Synthesis and properties of biodiesel obtained from fatty waste materials.

Vegetable waste oils, rapeseed oil.

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Content

1. Goal

In this project we will discuss all the important issues related with biodiesel, production in laboratory and industrial scale, comparing the different methods to make the transesterification, raw materials and their differences; focusing in vegetable oils, explaining the most important oils in different parts of the world and their differences, and of course analysing the final properties of the different biodiesels we can find in the world industry.

The main objective in the laboratory is to obtain biodiesel by transesterification of a mixture of rapeseed oils and compare their properties with the conventional diesel we can find in the gas station to see the possible behaviour of our biofuel in a combustion engine.

2. Introduction

First of all I would like to explain clearly the concept of biofuel and biodiesel, a biofuel is any material that can react with other substance to provide energy, could be for work or heating energy; which comes from the agriculture, some renewable source or waste material, or has been produced by some biological process, such as anaerobic digestion or transesterification of oils, of course biomass and a lot of different products are included here; but we will focus in the biodiesel.

Biodiesel is one type of biofuel mainly composed by alkyl esters, usually created by the reaction of an alcohol (methanol, ethanol or isopropanol) with the fats (triglycerides), coming from different sources, and usually with the presence of a catalyst. The different fatty acids contained in the triglycerides will be determining for the properties of our oil or fat, what will be very important for the chemical reaction and conditions, and of course for the final product. We can produce biodiesel from a wide range of triglycerides sources, the most important are: the most common vegetable oils (palm, canola, sunflower, soy or coconut), waste oils, and animal fats. Referring to the alcohol I have to mention that many alcohols can be used for the transesterification reaction, however usually methanol is used in industry not only because of the prize but also because methanol is more reactive than bigger alcohols.

Biodiesel can be used directly in conventional engines, however in many countries it is very usual to create blends with petrodiesel because they are completely miscible, however these blends are not proper biofuels, so we will not discuss so much about them but they are quite important nowadays because a lot of countries started with this before using pure biodiesel because less modifications are needed in the engines, for example there are some trains in the United Kingdom that run witch some of these blends, for them we use some acronyms referring to the amount of biodiesel in the blend, for example B100 will be pure biodiesel and B5 will be a mixture with 5% biodiesel.

Vegetable oils and animal fats were investigated as fuels a long-time ago and we now that Rudolf Diesel (Diesel engine inventor) was very interested in these type of fuels. It was in 1900 when the world first saw a small diesel engine running with peanut oil during the Paris exposition, the main problem and the main reason why oils are not used directly in engines is the high viscosity (around 10 times higher than pterodiesel), as well as some other important properties like low volatility and problems with injection systems. A lot of different ideas related to solve these problems with oil properties have been carried out, such as mixing oil with petrodiesel, designing specific engines for vegetable oil or preheating the oil, however the most successful idea was to treat oil and obtain a different substance with better properties for the diesel engines. In 1937 in the University of Brussels we can find the first patent in the world related with the usage of alkyl esters as a fuel, in this case it was ethyl esters coming from palm oil; however it was not until 1980 when two different patents (one in Brazil and the other in Germany) were registered related with the utilisation of methyl esters as a substitute for conventional diesel. The first Biodiesel factory was developed in Austria in 1991, in which they used rapeseed oil as the triglyceride source, in the same year the Austrian Standardisation Institute published the first quality standards for alkyl esters coming from fatty acids, since then biodiesel industry has not stopped growing, gaining importance all over the world, with soy oil in the USA, sunflower and canola oil in Europe and palm oil in tropical countries. Nowadays the research is focused in a renewable source of the triglycerides and the optimization of the industrial process, we have several examples such as non-eatable oils, waste fried oils, animal waste fats or microalgae oil.

2.1. Oil and fat composition

Oils and fats are mainly the essential raw materials for biodiesel production, in this section we will discuss the chemical properties and characteristics, we will focus on the vegetable oils, comparing their composition and properties for biodiesel production.

Triglycerides

Vegetable oils are mainly constituted by triglycerides (95-99% in weight), these triglycerides can be simple, when the three substituting groups are formed by the same molecules, and mixed, in which they are formed by different groups. Of course natural oils are complex mixtures of these two types of triglycerides. [1]

Mono and diglycerides

Due to the three hydroxyl groups that we have in one molecule of glycerine, this molecule can be mono, di or triesterified, mono and diglycerides appear in small amounts in nature, it is between 0.3 and 1% of the composition of vegetable oils. They are used as emulsion agent in food industry, that is why we have to avoid the appearance of these compounds as much as possible. [1]

Fatty acids

They are basically one carboxiylic group attached to a long chain of carbons, what we consider long is more or less 10 or more carbon atoms. By hydrolysis of the triglycerides we can obtain three fatty acids for each triglyceride. Fatty acids are divided in saturated and unsaturated depending on the presence of double bonds in the long chain, unsaturated can be divided in monounstarated or poliunsaturated fatty acids. Double bonds involve the presence of geometric isomers cis and trans, most of the fatty acids in nature (specially vegetable oils) present cis configuration whereas trans isomers appear usually in artificially hydrogenated fats and in some animal fats. Saturated and unsaturated fatty acids have different properties due to the orientation of the long chains, mainly because saturated can be packaged much better, which implies higher melting points, that is why oil is liquid at room temperature while some fats are not.

Free fatty acids (FFA) are present in fresh oils, they can have from less than 1% to more than 20% (refined oils usually have lower concentration than 0.1%). When our oil has an important presence of these FFA it is usually linked with the presence of mono and diglycerides, just because this FFA comes from the degradation of a triglyceride, and as mentioned before these molecules are not interesting for the industrial process, in fact, it will create additional costs in our production due to some problems during the separation of phases (which I personally suffered) because it difficulties the cleaning phases due to the emulsion that is formed between water and oil thanks to this molecules.[1] [2]

Phospholipids

Phospholipids or phosphooglycerides are present in a lot of different fatty substances like eggs and soy oil, they act like emulsifiers in a similar way to mono and diglycerides because they have a hidrofilic part (phosphate group and amine group) and a hidrofobic part (the hydrocarbon chain). For the soy oil for example we can have around 3.5% of fosfolipids which should be eliminated during the refine process. [1]

2.2. Classification of raw materials

Focusing in vegetable sources of triglycerides we have a wide variety of oils coming from totally different plants or fruits.

Rapeseed oil

The oil coming from the different varieties of rapeseed is mainly composed by monounsaturated fatty acids, this makes rapeseed oil a very good candidate for making the biodiesel, this monounsaturated fats have only one double bond in their structure and they are ideal for us because saturated fats put up the melting point and could be a problem in cold countries and a lot of polyunsaturated can imply problems with stability. Rapeseed oil composition is around 7% saturated and 93% unsaturated, being the predominant the erucic acid (22:1) with around 45% in weight. Rapeseed oil usually have between 1-7% of glucosinolates, a derivated from glucose which contains sulphur and nitrogen.

Canola oil is a special variety of rapeseed oil developed in Canada with very similar distribution of saturated and unsaturated fats but the amount of glucosinolates is reduced and it changes the type of unsaturated fats, in conventional rapeseed oil we have around 15% oleic (18:1) and 45% (22:1) erucic and in canola oil we have 60% oleic oil. This composition gives canola oil very good properties, it is highly homogenous because its composition is around 30% for the simple triglyceride triolein and the fatty acids are 93% formed by 18 carbon atoms chains oleic acid and polyunsaturated fats (18:2 and 18:3). [1] [2]

Sunflower oil

Sunflower oil is mainly composed by linoleic acid (18:2) around 68%, this gives this oil good alimentary properties, the main problem is the stability of alkyl esters due to the big percentage of polyunsaturated fats, there is a special variety of sunflower oil obtained by genetic modification with big amount of oleic acid that gives a lot of advantages for biodiesel production, even better than canola oil. [1] [2]

Soy oil

Soy oil is chemically quite similar to conventional sunflower oil despite the amount of polyunsaturated fats is reduced from 68% to 60% and that’s why soy oil gives better properties than sunflower oil, it is chemically more stable due to bigger proportions of saturated and monounsaturated fats. [1] [2]

Palm oil

Palm oil is extracted from the fruit of the palm tree, it is not very good for human health due to the big amount of saturated fats (almost 50%) that are present in it whereas that saturated fats give palm oil and to the derivate alkyl esters very good chemical stability. Palm oil has a different room temperature behaviour, it looks like semi-solid, more like butter than oil. The good point about palm oil is that we can separate it in two phases, one called palm olein and palm stearin.

