Chapter 2

Advanced Techniques in Soybean Biodiesel

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1. Introduction

The planet where we inhabit, live, has experienced a great transformation period in the most different fields. The evolution followed by a great technological development, on the other side has caused an imbalance both in society itself, as in the material environment in which we live. The planet earth has visibly demonstrated how has been affected by this imbalance and how it has naturally reacted. In recent years, all this has being reported through the literature, studied by different scientific research groups, as also observed by what is reported in the media in general, even in the form of documentaries and films, as the documentary performed by former USA vice president Al Gore, an inconvenient truth (an inconvenient truth, 2006). All learning takes a certain time to begin to be assimilated and been put in practice effectively, so humanity has learned, been advised by the latest natural disasters of this century, as in the case of Japan's earthquake, tsunami, the strong hurricanes that plague the northern hemisphere summer, as in fact glaciers melting that were called eternal, the poles of this planet, strong climate change experienced over the past years and the major pollution in large urban cities where population are forced to live in many different fields, has signaling how much real acts, changes are necessary to continue to be possible living an inhabited planet.In this century, XXI, the world main problems, which it has experienced, are related to the scarcity of natural resources such as water, which had been mismanaged, contaminated by urban and industrial solid waste disposal, and in relation to generation and use of energy the most diverse shapes.

These energy sources can be broadly classified into three categories: fossil fuels (coal, oil and natural gas), renewable (hydroelectric, wind, solar and biomass) and nuclear sources. Among those can be highlighted Biomass, where all organic matter that is produced by this process is called biomass. This has a great advantage over fossil fuels, it's less polluting, because its processes do not add carbon dioxide to the atmosphere, the environment. The biomass process reduces the carbon dioxide amount in atmosphere through the photosynthesis, performed by increasing the planted green areas, to cultivate the seeds crops. Research and development departments have been engaged in fuels discovery that do not cause much environment damage and that can replace fossil fuels, reducing the toxic emissions level, replacing the rare fossil fuel used to date. In the midst of these researches has been observed that the use of vegetable oils has shown great ability to make this one a possible alternative renewable energy (Agarwal & Das, 2000).A related problem in the replacement of diesel for oil plant was related to physical and chemical factors such as high viscosity, low volatility which results in incomplete combustion, leading to formation of carbon deposits in the engine and a high unsaturations degree (Meher et al, 2008), factor that reduces the power of the fuel at the lowest level of cetane,but also favors oxidation. Studies have shown that vegetable oils characteristics can be modified through four ways (Shrivastava & Presad, 2002): By pyrolysis, microemulsification, dilution and transesterification process. The latter originates the alkyl esters that constitute what is called biodiesel.

2. Biodiesel

The use of vegetable oils as an alternative fuel for diesel engine was discovered more than100 years ago, in the Paris world exhibition in 1900, when Rudolph Diesel used peanut oil in an engine ignition (Shay, 1993).This predicted saying, "The use of vegetable oils as fuel engine may be negligible in the present moment, but in the future may become so important as oil and coal as energy sources. The biodiesel term is a subject still under discussion. Some definitions consider biodiesel as a mixture of any vegetable oils with fuel, diesel and fossil derivative others consider the alkyl esters mixture from vegetable oils or animal fats with fossil fuels. Under the chemical aspect biodiesel, an alternative fuel can be defined as alkyl esters derived from fatty acids obtained from oils, vegetables or animal fats, which suffering a chemical reaction, transesterification with short chain alcohols such as methanol and ethanol (Pinto et al, 2005). Transesterification: Chemical reaction between an ester (RCOOR ') and an alcohol (R''COH) resulting in a new ester (R''COOR') and an alcohol (RCOH).

This reaction type, used in biodiesel production is the reaction between the triglycerides, main components of vegetable oils and fats that react with short chain alcohols, methanol and ethanol, resulting in two products, methyl esters derived from fatty acids, and the second product glycerol formation. Transesterification reaction rates can be affected by some aspects: The catalyst type (acid or alkaline), purity of reactants (mainly water content), free fatty acid content and alcohol/vegetable oil molar ratio (Helwani et al, 2009). The biodiesel reaction can be optimized specially by three factors: The first is an increase in the temperature. An increase in temperature increases reaction rate in exponential, allowing the reactants to be more miscible, obtaining a higher reaction rate to take place.

