.3	1.5	0.5
240	0.18	0.8	0.5
270	0.23	0.8	0.5
300	0.3	0.8	0.5

## EXPERIMENT 4

PTSA as a catalyst, 70°C and 25% and 8% in mass of methanol respectively.

Mass of raw material: 50 grams

First addition:

$$\text{Volume of methanol} = \frac{50g * 0.25}{0,79g/ml} = 15,82 \text{ ml}$$

$$\text{Mass of PTSA} = 50g * 0.02 = 1 \text{ g}$$

Second addition:

$$\text{Volume of methanol} = \frac{50g * 0.08}{0,79g/ml} = 5.06 \text{ ml}$$

$$\text{Mass of PTSA} = 50g * 0.01 = 0.5g$$

*Table 5. Experiment 4. Titration data.*

Time (min)	Mass (g)	Volume KOH(ml)	Blank Volume (ml)
0	0.31	10.4	0.5
5	0.29	6.1	0.5
15	0.33	5	0.5
30	0.31	4.4	0.5
45	0.31	3.9	0.5
60	0.32	3.2	0.5
90	0.32	3	0.5
120	0.35	2.85	0.5
180	0.3	2.4	0.5
185	0.3	2.3	0.5
195	0.32	2.1	0.5
210	0.3	1.9	0.5
225	0.3	1.7	0.5
240	0.3	1.5	0.5
270	0.32	1.5	0.5
300	0.31	1.3	0.5

## EXPERIMENT 5

H<sub>2</sub>SO<sub>4</sub> as a catalyst, 60°C and 30% and 10% in mass of methanol respectively.

Mass of raw material: 49.92 grams

First addition:

$$\text{Volume of methanol} = \frac{49.92g * 0.3}{0,79g/ml} = 18.98 \text{ ml}$$

$$\text{Volume of sulfuric acid} = \frac{49.92g * 0.02}{0.95 * 1,84g/ml} = 0,57 \text{ ml}$$

Second addition:

$$\text{Volume of methanol} = \frac{49.92g * 0.1}{0,79g/ml} = 6.32 \text{ ml}$$

$$\text{Volume of sulfuric acid} = \frac{49.92g * 0.02}{0.95 * 1,84g/ml} = 0.285 \text{ ml}$$

Table 6. Experiment 5. Titration data.

Time (min)	Mass (g)	Volume KOH(ml)	Blank Volume (ml)
0	0.29	10.7	0.3
5	0.22	5.2	0.3
15	0.31	6.6	0.3
30	0.19	4.1	0.3
45	0.25	4.3	0.3
60	0.22	3.6	0.3
90	0.21	3.5	0.3
120	0.21	3.5	0.3
180	0.18	2.7	0.3
185	0.2	2.5	0.3
195	0.2	2.2	0.3
210	0.15	1.7	0.3
225	0.3	2.7	0.3
240	0.18	1.5	0.3
270	0.23	1.8	0.3
300	0.23	1.6	0.3

## EXPERIMENT 6

PTSA as a catalyst, 60°C and 30% and 10% in mass of methanol respectively.

Mass of raw material: 50.06 grams

First addition:

$$\text{Volume of methanol} = \frac{50.06g * 0.30}{0,79g/ml} = 19.01 \text{ ml}$$

$$\text{Mass of PTSA} = 50.06g * 0.02 = 1 \text{ g}$$

Second addition:

$$\text{Volume of methanol} = \frac{50.06g * 0.1}{0,79g/ml} = 6.33 \text{ ml}$$

$$\text{Mass of PTSA} = 50.06g * 0.01 = 0.5g$$

*Table 7. Experiment 6. Titration data.*

Time (min)	Mass (g)	Volume KOH(ml)	Blank Volume (ml)
0	0.18	7.5	0.3
5	0.23	5.3	0.3
15	0.31	4.7	0.3
30	0.17	2.7	0.3
45	0.23	3.2	0.3
60	0.2	2.7	0.3
90	0.19	2.7	0.3
120	0.29	3.8	0.3
180	0.15	1.5	0.3
185	0.2	1.6	0.3
195	0.25	1.9	0.3
210	0.27	2	0.3
225	0.24	1.8	0.3
240	0.2	1.4	0.3
270	0.23	1.3	0.3
300	0.22	1	0.3

## EXPERIMENT 7

H<sub>2</sub>SO<sub>4</sub> as a catalyst, 70°C and 30% and 10% in mass of methanol respectively.

Mass of raw material: 49.95 grams

First addition:

$$\text{Volume of methanol} = \frac{49.95g * 0.3}{0,79g/ml} = 18.96 \text{ ml}$$

$$\text{Volume of sulfuric acid} = \frac{49.95g * 0.02}{0.95 * 1,84g/ml} = 0,57 \text{ ml}$$

Second addition:

$$\text{Volume of methanol} = \frac{49.95g * 0.1}{0,79g/ml} = 6.33 \text{ ml}$$

$$\text{Volume of sulfuric acid} = \frac{49.95g * 0.02}{0.95 * 1,84g/ml} = 0.285 \text{ ml}$$

Table 8. Experiment 7. Titration data.

Time (min)	Mass (g)	Volume KOH(ml)	Blank Volume (ml)
0	0.23	9.7	0.3
5	0.09	3.3	0.3
15	0.19	4.4	0.3
30	0.17	3.8	0.3
45	0.23	4.2	0.3
60	0.19	3.3	0.3
90	0.22	3.6	0.3
120	0.18	3	0.3
180	0.21	2.8	0.3
185	0.17	2.1	0.3
195	0.14	1.8	0.3
210	0.12	1.5	0.3
225	0.24	2.3	0.3
240	0.13	1.3	0.3
270	0.23	1.9	0.3
300	0.23	1.95	0.3

## EXPERIMENT 8

PTSA as a catalyst, 60°C and 30% and 10% in mass of methanol respectively.

Mass of raw material: 49.95 grams

First addition:

$$\text{Volume of methanol} = \frac{49.95g * 0.30}{0,79g/ml} = 18.96 \text{ ml}$$

$$\text{Mass of PTSA} = 49.96g * 0.02 = 1 \text{ g}$$

Second addition:

$$\text{Volume of methanol} = \frac{49.95g * 0.1}{0,79g/ml} = 6.33 \text{ ml}$$

$$\text{Mass of PTSA} = 49.95g * 0.01 = 0.5g$$

*Table 9. Experiment 8. Titration data.*

Time (min)	Mass (g)	Volume KOH(ml)	Blank Volume (ml)
0	0.26	10.3	0.3
5	0.12	2.6	0.3
15	0.24	4.2	0.3
30	0.24	3.7	0.3
45	0.21	3	0.3
60	0.21	2.8	0.3
90	0.23	2.6	0.3
120	0.19	2.1	0.3
180	0.11	1.3	0.3
185	0.1	1.1	0.3
195	0.16	1.5	0.3
210	0.16	1.4	0.3
225	0.24	1.9	0.3
240	0.17	1.35	0.3
270	0.23	1.6	0.3
300	0.12	0.9	0.3



### 3.1.5 RESULTS DISCUSSION

After obtaining the volumes for all the samples, it is necessary to calculate the amount of free acids present in each one for all the experiments, using the equation 1, and represent the variation of the acid number depending of the reaction time:

$$\text{Acid number} = \frac{56.1 * (V - V_0) * C_{KOH}}{m} \quad (\text{equation 1})$$

Before calculating the acid number of all experiments, the acid number of the raw material is analyzed, obtaining a value of **205 mg KOH/g oil**

### EXPERIMENT 1

H<sub>2</sub>SO<sub>4</sub> as a catalyst, 60°C and 25% and 8% in mass of methanol respectively.

*Table 10. Experiment 1. Acid number results in titration.*

Time (min)	Mass (g)	Volume KOH(ml)	Blank Volume (ml)	Acid number(mg KOH/g oil)
0	0.41	9.5	0.4	110.19
5	0.51	9	0.4	83.72
15	0.4	5	0.4	57.09
30	0.55	3.5	0.4	27.98
45	0.43	2.5	0.4	24.24
60	0.3	0.8	0.1	11.58
90	0.49	0.7	0.1	6.07
120	0.59	0.9	0.1	6.73
180	0.49	0.8	0.1	7.09
185	0.51	0.7	0.1	5.84
195	0.31	0.9	0.1	12.81
210	0.34	0.7	0.1	8.76
225	0.33	1	0.1	13.54
240	0.32	0.8	0.1	10.86
270	0.42	0.8	0.1	8.27
300	0.26	0.5	0.1	7.63