Palm olein is the liquid phase we obtain, and it is sold as oil for cooking directly, stearin is used in chemical processes to obtain trans fats such as margarine. The main differences in composition is that, as said, palm oil is around 50-50% saturated and unsaturated but palm olein has less saturated fats (around 45%) and stearin has even more than 55%. [1] [2]

Palm kernel oil and coconut oil

Palm kernel oil and coconut oil have very similar compositions, palm kernel is obtained from the seeds of the palm fruit, both have very high content of saturated fats, even more than palm oil, as said before the main problem for these oils is the behaviour at low temperatures because saturated fats can be solid at room temperature, so imagine in a car engine in winter, we would need some additives or some chemical modifications in it that make this process less useful than other important oils for biodiesel industry. [1] [2]

Alternative oils

In different countries the development is this field is getting very important, the objective is to produce biodiesel using oil coming from non-edible, toxic, or non-conventional plants that also give a good yield for oil extraction. Here we have 3 important oils that could be interesting for the close future, jatropha, ricinus and sacha inchi.

Jatropha oil cannot be used for alimentary purposes due to its toxicity presents an intermediate distribution of saturated and unsaturated fats between rapeseed or sunflower and palm oil, around 20% saturated fats, so it can be very interesting for biodiesel production.

Ricinus oil is non-edible as well, this oil has a special property that makes it different from every oil in the world, it is the only oil with fatty hidroxiacids (OH groups in middle of the fatty chain). The presence of this OH groups makes ricinus oil less soluble in hexane, more soluble in ethanol and that is why this oil is very important in chemical industry, taking part for adhesives, inks, plastics or lubricants. It is mainly composed y ricinoleic acid (close to 90%) and mainly composed by the simple triglyceride, triricinolein.

Sacha inchi oil, in opposite to jatropha and ricinus oil is very recommended for human consumption due to the high content in polyunsaturated fats more than 85% between 18:2 and 18:3 acids. [1]

Microalgae oil

This type of oil is furthermore, one of the most important for the future, because they can grow almost everywhere, even more important they can do it faster, and they do not need as much space. The yield per hectare can be up to 200 times bigger than conventional fields for plants like rapeseed or soy. The research in this field is dedicated to apply genetic engineering to develop new species with bigger oil contents and to design good bioreactors to allow production in very big scale. [1]

Fried-waste oils

A very important source of triglycerides are waste oils, in addition they are much cheaper than refined oils and furthermore it is “closing the circle” using a waste material that will go to recycling plants or landfills and is considered a pollutant. This has been applied industrially in several countries with very good legislation related to waste oils and with experienced companies in collecting and treating this oils.

During the frying process oils suffer different changes in the structure related with the degradation of triglycerides, for example creating free fatty acids, mono and diglycerides and several by-products that can be created such as aldehydes ketones, alcohols or hydrocarbons. However, most of these compounds can be retired from oil by adsorption with different solids or using water to remove polar substances. Obviously this is not a good issue for biodiesel production but it can be compensated with the lower price of the raw material. [1]

Animal waste fats

Animal waste fats are a very big source of triglycerides, their composition depends on the animal it comes from but they usually have more saturated fats than vegetable oils and that is why they are solid or semi-solid at room temperature. We can find a big difference in animal waste fats between farm animals (pig, cow, chicken, turkey) and produced fish oils.

Beef tallow and lard (pig fat) are quite similar in composition and properties, depending on different factors they can reach more than 50% of saturated fats they are solid at room temperature and they have several uses such as lubricants, soaps and as ingredient for animal food.

Chicken fat is slightly different from the other two mentioned sources it has only around 30% of saturated fat and around 20% of polyunsaturated, maybe for biodiesel is one of the most appropriate one due to the less amount in saturated fats.

Fish oil is quite different from the other animal fats and there a lot of types of fish oil, but mainly they are obtained from different fish tissues, we can obtain around 1g of oil from 100g of fish, obviously depending on the fish but here we are talking about fishes with important amount of oil such as tuna, salmon, sardines and some more. Generally they have some other uses because they have what we call omega-3 acids which are very good for human and animal alimentation. [1] [2]

3. Main triglycerides reactions

The main industrial activity involving fatty acids like oils and fats is related with reactions in the carbonyle group (the most reactive part of this molecules), the double bonds and other functional groups that can appear, most of the processes we are going to discuss are equilibrium reactions that are usually catalysed to obtain better conversion. [1]

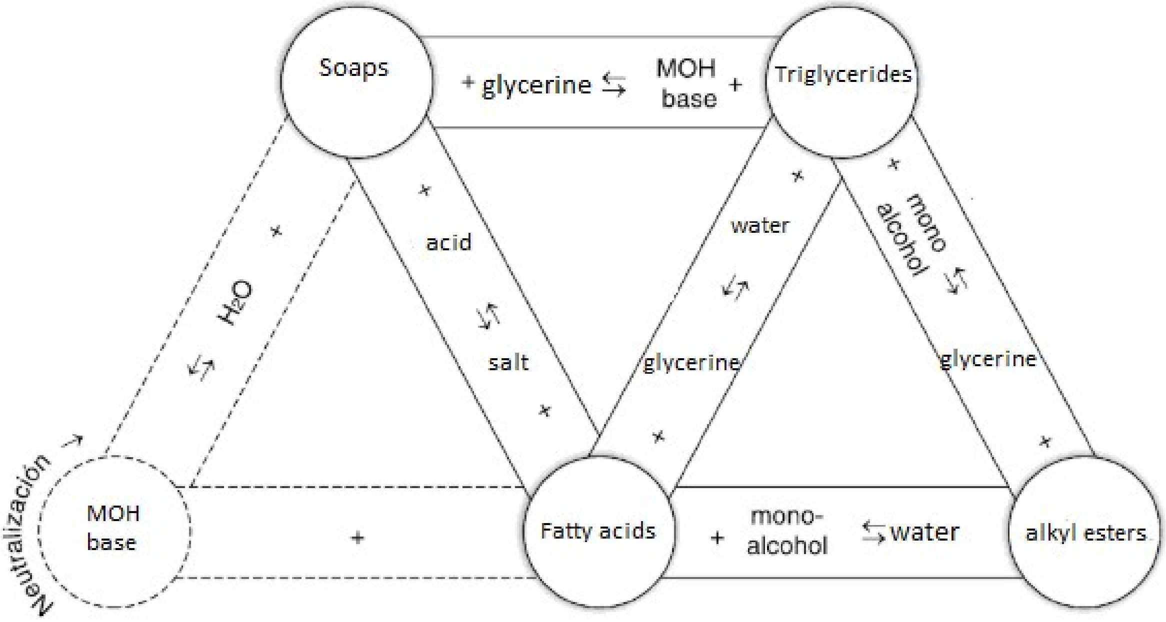


Figure 1. Representation of the main reactions related with triglycerides. Taken and adapted from reference [1].

3.1. Hydrolysis

Hydrolysis of triglycerides consists in the degradation of this big molecules with water into three fatty acids plus glycerine, usually catalysed by sulphuric acid or different oxides such as zinc, calcium or magnesium. This catalysts carry a double function, because they also have to work as emulsion agents to help the mixture of the two phases.

Industrially one of the most efficient and common methods is the Colgate-Emery, this reaction is not catalysed because it is carried at high pressure (5-6 MPa) and high temperature (250ºC). This process is carried out in continuous way using water steam in countercurrent. The result is two-phase mixture around 10% glycerol and oil, this oil phase is almost completely fatty acids. This method is quite expensive in equipment and energetically, furthermore it is not a good method when we have very high unsaturated fats because the temperature is very high for them. [1]

3.2. Saponification

Another way to call this reaction in industries is alkaline hydrolysis which is also working in continuous under moderate pressure (2 bar) and temperature (120ºC). In this reaction triglycerides react with KOH or NaOH dissolved in water or ethanol. The result is a mixture of the acid salts (soaps) and glycerol. In another reaction we can regenerate the fatty acids from the soaps using strong acids. This whole process after regenerating the fatty acids is an alternative to the direct hydrolysis process. This process is sometimes chosen before the Colgate-Emery process because at 120ºC there is no problem for unsaturated oils and the conditions of the reaction are less aggressive. [1] [2]

3.3. Esterification

Direct obtaining of alkyl esters from simple fatty acids making the reaction with methanol. The possibility to obtain alkyl esters directly from simple fatty acids gives two different alternatives for transesterification. The first alternative is the hydrolysis of triglycerides followed directly by esterification. The other possibility is to make saponification first, then with a strong acid we can obtain the simple fatty acids to make direct esterification. Quality in raw materials and some other factors can make this two alternatives interesting for industries, however the project will focus in the direct transesterification. [1]

4. Transesterification reaction

The transesterification reaction is the most important part in biodiesel production, there are different ways to carry this reaction but the general process is the following: Triglycerides react with methanol in a catalysed system resulting a mixture of alkyl esters that will depend on the composition of our triglycerides and glycerol. 1 mole of triglycerides reacts with 3 moles of methanol resulting 1 mole of glycerol and 3 moles of alkyl esters, this reaction is an equilibrium so it is necessary to use excess of alcohol to improve the conversion, another possibility is to remove the glycerol to obtain the same result, but in general it is easier to put excess of methanol.