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This parameter is limited by the solvent, reactant boiling point. The second factor to improve reaction yield, vigorous mixing, possibilities a higher collision rate between the reactants, been obtained a reaction mixture plus homogenized, yielding a higher rate of methyl esters obtained. In general alcohols and triglyceride sources are immiscible, vigorous mixing possibilities the obtaining of alcohol dispersed as fine droplets, increasing the contact surface between the two immiscible reactants (Stamenkovic et al, 2008). The use of a secondary solvent, a co-solvent as THF, possibilities a higher miscibility of the alcohol in the triglyceride phase, obtaining a better mixing of the two phases and hence a more reactions to take place, improving the biodiesel yield. The following Figure 1 illustrates a biodiesel type of reaction.

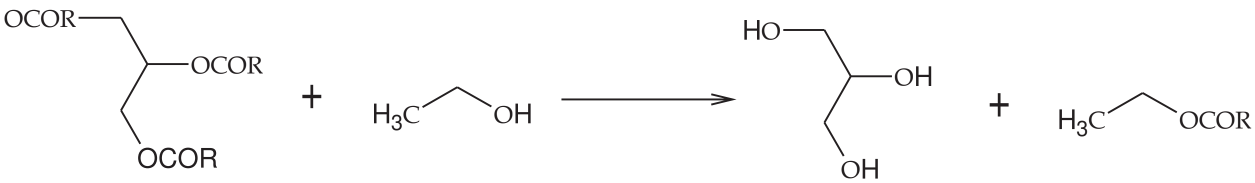

Figure 1. General transesterification reaction to produce biodiesel

In general terms, these reactions take place under homogeneous catalysts, acid or base catalysts, enzyme or through the use of heterogeneous catalysts. The selection of appropriate catalyst depends on the amount of free fatty acids in the oil. Heterogeneous catalyst provides high activity; high selectivity, high water tolerance properties and these properties depend on the amount and strengths of active acid or basic sites. Basic catalyst can be subdivided based on the type of metal oxides and their derivatives. Similarly, acidic catalyst can be subdivided depending upon their active acidic sites (Singh & Sarma, 2011). Generally, a basic catalyst gives better yields than the acids catalysts in both homogeneous and heterogeneous catalysts. The better results of homogeneous catalysts are related to the fact that base catalysts are kinetically much faster than heterogeneously catalyzed transesterification and are economically viable. There are many factors which govern the path of transesterification reactions, between these can be stand out the following parameters: the nature o raw material, the optimum experimental conditions, as the ratio oil/methanol, the temperature and the catalyst concentration, for example. Comparing heterogeneous catalyst with homogeneous catalysts can be observed that the use of solid heterogeneous use more extreme reaction conditions, higher pressure and temperature due the fact of the difficulty in the limited mass transfer between the three phase system solid-liquid-liquid immiscible (catalyst, oil, methanol). The main advantages in the use of solid catalysts are related to the easy work up when compared with homogeneous catalysts. Solid catalysts are separated just by filtration and centrifugation and are environmentally friendly, because they are reusable and reduce the amount of wasted, treated water used. Among the heterogeneous catalysts, we can highlight the use of zeolites (Suppes et al, 2004), clays, ion exchange resins and oxides.

3. Catalysts

3.1. Heterogeneous catalysts

The useof heterogeneous catalysts (Wang & Yang, 2007 and Leclercq et al, 2001) has as major advantage the reaction work-up, i.e., post-treatment reaction, separation and purification steps, since these can be easily removed and can be reused. Another interesting factor is the fact that this type of catalysis, there is no formation of by products, such as saponification (Suppes et al, 2001; Tomasevic et al, 2003 and Gryglewicz, 1999). The greatest difficulty encountered in using this reaction type is directly related to problems in relation between the diffusion systems, oil /catalyst /methanol.

3.2. Homogeneous catalysts

3.2.1. Basic catalysts

Basic Catalysis (Zhou et al, 2003) are procedures that use in general alkoxides of sodium and potassium, carbonates and hydroxides of these elements. Among these three groups it is found that alkoxides catalysts are financially unfavorable because they are more expensive but also difficult to handle because they are hygroscopic, and facilitate the achievement of side products such as derivatives of saponification, but have the advantage of carrying out the reactions in milder temperatures, produces high levels of esters derived from fatty acids and do not have corrosive properties as acid catalysts. A solution used to minimize the soap formation when biodiesel has a high free fatty acid content or water is the use of 2 or 3% mol of K_2CO_3 that will form the corresponding bicarbonate salt instead of water.

In the following, table 1, it's possible to find diverse types of heterogeneous catalysts used to obtain biodiesel of soybean, cotton seed, *Jatropha curcas*, palm, rape oil and sunflower.