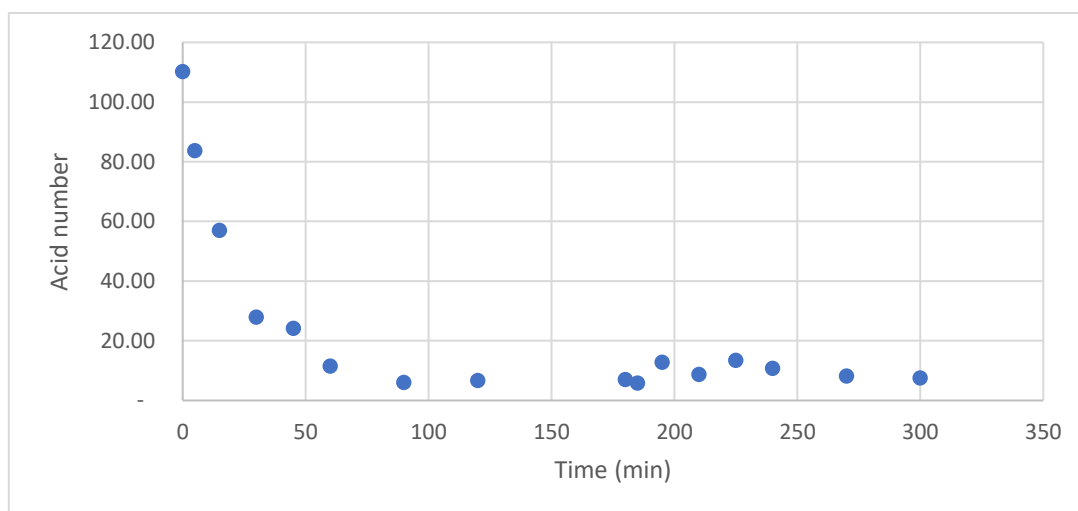


Figure 8. Experiment 1. Acid number vs time

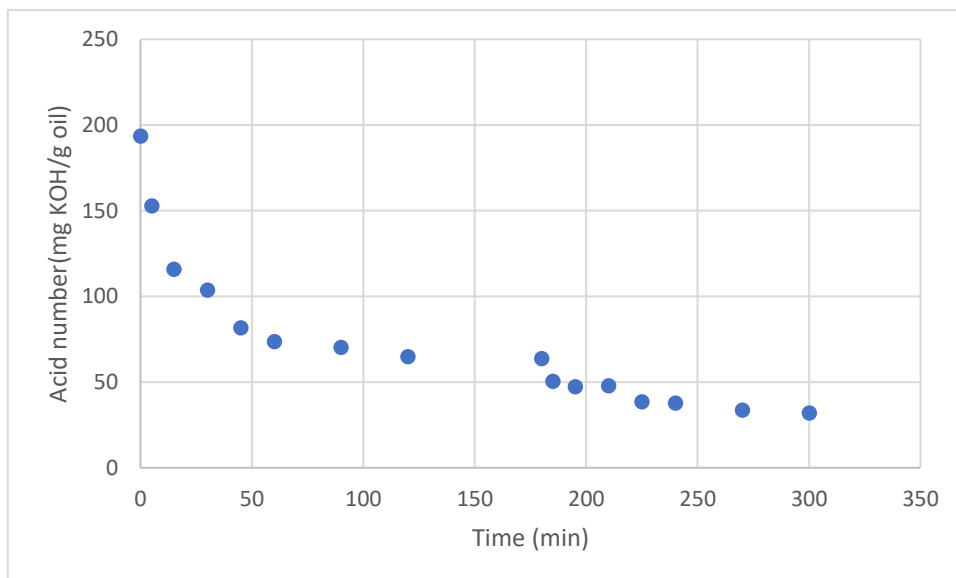
It can be observed how the acid number decreases with the passage of time, due to the reaction of the acid with methanol to produce biodiesel and glycerol. When the extra methanol and catalyst (sulfuric acid) is added, there is an increase in the acid number, obtaining quite different values that do not represent what should happen in reality. Since theoretically, this concentration should continue to decrease.

## EXPERIMENT 2

PTSA as a catalyst, 60°C and 25% and 8% in mass of methanol respectively.

Table 11. Experiment 2. Acid number results in titration.

Time (min)	Mass (g)	Volume KOH(ml)	Blank Volume (ml)	Acid number (mg KOH/g oil)
0	0.12	4.5	0.3	193.6
5	0.17	5	0.3	152.92
15	0.21	4.7	0.3	115.89
30	0.16	3.3	0.3	103.71
45	0.23	3.7	0.3	81.76
60	0.18	2.7	0.3	73.75
90	0.22	3.1	0.3	70.4
120	0.23	3	0.3	64.93
180	0.13	1.8	0.3	63.82
185	0.23	2.4	0.3	50.50
195	0.14	1.5	0.3	47.41
210	0.15	1.6	0.3	47.93
225	0.23	1.9	0.3	38.47
240	0.22	1.8	0.3	37.71
270	0.23	1.7	0.3	33.66
300	0.19	1.4	0.3	32.02



*Figure 9. Experiment 2. Acid number vs time*

As can be seen in the graph, the acid concentration quickly decreases during the first 60 minutes. Then, it stabilizes until 180 minutes. Once the extra methanol and catalyst is added, a slight decrease in the acid number is observed, to finally stabilize again around 32 mg KOH/g oil

## EXPERIMENT 3

H<sub>2</sub>SO<sub>4</sub> as a catalyst, 70°C and 25% and 8% in mass of methanol respectively.

Table 11. Experiment 3. Acid number results in titration

Time (min)	Mass (g)	Volume KOH(ml)	Blank Volume (ml)	Acid number (mg KOH/g oil)
0	0.31	9.9	0.5	150.54
5	0.3	7.3	0.5	112.53
15	0.31	6	0.5	88.08
30	0.29	5.4	0.5	83.88
45	0.31	5	0.5	72.07
60	0.31	4.5	0.5	64.06
90	0.32	4.5	0.5	62.06
120	0.3	4	0.5	57.92
180	0.3	3.7	0.5	52.95
185	0.33	3.1	0.5	39.11
195	0.31	2.6	0.5	33.63
210	0.31	1.9	0.5	22.42
225	0.3	1.5	0.5	16.54
240	0.18	0.8	0.5	8.27
270	0.23	0.8	0.5	6.47
300	0.3	0.8	0.5	4.96

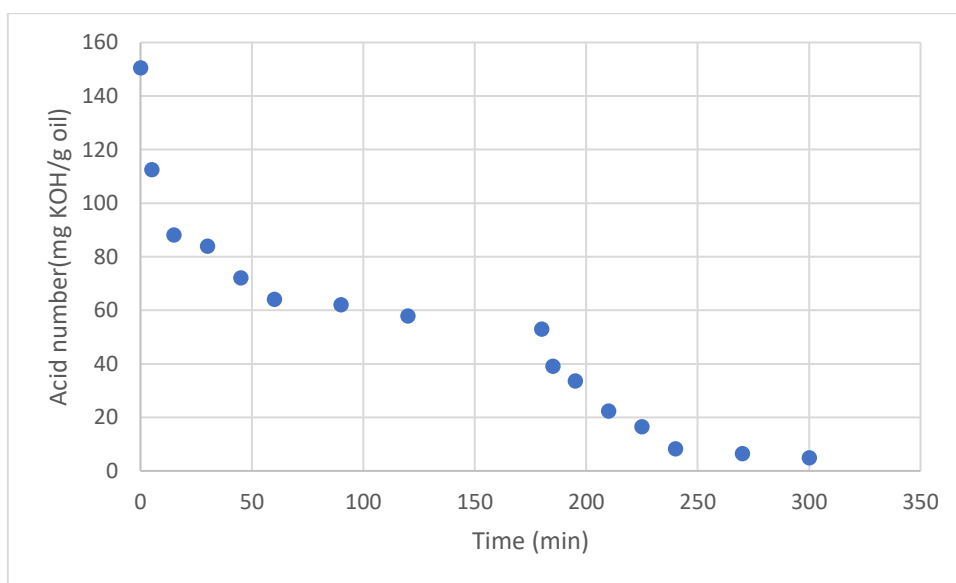


Figure 10. Experiment 3. Acid number vs time

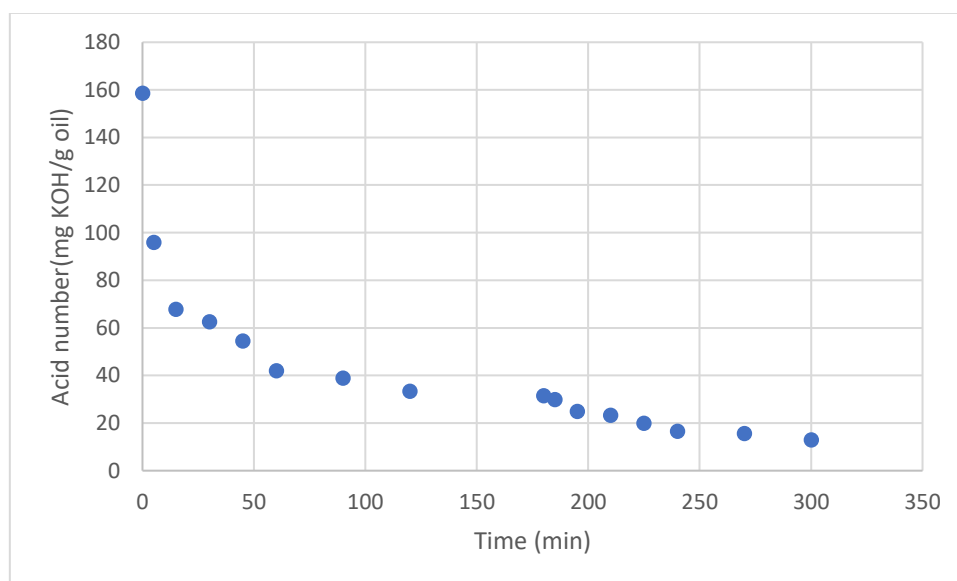
As can be seen in the graph, first, the acid concentration decreases rapidly and after 60 minutes it stabilizes. When the extra methanol and catalyst is added, there is a considerable decrease in the concentration of the acid.