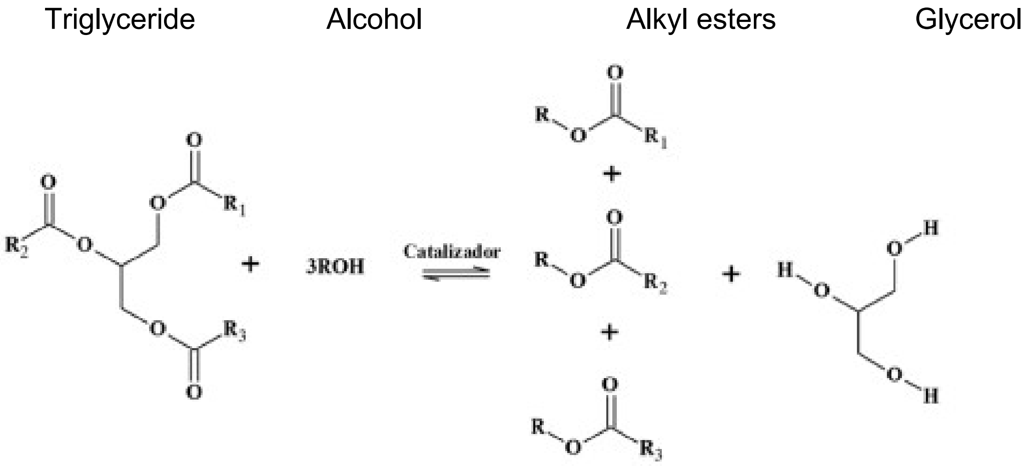


Figure 2. Transesterification reaction. Taken from reference [3]

This reaction appears as a global process but it is not what really happens, triglycerides start to react with methanol and they are first converted in a diglyceride, then in a monoglyceride and finally glycerol; so in every intermediate reaction an alkyl ester mole is created. During the first part of the reaction the concentration of mono and diglycerides is raising, however they reach a maximum and there one moment in which they start to disappear reacting with more methanol.

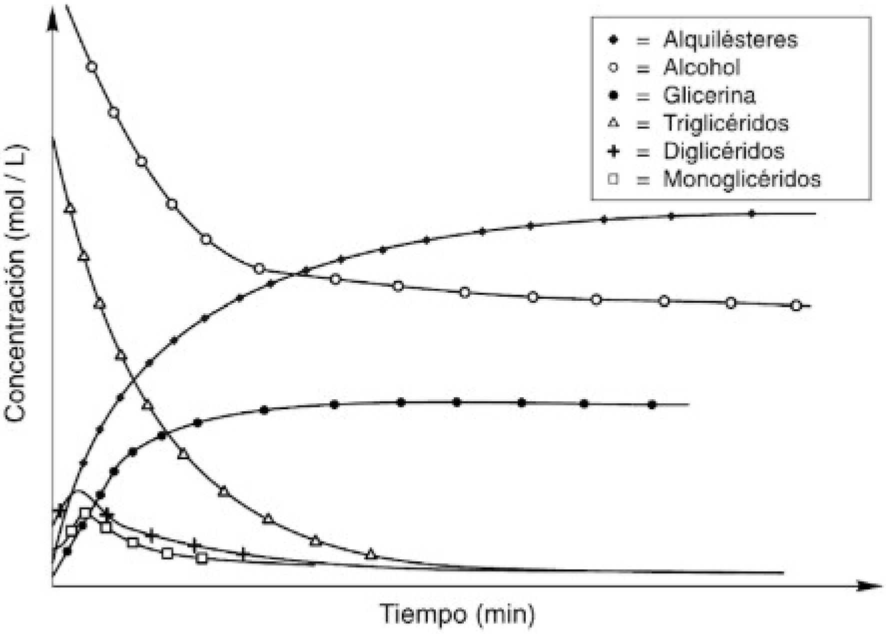


Figure 3. Concentration of the different substances involved in transesterification. Taken from reference [1]

The most important factors that affect this reaction are: quality of the raw materials, the kind and amount of alcohol, the mass transfer during the process, the catalytic system, and the reaction conditions. [1] [2] [3]

4.1. Quality of the triglyceride source

On the one hand the ideal raw material to obtain high yield biodiesel are refined oils, they have low amount of water, free fatty acids and non-saponificable materials. On the other hand from an economic point of view the best idea is to use lower quality and prize like crude oils or waste fried oils. Acidic value and moisture are the most important factors to take into account when we choose our raw material. The tolerance to this impurities will depend on our catalytic system. For example the acidic value is very important when use basic catalyst but if we use acidic catalyst it will not be a problem because free fatty acids can also react with methanol to form alkyl esters. In relation to moisture we want to avoid it as much as possible, it will raise separation costs and undesired products can appear, it is a big problem when using solid catalysts. [1]

4.2. Alcohol

Methanol is the chosen alcohol for these reaction not only because its reactivity but also because of the prize and availability in the market. Usually methanol is obtained in industrial processes from the syngas by a combustion reaction in presence of water. The fact that one of the main reactants comes from a mineral fuel puts in doubt if biodiesel is really renewable. Regarding this bioethanol appears as an alternative to obtain a really renewable biodiesel. Another thing to take into account is that ethylesters have even better properties than methylesters, higher cetane number and calorific power and lower cloud and pour point. There are several problems in relation to ethanol, it requires higher temperature, it is more complicated to reach very high conversions and a higher tendency to form emulsions, making very difficult the separation from glycerol. With bigger alcohols like propanol transesterification reaction is not always possible, even though alkyl esters from big alcohols could be interesting for biofuel purposes due to the much lower cloud and pour point.

The amount of alcohol is a very important thing to take into account, the required amount for the reaction is 3 moles of alcohol per mole of triglyceride, but as mentioned before an excess of alcohol is always used. Generally a higher relation alcohol oil will improve the yield of the reaction, however it is known that if we use too much alcohol it implies big separation costs because more alcohol will be dissolved in glycerol and in alkyl esters and we have to regenerate this alcohol to use it in future processes. Due to the importance of this relation the most recommendable is to obtain experimentally which is the best value for our system, depending on the raw material and the type of catalysis.

There is another way to keep the relation closer to 3:1 is to make this reaction in two or three different stages, dividing the amount of alcohol between them, this method maybe is not the best in the economic aspect but it can give very high conversions close to 100%. [1] [4]

4.3. Reaction conditions

Solubility between fats and alcohols is limited at moderate conditions of pressure and temperature, that is why high stirring is required to obtain a homogeneous mixture. Very different processes are carried out in different conditions, in general heating is necessary to help the solubility, 60ºC is a standard temperature to carry this type of reactions, however we have examples at much higher temperature (supercritical methane method) and room temperature method (enzymatic digestion). As the reaction goes forward product formation changes the structure of the mixture. When the reaction finishes and we stop stirring two different phases should appear, alkyl esters on the top and glycerol in the bottom. The biodiesel will be cleaned with water that will be necessary to remove all the water-soluble substances in the mixture (methanol, glycerol and the catalyst). However this is not always very easy, in fact it represents big costs in industrial scale and problems in laboratory scale. [1]

4.4. Catalytic systems

4.4.1. Homogeneous catalysis

Acidic and basic substances dissolved in the alcohol are the two main processes for transesterification. In acidic catalysis (usually H_2SO_4) the carbonyle group is more susceptible to be attacked by the alcohol and this process requires more time. In basic catalysis the mechanism is a little bit different, the goal is to form a nucleophilic alcoxide from the alcohol which can be able to attack the carbonyle group from the triglyceride. This process will be the chosen one for the laboratory experiments. As represented in the following figure the mechanism starts with the formation of a nucleophilic alcoxide from the alcohol. This alcoxide will attack the electrophilic part of the carbonyle group forming a tetrahedral intermediate. In the second step the intermediate is decomposed forming the alkyl ester and a diglyceride ion. In the last step the catalyst is regenerated with a proton. [3] [4]