Among the studies using soybean oil to obtain biodiesel, can be stand out the work developed by Wang et al, using CaO, SrO as a solid catalyst used in a heterogeneous process to obtain biodiesel. Cao, is a typical basic solid catalyst used in the most different ways. This compound has many advantages as a reusable due to its long catalyst lifetime, higher activity and requirement of only mild reaction conditions. At the example of table 1, is observed that in the best conditions to obtain biodiesel in yield of 95% is necessary a temperature of 65ºC, a molar ratio of MeOH/Oil of 5 and even a little reaction time from 0.5 to 3 hours. Even with all these specific positive factors, solid acid catalysts have been very useful at many industrial processes. Acid catalysts contain a large variety of acid sites with different strength of Bronsted, Lewis acidity, which is considered a good advantage at the transesterification process. These catalysts are even very useful, when is necessary to obtain biodiesel from oils rich in FFA, free fatty acids, because they convert the FFA into FAME prior to the biodiesel production, avoiding by this way the problem encountered at base catalysts, the soap formation.

Vegetable oil	Catalysts	Ratio MeOH/Oil	Reaction time (h)	Temperature (ºC)	Conversion (%)	References
Soybean	Calcined LDH (Li-Al)	15	1-6	65	71.9	Li
Soybean	La/zeolite beta	14.5	4	160	48.9	Furata
Soybean	$MgOMgAl_2O_4$	3	10	65	57	Schumaker
Soybean	MgO, ZnO, Al_2O_3	55	7	70-130	82	Trakarnpruk
Soybean	Cu and Co	5	3	70		Shu
Soybean	CaO, SrO	12	0.5-3	65	95	Wang
Soybean	ETS-10	6	24	120	94.6	Arzamendi
Cotton seed	Mg-Al-CO_3 HT	6	12	180-210	87	Wang
Jatropha Curcas	CaO	9	2.5	70	93	Albuquerque
Palm	Mg-Al-CO_3 (hydrotalcite)	30	6	100	86.6	Huaping
Rape	Mg-Al HT	6	4	65	90.5	Zeng
Sunflower	NaOH/Alumina	6-48	1	50	99	Liu
Sunflower	CaO/SBA-14	12	5	160	95	Suppes
Blended vegetable	Mesoporous silica loaded with MgO	8	5	220	96	Barakos

Table 1. Different heterogeneous catalysts used for transesterification of vegetable oils.

In the following figure 2, is exemplified the mechanism of base catalyzed transesterification. The mechanism can be resumed in the following way. In the first step the methoxide anion attaches to the carbonyl carbon atom of the triglyceride. In the second step, the oxygen picks up an acid H^+ from the alcohol. In the last step a rearrangement of the tetrahedral intermediate results in the formation of biodiesel and glycerol.

3.2.2. Acid catalysts

Sulfur and chlorides compounds are the most commonly used acid catalysts. This type of catalysis[(Mohamad & Ali, 2002) has as main advantages the absence of products derived from saponification reactions, higher yields but has some disadvantages such as the fact that the reactions are performed in a highly corrosive and reactive post-treatment, where the medium, the rinse water should be neutralized.

4. Enzymes

Enzimes are a fourth class of compounds used to produce biodiesel (Fukuda et al, 2001). In general its use is complicated by the fact that the enzyme generally are a specific material,