## EXPERIMENT 4

PTSA as a catalyst, 70°C and 25% and 8% in mass of methanol respectively.

*Table 12. Experiment 4. Acid number results in titration*

Time (min)	Mass (g)	Volume KOH(ml)	Blank Volume (ml)	Acid number (mg KOH/g oil)
0	0.31	10.4	0.5	158.55
5	0.29	6.1	0.5	95.87
15	0.33	5	0.5	67.70
30	0.31	4.4	0.5	62.46
45	0.31	3.9	0.5	54.45
60	0.32	3.2	0.5	41.89
90	0.32	3	0.5	38.78
120	0.35	2.85	0.5	33.33
180	0.3	2.4	0.5	31.44
185	0.3	2.3	0.5	29.78
195	0.32	2.1	0.5	24.82
210	0.3	1.9	0.5	23.16
225	0.3	1.7	0.5	19.85
240	0.3	1.5	0.5	16.54
270	0.32	1.5	0.5	15.51
300	0.31	1.3	0.5	12.81



*Figure 11. Experiment 4. Acid number vs time*

The behavior of the reaction is similar to the previous ones. First, it decreases drastically and after 60 minutes it stabilizes. In this case, when adding the methanol and the catalyst, a very noticeable decrease of the acid number in our reaction is not observed.

## EXPERIMENT 5

H<sub>2</sub>SO<sub>4</sub> as a catalyst, 60°C and 30% and 10% in mass of methanol respectively.

Table 13. Experiment 5. Acid number results in titration

Time (min)	Mass (g)	Volume KOH(ml)	Blank Volume (ml)	Acid number (mg KOH/g oil)
0	0.29	10.7	0.3	178.04
5	0.22	5.2	0.3	110.58
15	0.31	6.6	0.3	100.89
30	0.19	4.1	0.3	99.29
45	0.25	4.3	0.3	79.43
60	0.22	3.6	0.3	74.47
90	0.21	3.5	0.3	75.65
120	0.21	3.5	0.3	75.65
180	0.18	2.7	0.3	66.19
185	0.2	2.5	0.3	54.61
195	0.2	2.2	0.3	47.16
210	0.15	1.7	0.3	46.33
225	0.3	2.7	0.3	39.71
240	0.18	1.5	0.3	33.09
270	0.23	1.8	0.3	32.37
300	0.23	1.6	0.3	28.06

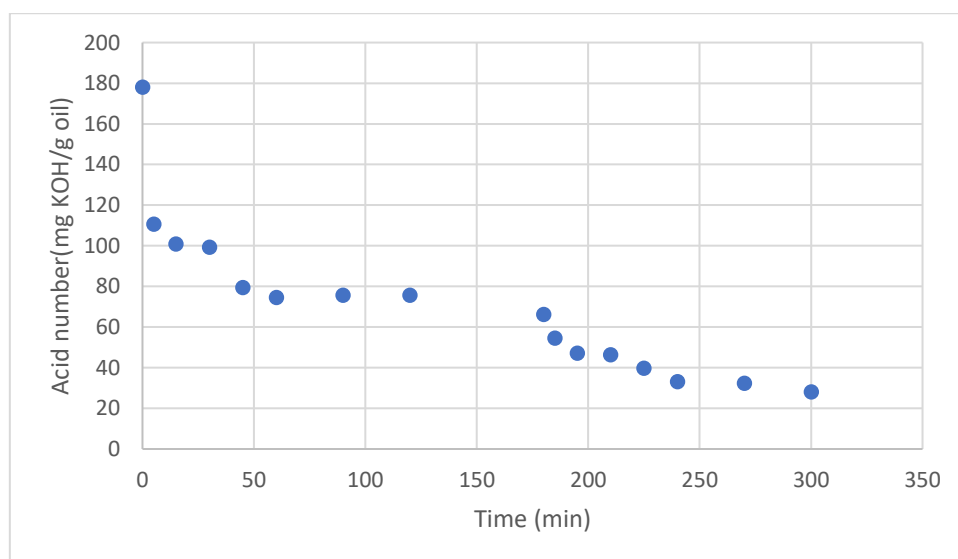


Figure 12. Experiment 5. Acid number vs time

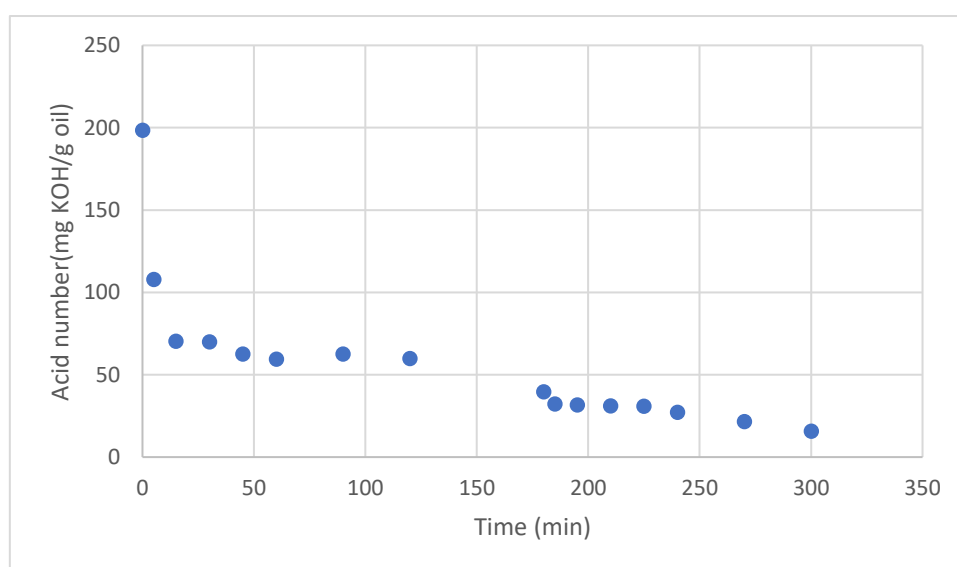
The behavior of the reaction is as expected, decreasing considerably the concentration of acid the first 60 minutes, to then stabilize until 180 minutes. Once the extra methanol and catalyst is added, the concentration of acid decreases due to the effect of these.

## EXPERIMENT 6

PTSA as a catalyst, 60°C and 30% and 10% in mass of methanol respectively.

*Table 14. Experiment 6. Acid number results in titration*

Time (min)	Mass (g)	Volume KOH(ml)	Blank Volume (ml)	Acid number (mg KOH/g oil)
0	0.18	7.5	0.3	198.59
5	0.23	5.3	0.3	107.93
15	0.31	4.7	0.3	70.46
30	0.17	2.7	0.3	70.09
45	0.23	3.2	0.3	62.6
60	0.2	2.7	0.3	59.57
90	0.19	2.7	0.3	62.71
120	0.29	3.8	0.3	59.92
180	0.15	1.5	0.3	39.71
185	0.2	1.6	0.3	32.27
195	0.25	1.9	0.3	31.77
210	0.27	2	0.3	31.26
225	0.24	1.8	0.3	31.03
240	0.2	1.4	0.3	27.30
270	0.23	1.3	0.3	21.58
300	0.22	1	0.3	15.79



*Figure 13. Experiment 6. Acid number vs time*

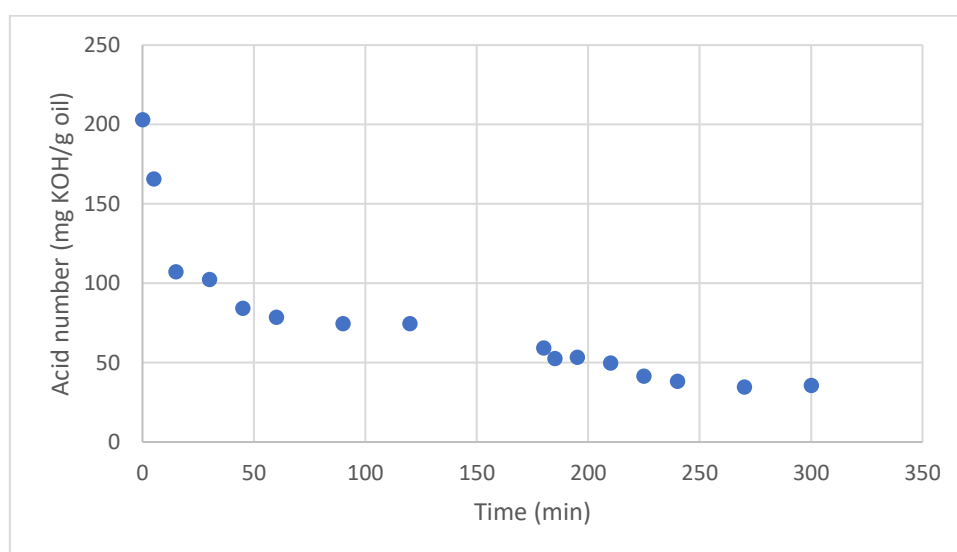
As can be seen in the graph, first, the acid concentration decreases rapidly and after 45 minutes it stabilizes. When the extra methanol and catalyst is added, there is a small decrease in the concentration of the acid.