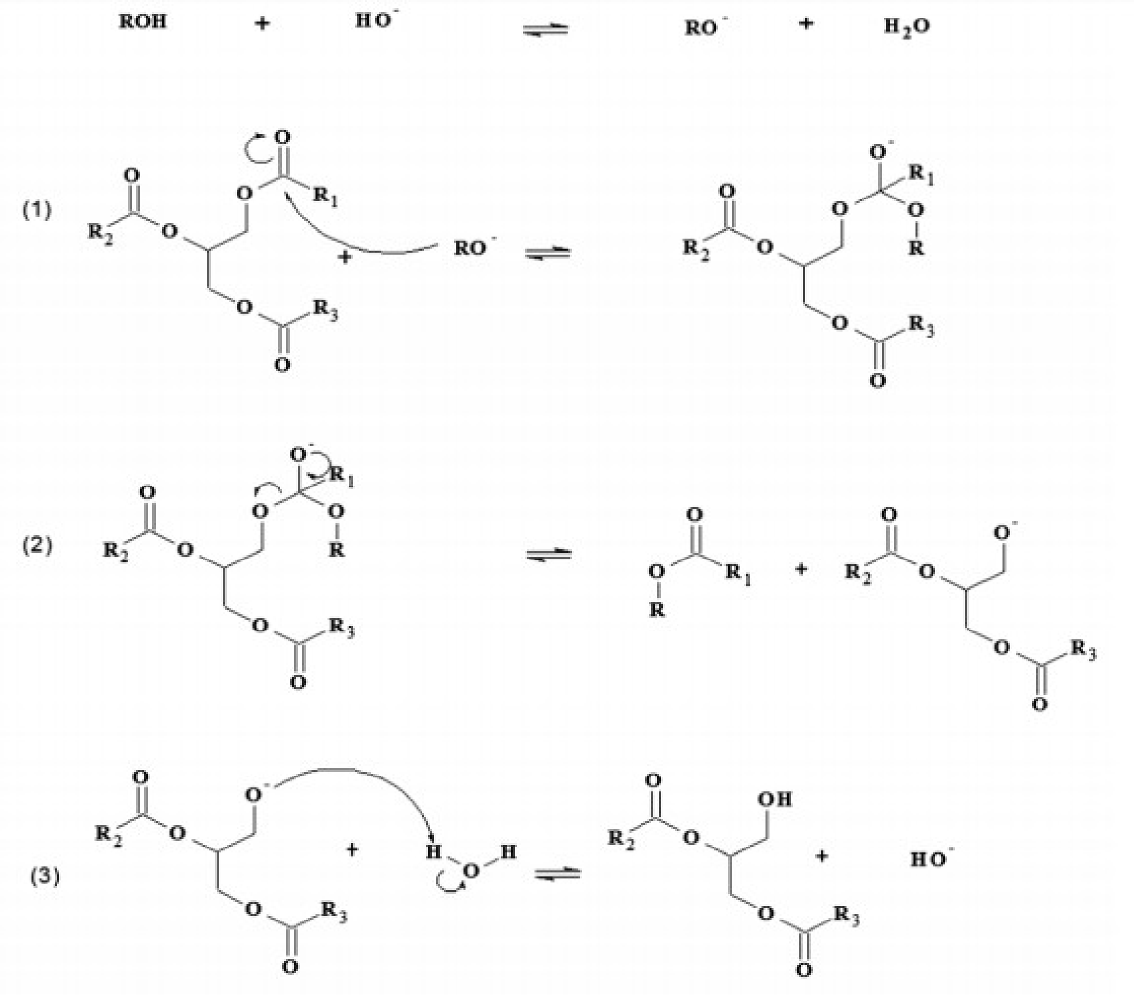


Figure 4. Homogeneous basic transesterification mechanism. Taken from reference [3]

4.4.2. Heterogeneous catalysis

Heterogeneous catalysis transesterification reaction mechanisms have certain similarities with homogeneous catalysis, however the main difference is that the reaction intermediates are formed in the surface of the catalyst. The most common heterogeneous catalysts are metal oxides and zeolites. Metal oxides are the most used and studied, MgO and CaO have been used with very good results, especially CaO is very interesting for biodiesel industry because it can be obtained from waste materials such as eggshell and mollusc shells which are a source of $CaCO_3$ that can be burnt to obtain CaO. [3]

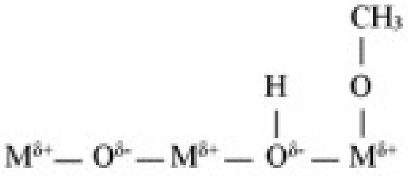
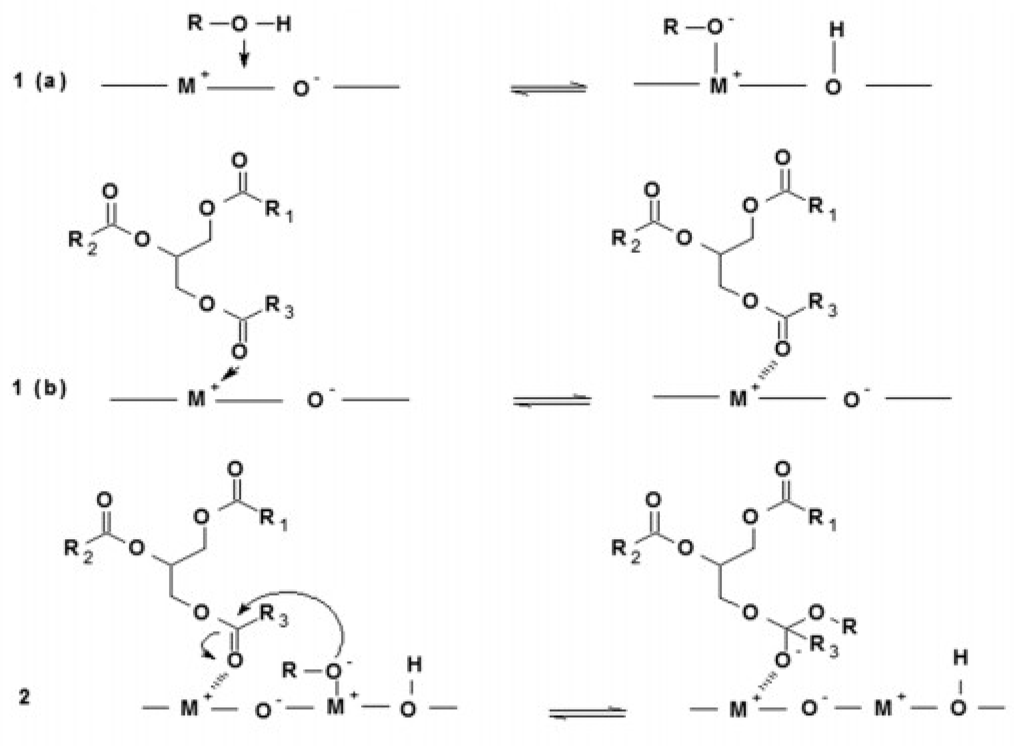


Figure 5. Surface structure of metal oxides. Taken from reference [3]

The mechanism of the heterogeneous basic transesterification follows the Langmuir-Hinshelwood (LH) model represented in the following figure, MgO has been tested in this process. Both reactants are adsorbed in the catalyst surface and then they react, this reaction has 4 main steps: the first step 1(a) and 1(b) is the adsorption of the reactants in the catalyst surface, in the second one (2) a tetrahedral intermediate is formed (very similar to homogeneous basic transesterifcation). In the third step the alkyl ester is formed, at the moment the alkyl ester is released the triglyceride is transformed into a diglyceride ion (or a diglyceride into monoglyceride ion, or monoglyceride into glycerol ion). In the last step the dygliceride ion takes a proton from the metal oxide. [3]