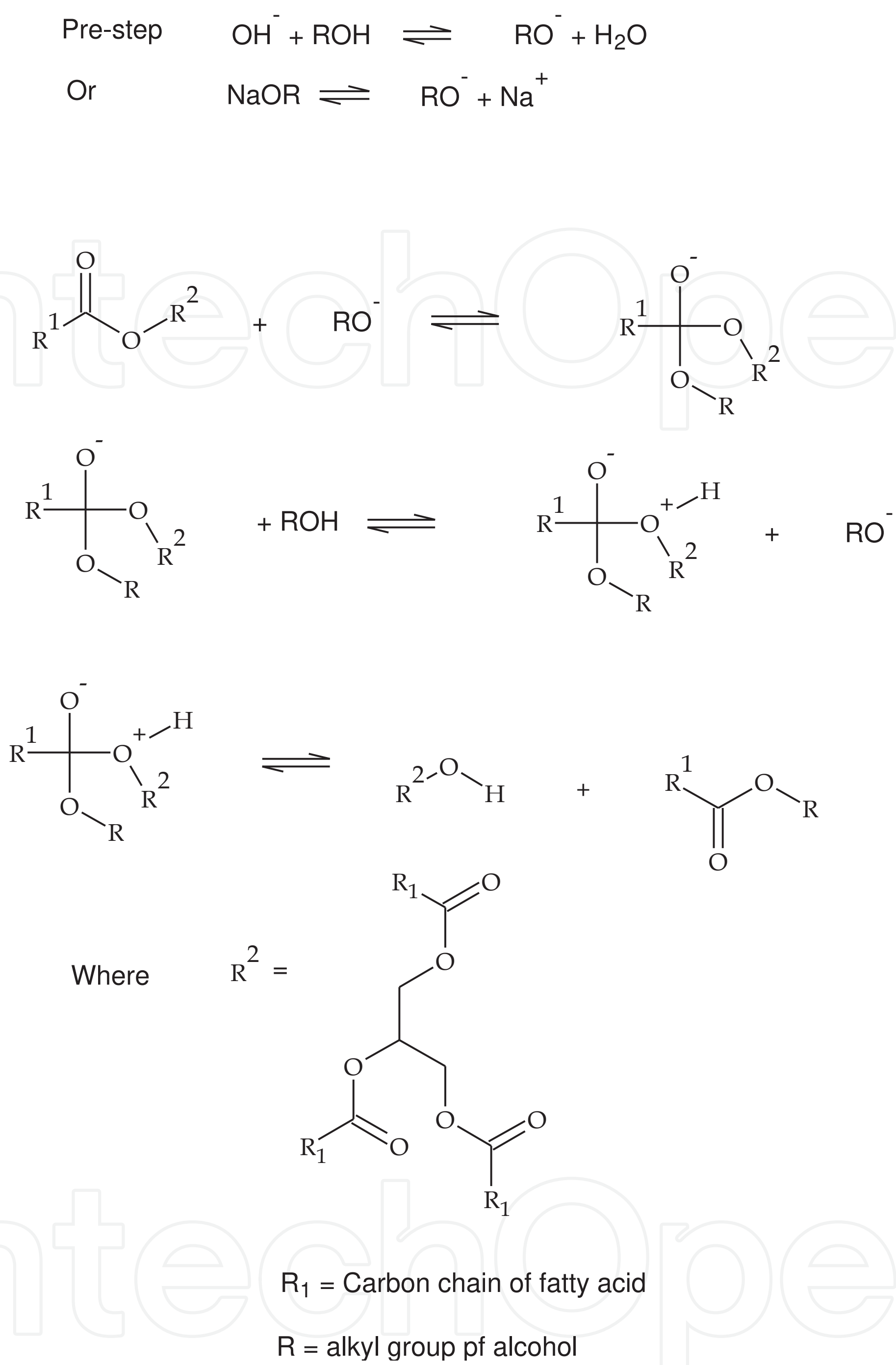

Figure 2. Mechanism of base catalyzed transesterification.

and extremely expensive in relation to this type of reaction, are sensitive to the presence of methanol and ethanol, which causes deactivation of the same (Salis et al, 2008). Literature (Modi et al, 2007) shows that this problem can be circumvented by the water (Kaieda et al, 2001 & Kaieda et al, 1998) use and organic (Raganathan, 2008 & Harding et al, 2008) solvents such as dioxanes and petroleum ether, for example.