## EXPERIMENT 7

H<sub>2</sub>SO<sub>4</sub> as a catalyst, 70°C and 30% and 10% in mass of methanol respectively.

*Table 15. Experiment 7. Acid number results in titration.*

Time (min)	Mass (g)	Volume KOH(ml)	Blank Volume (ml)	Acid number (mg KOH/g oil)
0	0.23	9.7	0.3	202.91
5	0.09	3.3	0.3	165.49
15	0.19	4.4	0.3	107.13
30	0.17	3.8	0.3	102.21
45	0.23	4.2	0.3	84.18
60	0.19	3.3	0.3	78.39
90	0.22	3.6	0.3	74.47
120	0.18	3	0.3	74.47
180	0.21	2.8	0.3	59.10
185	0.17	2.1	0.3	52.56
195	0.14	1.8	0.3	53.19
210	0.12	1.5	0.3	49.64
225	0.24	2.3	0.3	41.37
240	0.13	1.3	0.3	38.19
270	0.23	1.9	0.3	34.53
300	0.23	1.95	0.3	35.61



*Figure 14. Experiment 7. Acid number vs time*



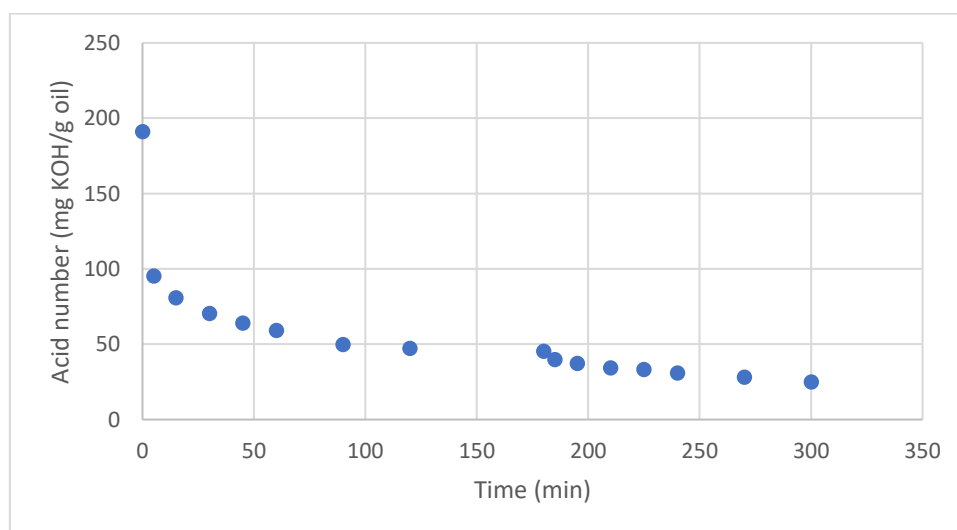
In this case, it is observed how the acid concentration decreases a lot initially, and after 30 minutes, it continues decreasing but more slowly. When the extra methanol and catalyst is added, the reaction continues decreasing at the rate that it did before adding it.

## EXPERIMENT 8

PTSA as a catalyst, 60°C and 30% and 10% in mass of methanol respectively.

*Table 16. Experiment 8. Acid number results in titration*

Time (min)	Mass (g)	Volume KOH(ml)	Blank Volume (ml)	Acid number (mg KOH/g oil)
0	0.26	10.3	0.3	190.95
5	0.12	2.6	0.3	95.15
15	0.24	4.2	0.3	80.67
30	0.24	3.7	0.3	70.33
45	0.21	3	0.3	63.83
60	0.21	2.8	0.3	59.1
90	0.23	2.6	0.3	49.64
120	0.19	2.1	0.3	47.03
180	0.11	1.3	0.3	45.13
185	0.1	1.1	0.3	39.71
195	0.16	1.5	0.3	37.23
210	0.16	1.4	0.3	34.13
225	0.24	1.9	0.3	33.09
240	0.17	1.35	0.3	30.66
270	0.23	1.6	0.3	28.06
300	0.12	0.9	0.3	24.82



*Figure 15. Experiment 8. Acid number vs time*

As can be seen in the graph, first, the acid concentration decreases rapidly and after 45 minutes it stabilizes. When the extra methanol and catalyst is added, there is a small decrease in the concentration of the free fatty acids.

### 3.1.6 EXPERIMENTS COMPARISON

After presenting the results and graphs of all the experiments, it is important to compare the results among them in order to see more clearly the differences between the different conditions in which the transesterification reaction has been carried out to obtain biodiesel.

Before comparing the different results, it is obvious that the behavior of the reaction of experiment 1 is very different from the rest of the reactions, so it is done again, taking a sample after 120 minutes of reaction as a check, and as expected, we obtain a result that is far from that obtained during the experiment. the acid number obtained in this sample is 62.85 mg KOH / g oil, much higher than other acid numbers for that time. So it is decided not to consider this experiment when comparing and drawing our conclusions.

#### SAME CATALYST

#### SULFURIC ACID

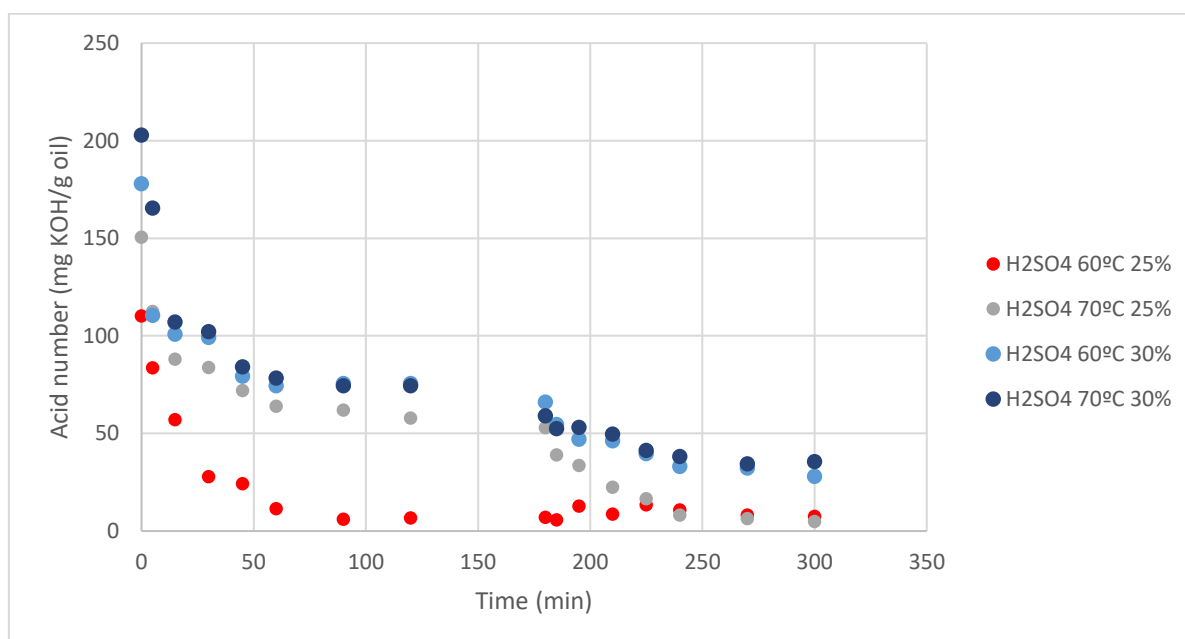


Figure 16. Comparison of all the reactions with  $H_2SO_4$  as a catalyst vs time

As can be seen in the graph, the reaction at 70°C and 25% methanol yields a higher yield and a higher conversion. Before performing this experience, the expected result was that the higher the temperature and the amount of reagents (methanol in this case) the higher the degree of

conversion, something that is not fulfilled in our experience, since at all times the reaction at 70 °C and 25% methanol has a lower acid number.

Another important fact to comment is the behavior of this reaction after the second addition of methanol and catalyst, since it undergoes a large decrease in the acid number, unlike the other two reactions.

The final acid concentration for the most favorable conditions is 4.96 mg KOH/g oil, so the conversion is of 97.57%