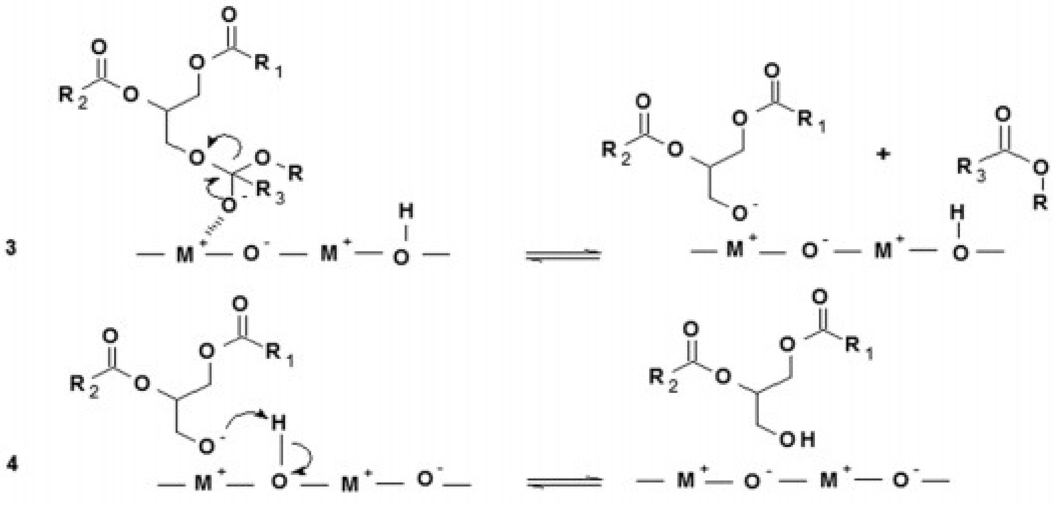
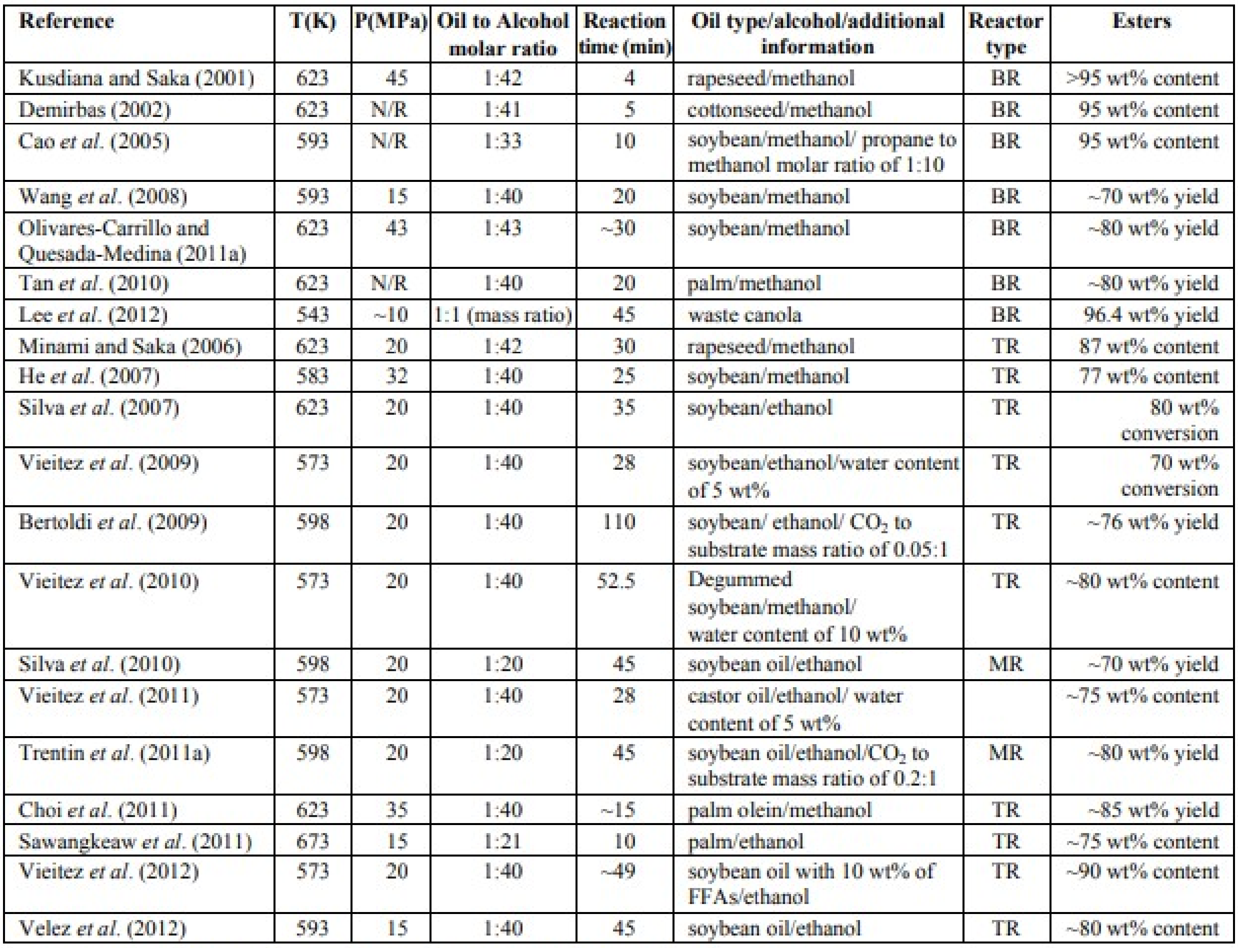


Figure 6. Langmuir-Hinshelwood (LH) mechanism for transesterification of triglycerides with alcohol. Taken from reference [3].

4.4.3. Non-catalytic systems

The non-catalytic transesterification of vegetable oils is characterized by the use of supercritical alcohol. In the following chart several studies are represented for different raw materials and different conditions.



Reference	T(K)	P(MPa)	Oil to Alcohol molar ratio	Reaction time (min)	Oil type/alcohol/additional information	Reactor type	Esters
Kusdiana and Saka (2001)	623	45	1:42	4	rapeseed/methanol	BR	>95 wt% content
Demirbas (2002)	623	N/R	1:41	5	cottonseed/methanol	BR	95 wt% content
Cao *et al.* (2005)	593	N/R	1:33	10	soybean/methanol/ propane to methanol molar ratio of 1:10	BR	95 wt% content
Wang *et al.* (2008)	593	15	1:40	20	soybean/methanol	BR	~70 wt% yield
Olivares-Carrillo and Quesada-Medina (2011a)	623	43	1:43	~30	soybean/methanol	BR	~80 wt% yield
Tan *et al.* (2010)	623	N/R	1:40	20	palm/methanol	BR	~80 wt% yield
Lee *et al.* (2012)	543	~10	1:1 (mass ratio)	45	waste canola	BR	96.4 wt% yield
Minami and Saka (2006)	623	20	1:42	30	rapeseed/methanol	TR	87 wt% content
He *et al.* (2007)	583	32	1:40	25	soybean/methanol	TR	77 wt% content
Silva *et al.* (2007)	623	20	1:40	35	soybean/ethanol	TR	80 wt% conversion
Vieitez *et al.* (2009)	573	20	1:40	28	soybean/ethanol/water content of 5 wt%	TR	70 wt% conversion
Bertoldi *et al.* (2009)	598	20	1:40	110	soybean/ ethanol/ CO_2 to substrate mass ratio of 0.05:1	TR	~76 wt% yield
Vieitez *et al.* (2010)	573	20	1:40	52.5	Degummed soybean/methanol/ water content of 10 wt%	TR	~80 wt% content
Silva *et al.* (2010)	598	20	1:20	45	soybean oil/ethanol	MR	~70 wt% yield
Vieitez *et al.* (2011)	573	20	1:40	28	castor oil/ethanol/ water content of 5 wt%		~75 wt% content
Trentin *et al.* (2011a)	598	20	1:20	45	soybean oil/ethanol/CO_2 to substrate mass ratio of 0.2:1	MR	~80 wt% yield
Choi *et al.* (2011)	623	35	1:40	~15	palm olein/methanol	TR	~85 wt% yield
Sawangkeaw *et al.* (2011)	673	15	1:21	10	palm/ethanol	TR	~75 wt% content
Vieitez *et al.* (2012)	573	20	1:40	~49	soybean oil with 10 wt% of FFAs/ethanol	TR	~90 wt% content
Velez *et al.* (2012)	593	15	1:40	45	soybean oil/ethanol	TR	~80 wt% content

N/R: not reported; FFAs: free fatty acids; BR: batch reactor; TR: tubular reactor; MR: microtube reactor.

Chart 1. Experimental conditions for non-catalytic systems. Taken from reference [4].

As represented in the previous chart temperatures around 600K, very high pressures and very big alcohol amounts are required, however, this reactions are carried out in short periods of time and give a very high yield so they could be interesting for big productions in industries. Another goodthing of these type of processes is that ethanol can be used instead of methanol, and as mentioned in the previous paragraph 4.2. Alcohol, bioethanol is a very good alternative to produce really renewable biodiesel.

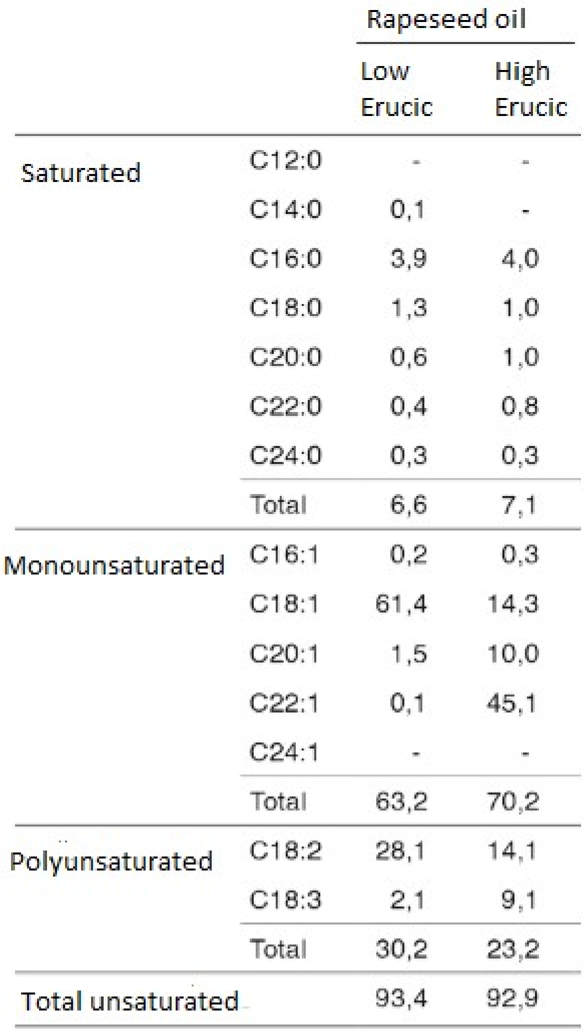
4.4.4. Enzymatic transesterification

To overcome several problems associated with chemical catalysis for biodiesel production enzymatic processes using lipases have been developed as an alternative. The advantages of enzymatic processes are: no soap formation, ability to esterify triglycerides and free fatty acids (very important thing when the main objective is to produce biodiesel from low quality waste materials), no need of a washing step to separate glycerol and better quality glycerol thanks to the no need of water. However, this type of technology has not received much commercial attention except in china with lipase as a catalyst. This may be due to the next disadvantages of enzymatic transesterification: longer time required for the reaction, high cost for the enzyme production and although enzymes can be reused in several processes, after 100 days they lose their activity. [5]

5. Laboratory experience

The main goal of the laboratory experience is the synthesis and characterization of biodiesel obtained from transesterification vegetable oil, studying different properties and comparing them with traditional diesel and with industrial biodiesel. We had different vegetable oils in the laboratory so we decided to create a mixture, they were not waste oils because they haven’t been used for cooking but they may not be of the best quality, so the first step is to analyse that oil to obtain as much information as possible to design a good process for it. The mixture was mostly formed by rapeseed oil, we also added some universal oil and a little bit of oleic acid. The first thing I want to mention about rapeseed oil is that there are two main varieties, as represented in the Chart 2 below, the traditional rapeseed crude oil is the high erucic acid (22:1) variety and canola oil is a genetic modified variety with lower amount of erucic (22:1) acid and higher percentage of oleic acid. The oils we had in the laboratory were traditional rapeseed oil so for the different calculations I used some bibliography data from rapeseed oil such as average molecular weight. [1]

The first observation I can make from the oil is that it is a homogeneous mixture with a dark yellow colour quite darker than usual refined vegetable oils we use for cooking. Seemingly there are no impurities like water bubbles or solids so we can assume that our mixture is completely oil we don’t have to make any initial pre-treatment.



		Rapeseed oil	
		Low Erucic	High Erucic
Saturated	C12:0	-	-
	C14:0	0,1	-
	C16:0	3,9	4,0
	C18:0	1,3	1,0
	C20:0	0,6	1,0
	C22:0	0,4	0,8
	C24:0	0,3	0,3
	Total	6,6	7,1
Monounsaturated	C16:1	0,2	0,3
	C18:1	61,4	14,3
	C20:1	1,5	10,0
	C22:1	0,1	45,1
	C24:1	-	-
	Total	63,2	70,2
Polyunsaturated	C18:2	28,1	14,1
	C18:3	2,1	9,1
	Total	30,2	23,2
Total unsaturated		93,4	92,9

Chart 2. Composition of rapeseed oil varieties. Taken from reference [1].

5.1. Equipment

We will carry out different experiments related to the biodiesel synthesis and the analysis of its properties, we will need specific equipment that will be exposed in this section.

General equipment: Safety goggles, gloves and general safety equipment, beakers, Erlenmeyer flasks, funnels, pipettes, balance, separation funnels, filter paper, retort stands and different accessories.

Equipment for titration: Burette, phenolphthalein, a mixture of ethanol:heptane or ethanol:toluene (1:1) and KOH.

Equipment for oil treatments: For the different treatments that will be tested in these project we will use, methanol, BF3-Methanol 10% solution, Acidic resins, $Ca(OH)_2$, sodium bicarbonate ($NaHCO_3$) and water.

Main reaction equipment: Round-bottom flask, stir bar, magnetic stirrer with heating, digital thermometer, big bowl to make a water bath, oil, methanol and KOH.

Density test: distilled water, thermometer, pycnometer and precision balance.

Viscosity test: Cannon-Ubbelohde viscometers, big water bath for analysis at 40ºC and chronometer.

Smoke and flash point test: special ceramic containers, heater, test flame, lighter and thermometer. The equipment represented in the following figure is not exactly like the one I used in the laboratory but it is quite representative for what we need.

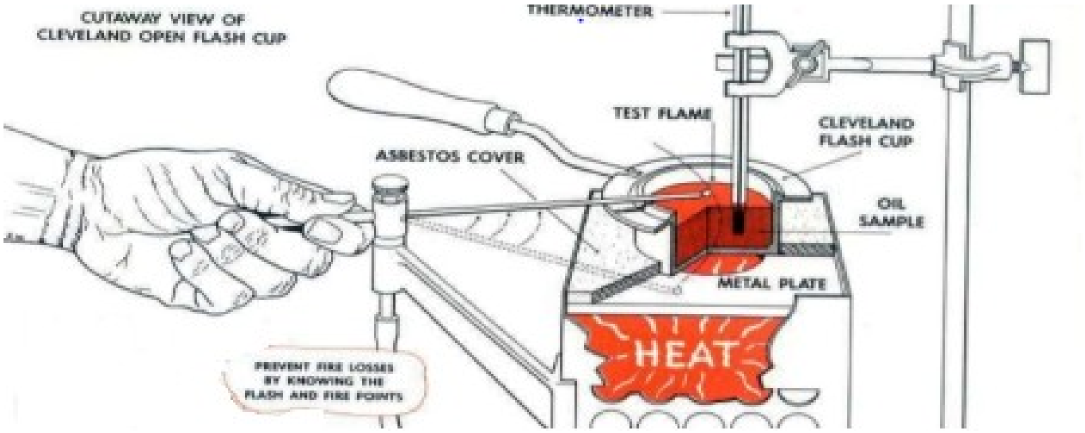


Figure 7. Smoke and flash point test. Taken from reference [6].

Cloud and pour point: cooling alcohol bath, thermometer, test tubes and special cork.

5.2. Laboratory Experiments

5.2.1. Biodiesel synthesis.

Determination of fat acid number by titration with phenolphthalein, using a mixture of alcohol as a solvent and 0.1M KOH. First of all we have to determine the acidic value of the solvent solution (the blank), in our case only 0.1ml of KOH was necessary for the neutralization. We will use 3 grams of the oil for each test and 25 ml of the alcoholic solution and KOH in the burette.

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

Where LK value is the amount of KOH in mg per gram of oil required to neutralize the oil, V and V_0 are respectively the volumes required for neutralization of the objective solution and the blank, m is the exact mass of oil and C_{KOH} is the concentration of the KOH solution, 0.1M in our case.

This test will be determining for the future procedures, as explained in previous sections the LK value represents the amount of free fatty acids, the ideal oil for tranesterification will have a very low LK, free fatty acids are usually a problem due to some side-reactions that can affect the biodiesel production. Especially in our process, homogeneous basic system, free fatty acids can react with KOH, forming soaps and water, as represented in figure X, two undesired products.

We made two tests for the oil mixture and the average LK value was 10,89, in the first titration 5.6ml of KOH was required to neutralize 2.99g of oil and in the second one 6.5ml for 3.15g of oil.

There are different paths to follow depending on the LK value, in this case this value is quite high and is necessary to eliminate or transform the free fatty acids, there are mainly two methods to eliminate this FFA in the laboratory, neutralization of the FFA producing soaps and acid esterification of FFA; to determine which method was the best for our oil we made some tests with small amounts of oil (50g). Every reaction will be carried out in a round-bottom flask with stirring, the reactions in which temperature is important, bowls with water will be used for the hot bath and a thermometer to control the temperature.

Neutralization

This method may seem to be effective to neutralize completely the fatty acids, however the soap formation gave a lot of problems when separating the final product, especially when washing with water emulsions were created. This problems resulted in yield loss and obtaining milky mixtures containing water that is complicated to eliminate, filtration helped to separate the water and the soaps from the oil, however it took more than two or three days sometimes.