## PTSA

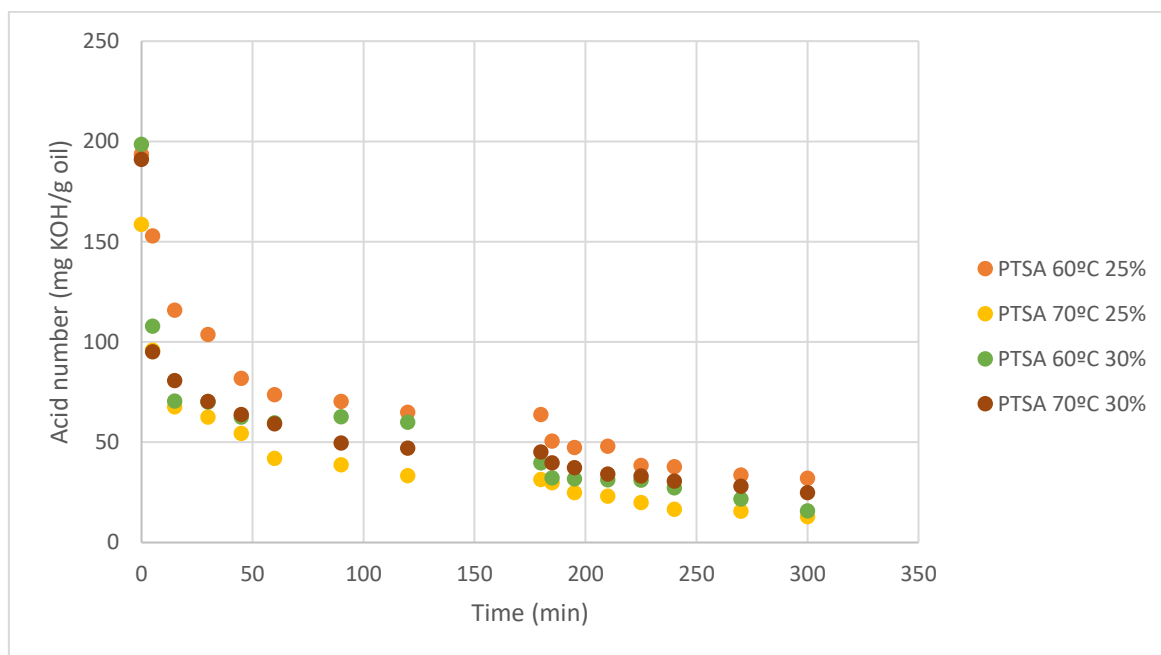


Figure 17. Comparison of all the reactions with PTSA as a catalyst vs time

Observing the graph of the 4 different reactions with the PTSA catalyst, it is observed that the best conditions are at 70°C and 25% by mass of methanol. It is somewhat surprising because in theory, with more reagent (methanol) should react more acid, however, in our case it reacts more acid with 25% than with 30% methanol at 70 °C.

Another conclusion that can be obtained is that without a doubt, the worst conditions would be at 60°C and with 25% methanol. This condition is more logical, because a temperature and a low amount of reagent generates a worse reaction kinetic.

Finally, note that the final acid number obtained with the most favorable reaction for the PTSA catalyst is 12.81 mg KOH / g oil

The final acid concentration for the most favorable conditions is 12.81 mg KOH/g oil, that means a conversion of 93.75%

## SAME TEMPERATURE

60°C

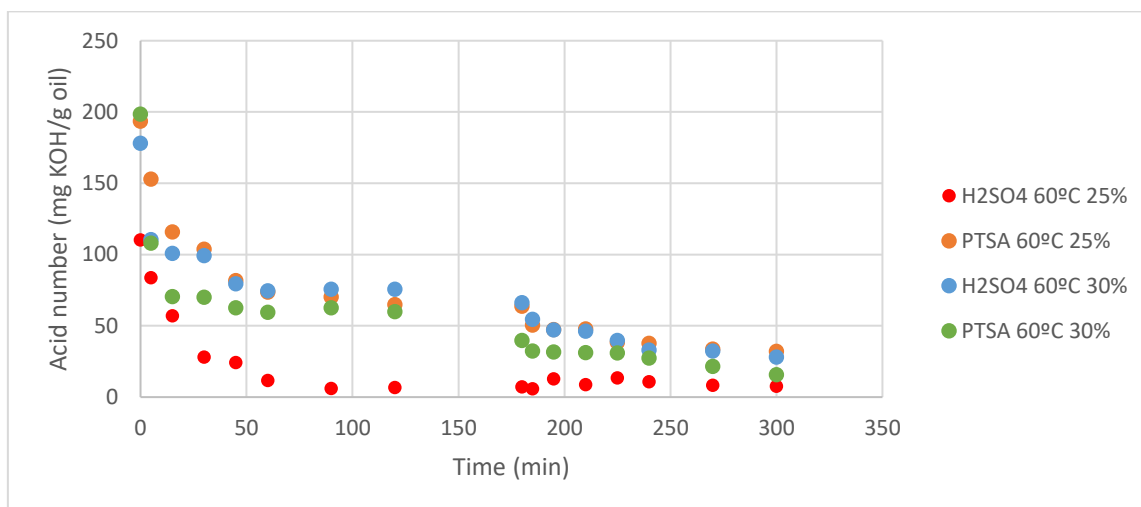


Figure 18. Comparison of all the reactions at 60°C vs time

Comparing the data obtained at the same reaction temperature, it can be concluded that they are completely logical, since despite not being able to count on information about sulfuric acid with 25% methanol, it is found that the most unfavorable reaction is that which has a lower amount of methanol.

On the other hand, comparing the results for the two reactions with the same amount of methanol (30%), it can be concluded that the PTSA catalyst is more effective than sulfuric acid, since it obtains lower acid numbers throughout the reaction.

The final acid concentration for the most favorable conditions is 15.79 mg KOH/g oil with a conversion of 92.29%

70°C

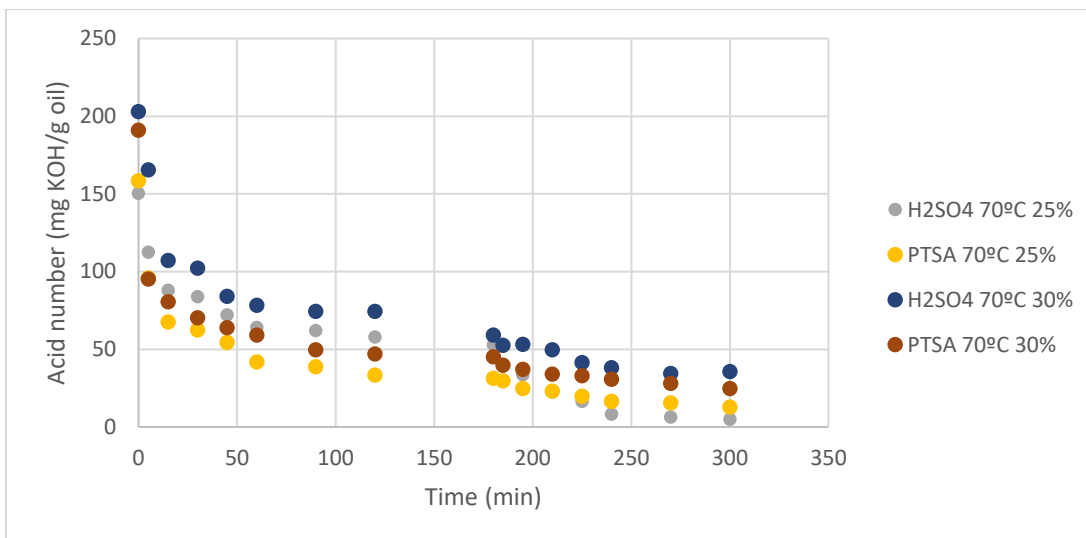


Figure 19. Comparison of all the reactions at 70°C vs time

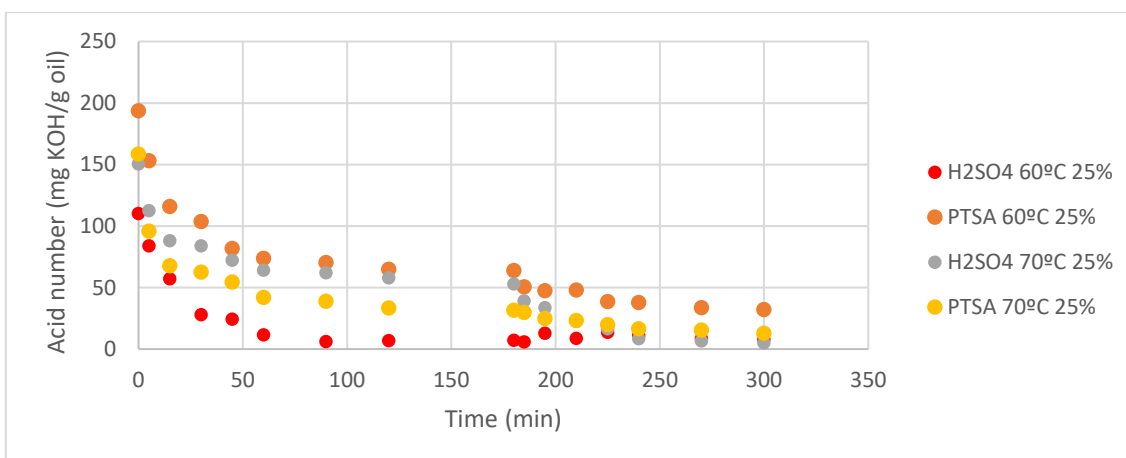
Observing the graph it can be verified that once again, reactions with 25% methanol are more efficient compared to those with 30% methanol.

Another important fact that can be extracted from the graph is that for shorter times, in this case 3 hours, the reaction with 25% methanol and PTSA as the reactant is the most efficient. However, for longer times, in this case 5 hours, the reaction with 25% methanol and sulfuric acid as catalyst is the most efficient.

The final acid concentration for the most favorable conditions is 4.96 mg KOH/g oil (97.57% conversion)

## SAME QUANTITY OF METHANOL

25%



Graphic X. Comparison of all the reactions with 25% methanol vs time

In the graph it can be seen that in the first part of the reaction, before adding the extra methanol and catalyst, the reaction with the lowest acid number is that of the PTSA and 70°C, followed by that of sulfuric acid at 70°C. However, when adding the extra methanol and catalyst, a considerable reduction occurs by the reaction at 70 ° C of sulfuric acid, which means that after 5 hours of reaction, it is the one that possesses the lowest acid number, with a value of 4.96 mg KOH / mg oil.