Neutralization with $Ca(OH)_2$

In this experiment we will use the stoichiometric amount of $Ca(OH)_2$ to neutralize the fatty acids. The reaction was carried during 30 minutes at 60ºC with stirring using methanol as the solvent, in this case we were using 50g of oil, and the LK value for this oil is 10,89mgNaOH/gOil, so the necessary amount of $Ca(OH)_2$ is:

$$moles\,Ca(OH)_2 = \frac{50\,\dfrac{g*10.89\,mgNaOH}{goil}}{\dfrac{56.1\,g}{moleNaOH}*2*1000} = 0.00485\,moles\,Ca(OH)_2$$

$$0.00485\,moles\,\frac{Ca(OH)_2*74.093\,g}{mole\,Ca(OH)_2} = 0.359\,g\,Ca(OH)_2 = 359\,mg\,Ca(OH)_2$$

This reaction may have neutralized all the FFA in our oil, however the soap formation affected negatively the following steps, giving a very milky mixture. Even though I proceeded with the LK value analysis with not very good results.

As in previous steps we made two tests for the acidic value, in the first one 4.6ml of KOH was necessary to neutralize 3.01g of oil, and 5ml for 3.12g of oil, the average LK value was 8.59mgNaOH/gOil. This value should have been lower due to acids neutralization, however, as I said, maybe the soap formation and the water emulsions created during the washing affected this process, so we decided to avoid this method in future experiments.

Neutralization with $NaHCO_3$

This reaction is quite similar to the previous one because, in fact, we are creating soap using Na^+ in this case, however the reaction is a little bit different, due to the structure of $NaHCO_3$ when it is hydrolysed in Na^+ and bicarbonate ion the equilibrium described in the following figure takes place, so H_2O and CO_2 are indirect products in this process. The reaction was carried out during 30 minutes at room temperature using water, around 5% of the oil weight, as a solvent.

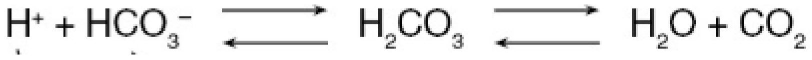


Figure 8. Bicarbonate equilibrium.

$$moles\,NaHCO_3 = \frac{50\,\frac{g*10.89\,mgNaOH}{goil}}{\frac{56.1\,g}{moleNaOH}*1000} = 0.0097\,moles\,NaHCO_3$$

$$0.0097\,moles\,\frac{NaHCO_3*84.01\,g}{mole\,NaHCO_3} = 0.815\,g\,NaHCO_3 = 815\,mg\,NaHCO_3$$

In the first test for acidic value 3.8ml of KOH was necessary to neutralize 3.21g of oil, and 3.3ml for 3.09g of oil, the average LK value was 6.13mgNaOH/gOil. In this case the acidic value was quite better than in the $Ca(OH)_2$, however we also discarded this method because the mixture didn't look homogeneous and was a little bit milky, with emulsionated water due to the soap formed.

Acid esterification of FFA.

In this process FFA are transformed in methyl esters by esterification reaction, no soaps are formed in this process, so apparently this method could be a better alternative in this case. Small water bubbles were formed as well after the washing, however they could be eliminated after filtering the oil. The result was a more or less homogeneous mixture with a lighter colour than the original oil.

10% alcoholic solution of BF3

In this case the process will be carried out with the mentioned solution, 90% methanol and 10% BF3, for the calculations of the reagents amount we will calculate approximately the molar mass of our oil assuming the composition is the same as rapeseed oil high erucic acid version, I obtained 955g/mole. In bibliography I could find data in the following range (920-975g/mole) so I assume that 955g/mole is an average value for rapeseed oil molar mass. The relation methanol oil will be 12-24:1 mole/mole.

$$50\,g\frac{\frac{\frac{\frac{oil*1\,mol\,oil}{955\,g}*18\,mol\,Methanol}{1\,mol\,oil}*32\,g}{1\,mol\,Methanol}*100\,g\,solution}{90\,g\,Methanol}=33.5\,g\,of\,10\%\,Alcoholic\,solution\,of\,BF3$$

The mixture will be mixing during 1 hour at 60ºC, after this the solution should be cleaned with water, then filtered and finally the LK value was determined. The average LK value after this test was 6.64 mgNaOH/gOil, and the mixture looked cleaner than in previous experiments, so we decided this method will be interesting for our experiment.

Acidic resins

In this method acidic resins were used instead of BF3 in a mixture of ethanol with the same calculations as the previous experiment, 50g of oil and a relation 18:1 Methanol oil, so we needed 30.15g (0.9*33.5g) of Methanol for this reaction. In this case there was a small difference, one extra filtration is required after the reaction to separate the solution from the resin. The results were very good with this method, using 5% acidic resins and after washing and filtering we obtained a clean oil with LK = 3.95mgNaOH/g oil. So definitely we continued with this method for the final tests.

Final tests

Once we were sure about what methods were the most effective in our case, we will proceed with the real experiment, using 200g of oil, and we will use the two acidic esterification of fatty acids. Exactly the same procedure was followed, the proportions were maintained in the same way so we used the following amounts for the experiments: in the alcoholic solution of BF3 experiment we used 134g of this solution and in the acidic resins we used 10g of acidic resins and 120.6g of methanol. I will not explain this calculations because we only need to follow the stoichiometry and multiply by 4 what we calculated in the previous paragraphs, because we are using 200g instead of 50g.

After both reactions were completed, the solutions washed and filtered, the result was two homogeneous solutions, except for a little bit of water, remaining from the washing, which could be removed after filtration. The solution coming from the first method looked kind of milky due to the presence of emulsioned water. After this the LK value was determined for both solutions, the results were worse than I expected, for the BF3 experiment we obtained 8.87mgNaOH/gOil, which is a very high value, and 5.06mgNaOH/gOil in the case of the resin. The first method may have failed for different reasons, maybe the reaction needed more time to be completed, maybe the presence of mono and digilycerides, or other impurities coming from the original oil helped the water emulsioning or maybe the extra filtration required in the resin process helps the elimination of these substances.

Anyway, the selected oil for the biodiesel synthesis was the oil treated with acidic resins, it is important to say that only 101.3g of oil remained from the previous stage, so maybe the different methods used for treating, cleaning and filtering the oil were not the optimal. The chosen system for the transesterification reaction is homogenous basic catalysis with KOH, as explained previously. The relation methanol:oil will be 6:1 and the amount of KOH will be the necessary to neutralise the acidic value plus 1% of the oil weight for the catalysis. Maybe 6:1 is not the optimal relation, because as explained in 4.2. Alcohol, this relation should be estimated for each specific process, this is very important for industrial activity, however 6:1 is a quite standard relation, taking into account that 3:1 is the required amount of methanol.

The calculated amounts for the reactants are the following:

$$101.3\,g\,\frac{\frac{\frac{Oil*1\,mole}{955\,g\,Oil}*6\,moles\,MeOH}{1\,mole\,Oil}*32\,g}{1\,mole}=20.36\,g\,MeOH$$

$$0.01*101.3+101.3\,g\,\frac{\frac{\frac{\frac{Oil*5.06\,mg\,NaOH}{1\,g\,Oil*1000}*1\,mole\,NaOH}{39.997\,g}*1\,mole\,KOH}{1\,mole\,NaOH}*56.1056\,g}{1\,mole\,KOH}=1.73\,g\,KOH$$

The reaction will be carried at 60ºC during 1 hour, after this time the solution should be left in a separation funnel to wait for the glycerol to separate from the biodiesel, after this remove the glycerol and clean several times with hot and cold water respectively. After this washing the mixture had a milky colour similar to other experiments, anyway we proceed with filtration. After more than two days of filtration we finally had the biodiesel, small portions of water were removed from the bottom of the flask after the filtration, and the result was an oily mixture with a light yellow colour, that looked pretty different from the original oil. It is important to mention that I had around 80ml of biodiesel, so it is obvious that the yield of the whole process was not good at all, anyway we will study the properties of our biodiesel and compare them with petrodiesel and industrial vegetable oil biodiesel.

5.2.2. Determination of the properties

Density

Density was calculated with the help of a pycnometer using the following equation. Using the same pycnometer for the three samples makes the calculations easier. Density of water was taken from bibliography at 25ºC.

$$Vbiodiesel=Voil=Vwater$$

$$\frac{17.3022\,g biodiesel}{density}=\frac{17.47736\,g Oil}{density}=\frac{18.2924\,g water}{997.044\,g/L water}$$

$$Biodiesel\,density=943.07\,g/L$$

$$Oil\,density=952.62\,g/L$$

Viscosity

Viscosity was studied at room temperature (25ºC) and 40ºC for the oil and the biodiesel, to obtain a more precise number I used two different viscometers in both temperatures for the biodiesel measure. As mentioned in 5.1. Equipment, we used Cannon-Ubbelohde viscometers with known constant (k), η represents the dynamic viscosity and v the kinematic (in mm^2/s). During the following experiments we will focus in the kinematic viscosity.

$$K=\frac{\eta(water)}{density(water)*t(sec)}=\frac{v(water)}{t(sec)}$$

$$kinematic\ viscosity\,(substance)=K*time\,(seconds)$$

In total I used 3 different viscometers, one for oil and two for biodiesel. For the oil we used one viscometer with high K, due to the very high viscosity of oils, with a smaller K viscometer the measure can take more than half an hour. Two tests were done for each fluid and temperature, the average time is shown in the following equations. Time was measured in minutes, for example for the first experiment the average time was 18min 21sec.

Oil 25ºC $v(oil\,25\,ºC)=0.05636*(18*60+21)=62.052\,\frac{mm^2}{sec}$

Oil 40ºC $v(oil\,40\,ºC)=0.05636*(9*60+46)=33.026\,\frac{mm^2}{sec}$

For the biodiesel test we used two different viscometers to obtain a more accurate result.

Biodiesel 25ºC $v(biodiesel\,25\,^oC)=0.02837*(28*60+50)=49.08\,\frac{mm^2}{sec}$

Biodiesel 25ºC $v(biodiesel\,25\,^oC)=0.0516*(16*60+45)=51.858\,\frac{mm^2}{sec}$

Biodiesel 40ºC $v(biodiesel\,40\,^oC)=0.02837*(17*60+25)=29.646\,\frac{mm^2}{sec}$

Biodiesel 40ºC $v(biodiesel\,40\,^oC)=0.0516*(9*60+35)=29.67\,\frac{mm^2}{sec}$

Smoke and flash point

As represented in figure X, special equipment is required in this test, we will need heating the whole time, it is very important not to exceed 350ºC to avoid the oil cracking, however flash point of rapeseed oil is around 250ºC, so this should not be a problem. When the mixture starts releasing smoke we should write down the temperature, this will be the smoke point. The test flame will be passed over the tested substance every certain lapse of time, when we see and listen like a very small explosion, this is the flash point and the temperature should be written.

Smoke Point for the biodiesel was 145ºC, for oil it was 160ºC

Flash point was 243ºC for biodiesel and 260ºC for oil.

Cloud and pour point

In this experiment the biodiesel and the oil will be submerged in a cold alcoholic bath to study the low temperature properties. Cloud point is the moment in which it is complicated to see through the substance because some fog appeared, it is due to the apparition of the first crystals. Pour point is the moment in which the substance stays more than 5 second inclined 45º without moving, in this moment it is practically frozen.

For the biodiesel and the oil the results were the following:

Cloud point: -1 for the biodiesel and -4 for the oil

Pour point: -19 for the biodiesel and -24 for the oil.

5.3. Security in the laboratory

Generally all of the chemical and physical experiments exposed before are completely safe and do not present any risks for human health, there are a few issues I want to talk about in this section related with security.

The exception and more dangerous part is flash and smoke point test due to the high temperatures reached in the process, during the biodiesel flash point test, between 90 and 105ºC a some water started to boil and it could be dangerous if you don't carry this experiment in the security fume hood with protecting glass; this didn't happen with the oil because biodiesel had some remaining water from washing steps and oil was "pure" oil. You have to be especially careful in the moment of turning on the test flame, the flame comes from a gas tank and it has to be turned on manually with a lighter, it is important to be sure we didn't open too much de gas tank.

For the rest of the experiences with the lab coat, gloves and glasses will be enough for security, we are not using any strong acid or base and no hazardous materials, so any additional security measures will be taken.

5.4. Waste management

Most of the reactants used during the experiments were not toxic or dangerous, anyway most of organic waste material was poured in a specific container for future treatment.

6. Results

Results are presented in the following chart, most of the properties of our obtained biodiesel are quite far away from specifications, the properties with (-) could not be found in bibliography. In the following chart we use this acronyms: SP (smoke point), FP (flash point), CP (cloud point) and PP (pour point).

	Oil	Biodiesel	Petrodiesel*	Biodiesel specifications*	Units
Density	952,62	943,07	780-960	860-900	kg/m3
Viscosity(25°C)	62,052	50,469	-	-	mm2/sec
Viscosity(40°C)	33,026	29,658	2-4	3,5-5	mm2/sec
SP	160	145	-	-	°C
FP	260	243	50	min 120	°C
CP	-4	-1	-	-	°C
PP	-24	-19	lower than -30	max 0	°C

Chart 3. Properties of oil and biodiesel and comparison with bibliography. Petrodiesel and Biodiesel specifications were taken from reference [2] and [7].

7. Conclusions

In this report I wanted to expose that biodiesel is a very good alternative for traditional fuels, using renewable sources to obtain a fuel, with similar properties and less pollutant than normal diesel. The main raw materials were explained as well as the technological issues related with industrial and laboratory production. In conclusion for this research project I have to mention that the biodiesel synthesis was accomplished, despite the several problems that appeared during the laboratory experience as I exposed in 5.2. Experiments we can see in the Chart 3 (properties of oil and diesel and comparison with bibliography) that the properties of our biodiesel are quite different from industrial biodiesel and are closer to the oil, such issue is due to the non-full conversion of the triglycerides in methyl esters. Anyway we can see how the properties of the obtained biodiesel show a tendency to the industrial biodiesel properties, viscosity and density are reduced, the same as high and low temperature properties. To sum up we can say that the main goal of the experiments was a success, however, different processes should be optimized to obtain a better biodiesel; everything that can be improved from our experiments was exposed in previous sections.

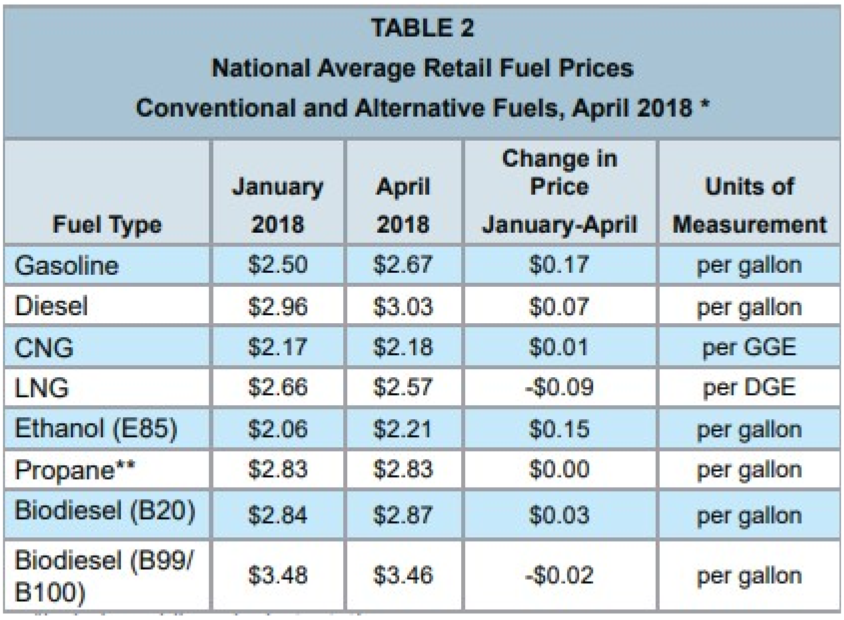


TABLE 2
National Average Retail Fuel Prices
Conventional and Alternative Fuels, April 2018 *

Fuel Type	January 2018	April 2018	Change in Price January-April	Units of Measurement
Gasoline	$2.50	$2.67	$0.17	per gallon
Diesel	$2.96	$3.03	$0.07	per gallon
CNG	$2.17	$2.18	$0.01	per GGE
LNG	$2.66	$2.57	-$0.09	per DGE
Ethanol (E85)	$2.06	$2.21	$0.15	per gallon
Propane**	$2.83	$2.83	$0.00	per gallon
Biodiesel (B20)	$2.84	$2.87	$0.03	per gallon
Biodiesel (B99/ B100)	$3.48	$3.46	-$0.02	per gallon

Chart 4. Main fuel prices in the USA. Taken from reference [8]

As you can see in the previous chart biodiesel is more expensive than traditional diesel, however the tendency during 2018 is shown and we can see that biodiesel price is getting lower. Biodiesel industry is still developing all over the world and hopefully research in the next few years will make biodiesel a real alternative for both domestic and industrial uses of traditional fuels.

8. References

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