On the other hand, the reaction at 60°C with PTSA shows the worst performance at all times and supposedly that of the sulfuric acid at that temperature should show a similar performance.

In this case, this result is the expected one, since a higher temperature increases the speed of the reaction and therefore the degree of conversion.

30%

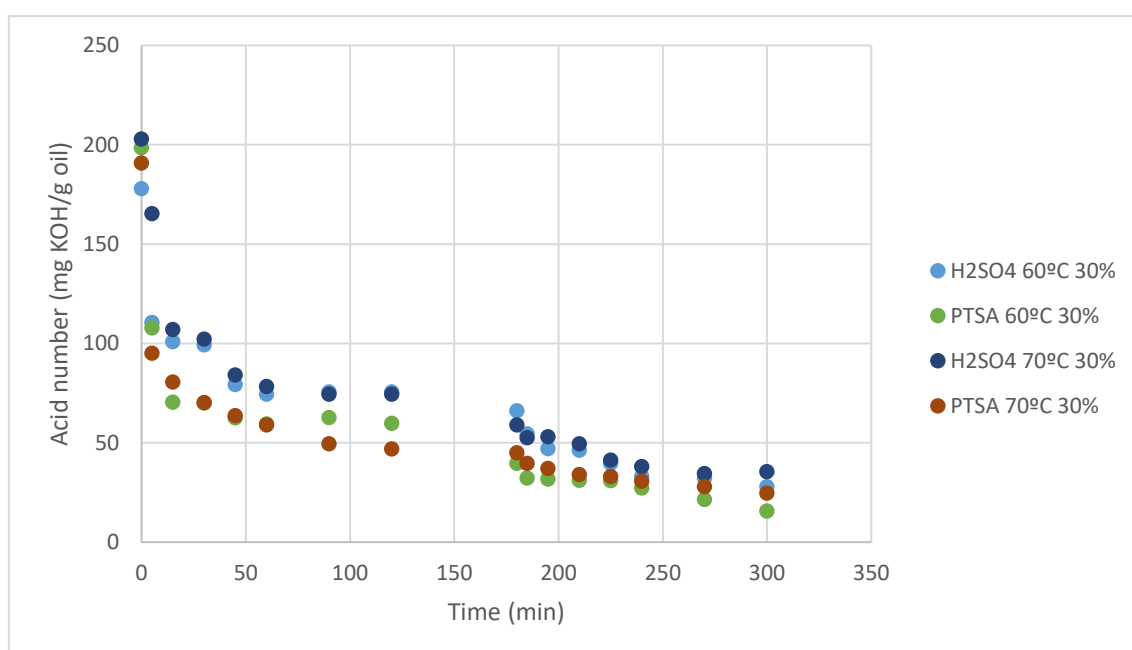


Figure 20. Comparison of all the reactions with 30% methanol vs time

Surprisingly, in this case, the reaction that obtains at the end a lower acid number is that of the PTSA at 60 ° C and the one that obtains a worse yield and degree of conversion is that of sulfuric acid at 70 ° C, so these results are totally opposite to those obtained for the reactions with 25% methanol.

It can be stated that for that amount of methanol, the PTSA catalyst obtains higher yields than sulfuric acid.

The minimum value of acid number obtained is 15.79 mg KOH/mg oil(02.25%), which is a value higher than that obtained with 25% methanol.

## ALL THE EXPERIMENTS

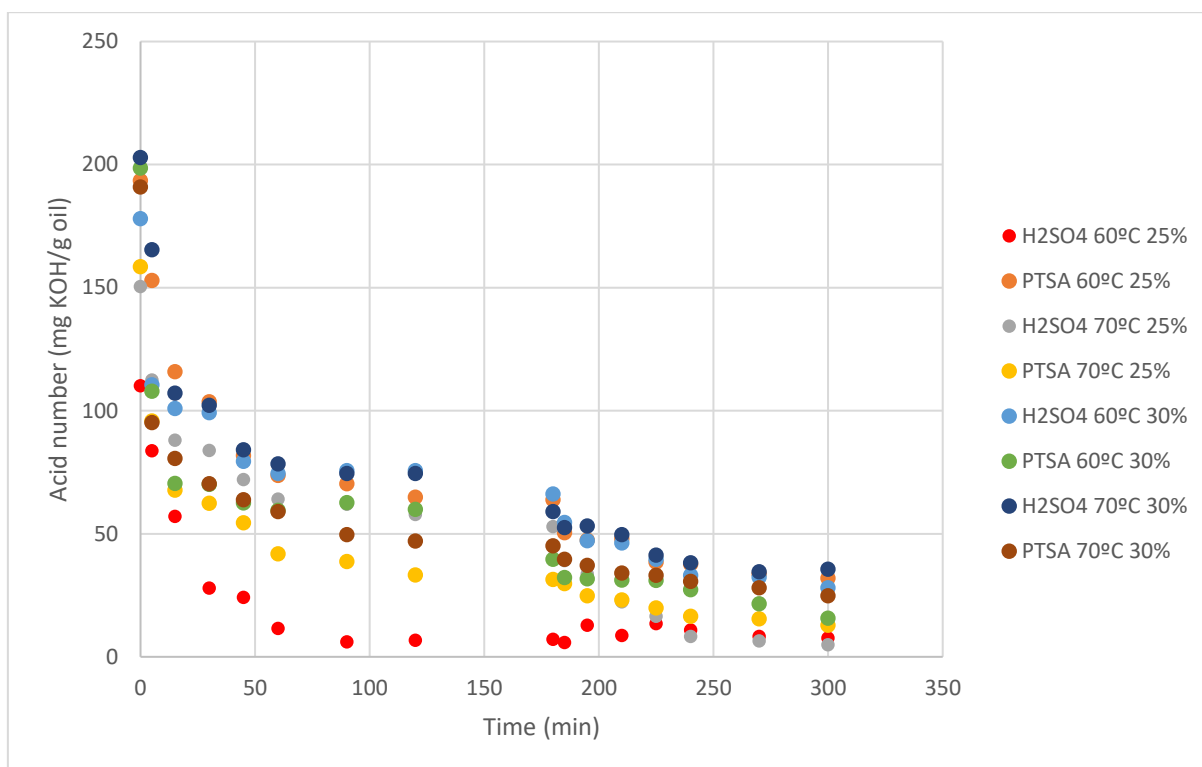


Figure 21. All experiments comparison. Acid number vs time

By exposing all the graphs together, several conclusions can be drawn:

Before making the second addition, the reactions with the lowest acid number are those that use PTSA as a catalyst, with the exception of the one that is carried out at 60°C and 25% methanol, which has an acid number lower than the rest due to the fact that the conditions of temperature and amount of methanol are not the most favorable.

On the other hand, after 5 hours of reaction, the reactions that use PTSA as a catalyst continue being the ones with less acid number, with the exception of the reaction with sulfuric acid with 25% methanol at 70°C, which is the lowest number acid possesses all the reactions performed.

Regarding the influence of temperature, quite different results are obtained. In theory, a higher temperature leads to a higher reaction rate and therefore a lower acid number. This is true for all reactions at 70 ° C except for sulfuric acid with 30%, which in fact is the reaction with the highest acid number of all.

Finally, as regards the influence of the amount of methanol used, in theory, a greater quantity of reagents facilitates the obtaining of the products, which would correspond to a lower acid number. However, the two lower acid numbers obtained correspond to reactions that have used 25% by weight of methanol, so this is not true for our study.

Another way to compare the different experiments is through the conversion percentage, which is calculated by the following expression:

$$\% \text{ conversion} = \left(1 - \frac{LK}{LK_{\text{raw material}}}\right) * 100 \quad (\text{equation 2})$$

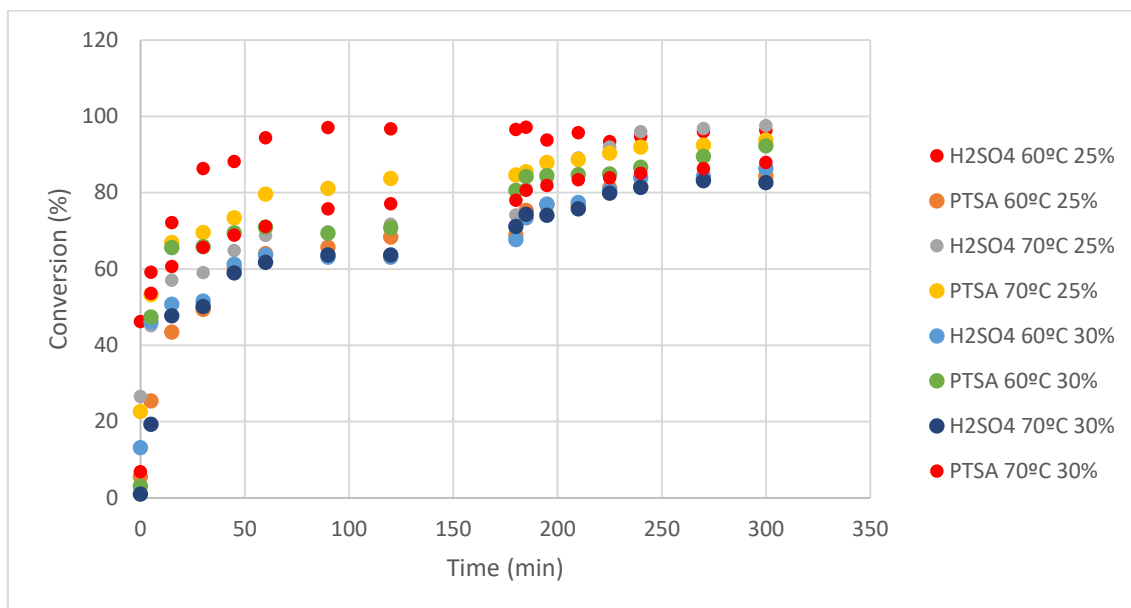


Figure 22. All experiments comparison. Conversion vs time

So, the total conversions of each experiments are the following:

Table 17. Final acid number and conversion of each experiment.

CONDITIONS	ACID NUMBER (mg KOH/g oil)	CONVERSION(%)
H2SO4 60°C 25%	7.63	96.27
PTSA 60°C 25%	32.02	84.37
H2SO4 70°C 25%	4.96	97.58
PTSA 70°C 25%	12.81	93.74
H2SO4 60°C 30%	28.06	86.31
PTSA 60°C 30%	15.79	92.29
H2SO4 70°C 30%	35.61	82.62
PTSA 70°C 30%	24.82	87.89



## 3.2 PART II: PROPERTIES OF BIODIESEL

As mentioned in the experimental procedure, at the end of all the experiments both biodiesel mixtures are analyzed to know their acid number. When analyzing the biodiesel sample produced using sulfuric acid as a catalyst, an acid number of 28.86 mg KOH/mg oil is obtained, while the biodiesel mixture using PTSA has an acid number of 17.6, so that the mixture of biodiesel obtained with PTSA as a catalyst will be used to analyze their properties and compare them with the raw material.

The properties to analyze are: density, viscosity, cloud point, freezing point, smoke point and ignition point.

### 3.2.1 DENSITY

The pycnometric method is used to determinate the density of biodiesel, it's a very precise method and it uses a working liquid with well-known density at different temperatures, such as water. The density can be calculated using the following equation:

$$\rho_{dest(T)} = \frac{\rho_{H2O(T)} * m_{dest}}{m_{H2O}} \quad (\text{equation 3})$$

Both biodiesel and the waste oil were at room temperature ( $T = 20^{\circ}\text{C}$ ). Using the table of the density of water provided in the instructions we can know the density of both liquids.

°C	0,0	0,1	0,2	0,3	0,4	0,5	0,6	0,7	0,8	0,9
15	999,0986	999,0834	999,0682	999,0528	999,0373	999,0217	999,0060	998,9902	998,9742	998,9581
16	998,9420	998,9257	998,9093	998,8927	998,8761	998,8593	998,8425	998,8255	998,8084	998,7912
17	998,7739	998,7565	998,7389	998,7213	998,7035	998,6856	998,6676	998,6495	998,6313	998,6130
18	998,5946	998,5760	998,5574	998,5386	998,5198	998,5008	998,4827	998,4625	998,4432	998,4238
19	998,4043	998,3847	998,3650	998,3451	998,3252	998,3051	998,2850	998,2647	998,2444	998,2239
20	998,2033	998,1826	998,1619	998,1410	998,1200	998,0989	998,0777	998,0564	998,0350	998,0134
21	997,9918	997,9701	997,9483	997,9264	997,9043	997,8822	997,8600	997,8376	997,8152	997,7927
22	997,7700	997,7473	997,7245	997,7015	997,6785	997,6554	997,6321	997,6088	997,5854	997,5618
23	997,5382	997,5144	997,4906	997,4667	997,4427	997,4185	997,3943	997,3700	997,3456	997,3210
24	997,2964	997,2717	997,2469	997,2220	997,1970	997,1719	997,1467	997,1214	997,0960	997,0706
25	997,0450	997,0193	996,9935	996,9677	996,9417	996,9157	996,8895	996,8633	996,8369	996,8105
26	996,7840	996,7574	996,7307	996,7039	996,6770	996,6500	996,6229	996,5957	996,5685	996,5411
27	996,5137	996,4861	996,4585	996,4308	996,4029	996,3750	996,3470	996,3190	996,2908	996,2625
28	996,2341	996,2057	996,1771	996,1485	996,1198	996,0910	996,0621	996,0331	996,0040	995,9748
29	995,9456	995,9162	995,8868	995,8573	995,8277	995,7980	995,7682	995,7383	995,7083	995,6783
30	995,6482	995,6179	995,5876	995,5572	995,5267	995,4962	995,4655	995,4348	995,4039	995,3730
31	995,3420	995,3109	995,2797	995,2485	995,2171	995,1857	995,1542	995,1226	995,0909	995,0591
32	995,0273	994,9953	994,9633	994,9312	994,8990	994,8667	994,8343	994,8019	994,7694	994,7368
33	994,7041	994,6713	994,6384	994,6055	994,5725	994,5394	994,5062	994,4729	994,4395	994,4061
34	994,3726	994,3390	994,3053	994,2716	994,2377	994,2038	994,1698	994,1357	994,1015	994,0673

Figure 23. Density of water ( $\text{kg}/\text{m}^3$  at various temperatures

So, the density of the water at  $20^{\circ}\text{C}$  is  $998,2033 \text{ kg}/\text{m}^3$ .

As 2 pycnometers of different volume (10 and 25 ml) have been used, the water is weighed for both volumes, obtaining values of 9.98 grams for the 10 ml and 24.96 grams for 25 ml. The density of the raw material and biodiesel is as follows:

$$\rho_{raw\ material} = \frac{998.2033 * 9.05}{9.98} = 905.18\ kg/m^3$$

$$\rho_{Biodiesel} = \frac{998.2033 * 21.81}{24.96} = 872.23\ kg/m^3$$

To know the density at 15°C, the next equation is used:

$$\rho_{T'} = \rho_T + \alpha * (T - T') \quad (\text{equation 4})$$

Where:

$\rho_{T'}$  is density at standard temperature kg/m

$\rho_T$  is density at T temperature kg/m<sup>3</sup>

T is measurement temperature, °C

T' standard temperature, °C

$\alpha$  temperature factor of density, g/cm<sup>3</sup>

With a good approximation (with minor differences between the measurement temperature and standard temperature), the following formula can be used to calculate the calculation factor value:

$$\alpha = -0.0013 * \rho_T + 0.0018 \quad (\text{equation 5})$$

$$\alpha_{biodiesel} = -0.0013 * 0.87223 + 0.0018 = 0.000665971\ g/cm^3$$

$$\alpha_{raw\ material} = -0.0013 * 0.90518 + 0.0018 = 0.000623266\ g/cm^3$$

So, the density at 15°C is:

$$\rho_{biodiesel,15^\circ C} = 872.23 + 0.665971 * (20 - 15) = 875.56\ kg/m^3$$

$$\rho_{raw\ material,15^\circ C} = 905.18 + 0.623266 * (20 - 15) = 908.29\ kg/m^3$$

So the density of the biodiesel is lower than the raw material used.

### 3.2.2 VISCOSITY

Viscosity is a very important property of biodiesel, because if it is too high it can cause problems in the functioning of the engine when used.

To calculate the viscosity, a capillary tube viscometer is used, consisting of 2 vessels connected by a long tube of small diameter known as a capillary tube. As the fluid flows through the tube with a constant velocity, the system loses energy, causing a pressure drop. To know the viscosity, the time it takes for the fluid to fall from one signaled point to another is measured, as can be seen in the Figure X. Each viscometer has a constant, that when multiplied by time, the viscosity of the liquid to be analyzed is obtained. The process is done in a bath of 40 degrees.



Figure 24. Two signaled points

For the biodiesel, the constant of the viscosimeter was  $0.02837 \text{ mm}^2/\text{s}^2$ . The experiment was done twice, obtaining times of 191 and 193 seconds, so the average time is 192 seconds.

$$v_{Biodiesel} = 192 \text{ s} * 0.02837 \frac{\text{mm}^2}{\text{s}^2} = 5.447 \text{ mm}^2/\text{s}$$

For the raw material, the constant of the viscosimeter was  $0.05657 \text{ mm}^2/\text{s}^2$ . The experiment was done twice, obtaining times of 344 and 342 seconds, so the average time is 343 seconds.

$$v_{Raw \text{ material}} = 343 \text{ s} * 0.05657 \frac{\text{mm}^2}{\text{s}^2} = 19.4 \text{ mm}^2/\text{s}$$

So as can be seen, the viscosity with the reaction has been decreased a lot.

### 3.2.3 CLOUD AND FREEZING POINT

It is very important to know both the temperature of the cloud point and the freezing point because when operating at low temperatures, these can cause engine problems.

To know the cloud point and the freezing point, biodiesel and raw material are introduced in a tube, with a subject thermometer (Figure X), and submerged in a  $-40^{\circ}\text{C}$  bath. The appearance of the samples is checked periodically. The cloud point corresponds to the temperature at which the sample presents a cloudy appearance, as shown in Figure X. The freezing point corresponds to the moment when you tilt the sample 45 degrees and it does not move, as can be seen in Figure X.

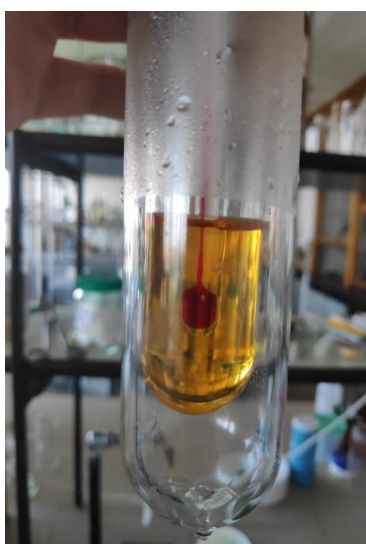


Figure 25. Normal liquid state



Figure 26. Cloud point



Figure 27. Freezing point

Table 18. Cloud and freezing

point

	Biodiesel	Raw material
Cloud point	$-6^{\circ}\text{C}$	$17^{\circ}\text{C}$
Freezing point	$-9^{\circ}\text{C}$	$10.5^{\circ}\text{C}$

Comparing the results, the low temperatures properties have changed a lot with the reaction. The freezing point of the oils varies according to the insaturations. For the case of oleic acid, which has an unsaturation, the melting temperature is  $16.3^{\circ}\text{C}$ . The melting temperature increases as the unsaturation decreases, so when mixing the oil with other saturated compounds, the melting temperature increases.

On the other hand, the melting and cloud temperatures for biodiesel have been quite low, which makes it quite resistant to low temperatures.

### 3.2.4 SMOKE AND IGNITION POINT

To calculate the point of smoke and ignition of both the raw material and biodiesel, both samples are heated separately in an oven as shown in Figure X. By using a thermometer, you can know the temperature of the oil in each moment.

In the case of the smoke point, you simply have to wait until you see smoke appear on the oil. At that moment the temperature is recorded. The sample is still heated, and a flame is passed over it. This flame does not remain fixed up, since it would burn the gases and we would not obtain the exact temperature of ignition. Therefore, the flame is periodically passed over, until a spark is heard, a flame appears or in the worst case, the oil is ignited.



Figure 28. Experiment assembly

Table 19. Smoke and ignition point

	Biodiesel	Raw material
Smoke point	126 °C	148 °C
Ignition point	204 °C	240 °C

It can be affirmed that both temperatures have decreased with the transesterification reaction. The ignition temperature of the oil varies depending on the composition and unsaturation, and always goes between 200-250°C, as in this case.

### 3.2.5 CONCLUSSION

Table 20. Properties comparison

	RAW MATERIAL	BIODIESEL	EN 14214:2003	ASTM D6751:07b	MS 2006:2008
ACID NUMBER (mg KOH/mg oil)	205	17.6	<0.5	<0.5	<0.5
DENSITY at 15°C (g/cm <sup>3</sup> )	0.908	0.875	0.86-0.9	-	0.86-0.9
VISCOSITY ( mm <sup>2</sup> /s)	19.4	5.447	3.5-5	1.9-6	3.5-5
CLOUD POINT (°C)	17	-6	-	-	-
FREEZING POINT (°C)	10.5	-9	-	-	-
SMOKE POINT (°C)	148	126	-	-	-
IGNITION POINT (°C)	240	204	>120	>130	>130

Comparing the properties of our biodiesel with the standard values of EN 14214:2003, ASTM D6751:07b and MS 2006:2008, the following conclusions can be drawn: the acid number obtained is not valid. This is a clear indication that the transesterification reaction has not had the appropriate degree of conversion. Therefore, it might be necessary more reaction time, more reactive, the use of another catalyst or increase the temperature and the pressure. On the other hand, the density obtained is adequate.

Regarding the viscosity, the value of this is higher than the one suitable for the standards EN 14214:2003 and MS 2006:2008, but it is adequate according to the ASTM D6751:07b regulation. Finally, our ignition point value is higher than the minima that are marked, so it would also be valid.

## 4. FINAL CONCLUSION

After this research work on the development of biodiesel from a raw material with a high content of free fatty acids in its interior, the following conclusions can be drawn.

In the first place, none of the experiences show a suitable result according to the biodiesel standards, since none of them has a final acid number lower than 0.5 mg KOH/g oil. This is because the transesterification reaction with an acid catalyst must be carried out above 100 degrees and at a pressure between 0.2 and 0.4 Mpa to achieve an adequate conversion, unfortunately, in the laboratory there were not enough means to perform it to those conditions. Another drawback that has been produced is that part of the methanol has evaporated and left the reactor during each of the sampling.

In spite of this, it is worth noting that the most favorable reaction has been carried out at 70°C, 25% methanol and sulfuric acid as catalyst, obtaining a final acid number of 4.96 mg KOH/g oil and a conversion of 97.58%.

On the other hand, the properties of biodiesel composed of the mixture of all the final products of the reactions with the PTSA catalyst have been analyzed, obtaining valid values of density and ignition point according to the standards values of EN 14214:2003, ASTM D6751:07b and MS 2006:2008. In terms of viscosity, it falls within the limits established by the ASTM D6751:07b standard only.

Finally, note that both cloud point values and freezing values are quite favorable for working at low temperatures.

## 5. LITERATURE REVIEW

- [1] Biodiesel Production Techniques. (2016, July). Retrieved June 20, 2019, from <http://factsheets.okstate.edu/documents/fapc-150-biodiesel-production-techniques/>
- [2] Biocombustibles: ventajas y desventajas - Escuelapedia - Recursos Educativos. (2014, June 9). Retrieved June 20, 2019, from <http://www.escuelapedia.com/biocombustibles-ventajas-y-desventajas/>
- [3] Botero, J. P. B., & Bedoya, A. B. (n.d.). Tipos de Biocombustibles. Retrieved June 20, 2019, from <http://biocombustibleseafit.blogspot.com/2011/04/tipos-de-biocombustibles.html>
- [4] Clarence Lehman, C. L., & Noelle Eckley Selin, N. E. S. (2008, August 2). biofuel | Definition, Types, & Pros and Cons. Retrieved June 20, 2019, from <https://www.britannica.com/technology/biofuel>
- [5] Colaboradores de Wikipedia. (2019a, June 11). Biodiesel. Retrieved June 20, 2019, from <https://es.wikipedia.org/wiki/Biodi%C3%A9sel>
- [6] Colaboradores de Wikipedia. (2019b, February 14). Índice de cetano - Wikipedia, la enciclopedia libre. Retrieved June 20, 2019, from [https://es.wikipedia.org/wiki/%C3%8Dndice\\_de\\_cetano](https://es.wikipedia.org/wiki/%C3%8Dndice_de_cetano)
- [7] M. Balat. Potential alternatives to edible oils for biodiesel production - A review of current work. *Energy Conversion and Management*, 52(2) 201, pp.1479-1492. doi: 10.1016/j.enconman, 2010.10.011.
- [8] M. M. Conceição, R. A., Candeia, F. C. Silva, A. F. Bezerra, V. J. Fernandes & A. G. Souza, Thermoanalytical characterization of castor oil biodiesel. *Renewable and Sustainable Energy Reviews*, 11(5), 2007, pp. 964-975. doi: 10.1016/j.rser.2005.10.001.
- [9] Moriana, L. M. (2018, September 25). Qué son los biocombustibles, ventajas y desventajas. Retrieved June 20, 2019, from <https://www.ecologiaverde.com/que-son-los-biocombustibles-ventajas-y-desventajas-1364.html>
- [10] Msc García-Muentes, S. A. G. M., Dr Lafargue-Pérez, F. L. P., & Dr Labrada-Vázquez, B. L. V. (2018, April). *SciELO - Scientific Electronic Library Online*. Retrieved June 20, 2019, from [http://scielo.sld.cu/scielo.php?script=sci\\_arttext](http://scielo.sld.cu/scielo.php?script=sci_arttext)
- [11] S. Sumathi, S. P. Chai, & A. R. Mohamed. Utilization of oil palm as a source of renewable energy in Malaysia. *Renewable and Sustainable Energy Reviews*, 12(9) 2008, pp. 2404-2421. doi: 10.1016/j.rser.2007.06.006.
- [12] Skrzyńska, E. S. (2017). *Biofuels and bioresources*. Retrieved from <https://dysk.pk.edu.pl/index.php/s/wiw5RrTGtYe2j2X#pdfviewer>
- [13] Y. Sharma, B. Singh, & S. Upadhyay, Advancements in development and characterization of biodiesel: A review. *Fuel*, 87(12) 2008, pp. 2355-2373. doi: 10.1016/j.fuel.2008.01.014.



- [14] Wikipedia contributors. (2019, June 18). burning point of oil and fats. Retrieved June 20, 2019, from [https://en.wikipedia.org/wiki/Smoke\\_point](https://en.wikipedia.org/wiki/Smoke_point)
- [15] Zapata, C. D. Z. (2007, January 1). PRODUCCIÓN DE BIODIESEL A PARTIR DE ACEITE CRUDO DE PALMA: 1. DISEÑO Y SIMULACIÓN DE DOS PROCESOS CONTINUOS | Zapata | DYNA. Retrieved June 20, 2019, from <https://revistas.unal.edu.co/index.php/dyna/article/view/894>
- [16] BENGOGOROSTIZA, P. B. (s.f.). SINTESIS DE BIODIESEL MEDIANTE CATALISIS ACIDA HETEROGENEA A PARTIR DE MEZCLAS DE ACEITE Y ÁCIDOS GRASOS. Recuperado de <https://academica-e.unavarra.es/bitstream/handle/2454/5984/577867.pdf?sequence=1&isAllowed=y>