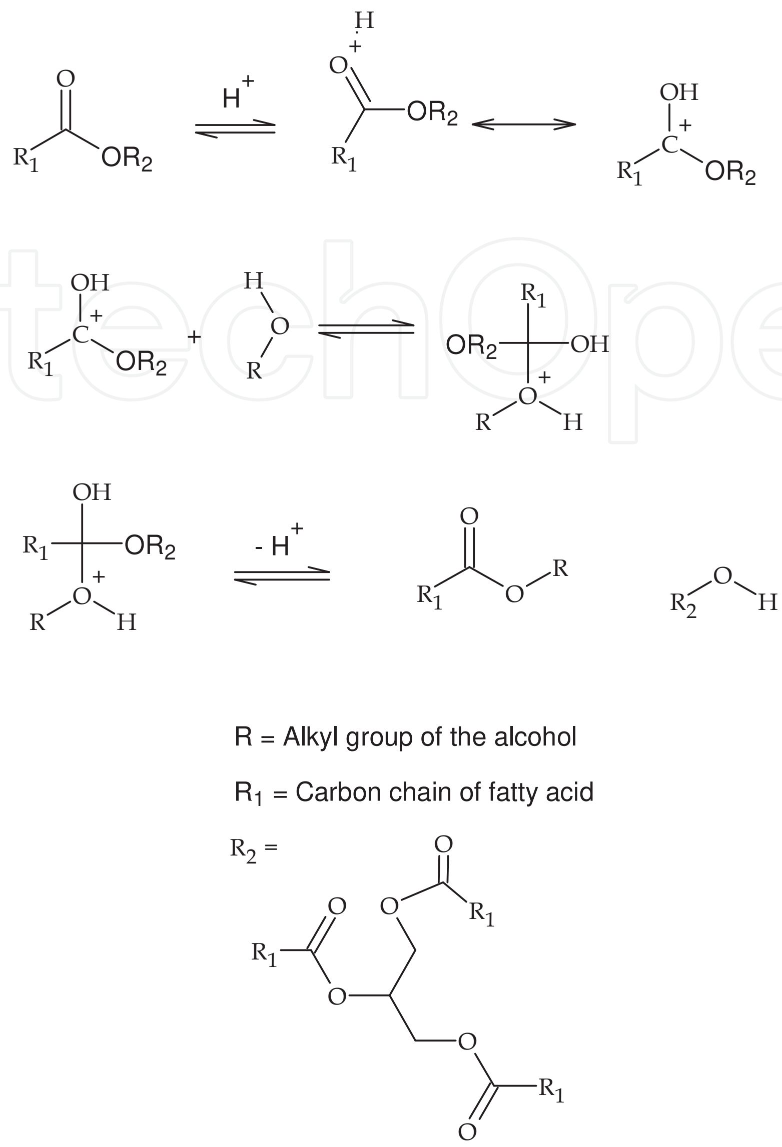

Figure 3. Mechanism of acid catalyzed transesterification

5. Non catalytic fatty acid alkyl ester production

The use of supercritical methanol process (Marulanda, 2012) to obtain biodiesel has been a useful method when the feed stock oil contains high amount of free fatty acids. This methodology has solved the problem encountered at the use of solid catalysts, low reaction rates due to low level of mass transfer, limitation between liquid and solid phase of catalysts and reactants. By this process, the dielectric constant of liquid methanol which tends to decrease in the supercritical state, increase the oil in to methanol solubility, resulting in a single phase oil/methanol system (Lee et al, 2012). In the next page, is exemplified the process of obtaining biodiesel by supercritical method, figure 4.

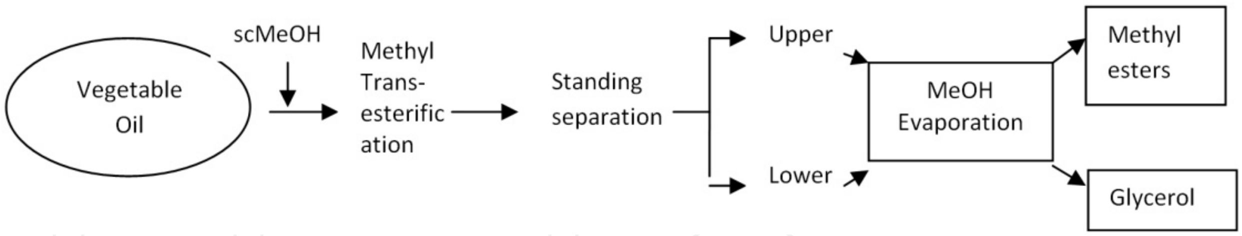

Figure 4. Schematic process of biodiesel production by supercritical method.

The methodology using supercritical methanol to obtain biodiesel by transesterification has reached the possibility to realize the reactions under mild, relatively moderate reactions to avoid the thermal degradation of fatty acid methyl esters (FAME). The reactions has been investigated in a wide range of reaction conditions (T = 200 – 425 ºC, time = 2 – 40 min. and P = 9.6 – 43 MPa). Thermal stability studies of methyl esters has showed that the best reaction conditions by supercritical methanol methodology to obtain biodiesel, consists in the temperature of 270ºC and reaction pressure of 8.09 MPa. The use of a co-solvent, as propane, CO_2 and heptane, diminishes, decrease the reaction temperature and the pressure needed to achieve a high yield of biodiesel obtained. The following table 2 exemplifies the investigated reactions conditions to obtain biodiesel.

Oil (co-solvent)	T (ºC)	P (MPa)	MeOH/Oil ratio	Time (min)	B/C	Yield (%)	Refs.
Soybean	100 -320	32	40	25	C	96	He H. et al
Soybean (CH_3H_8/MeOH = 0.05)	280	12.8	24	10	B	98	Cao W. et al
Soybean (CH_3H_8/MeOH = 0.05)	288	9.6	65.8	10	B	99	Hegel P. et al
Soybean (CO_2/MeOH = 0.1)	280	14.3	24	10	B	98	Han H. et al
Soybean (CO_2/MeOH = 0.1)	350-425	10 - 25	3-6	2 - 3	C	100	Anitescu G. et al

Table 2. Examples of biodiesel production, experiment data using supercritical methanol.

6. Sources to obtain biodiesel

The sources for biodiesel production are chosen according to availability of the same in each country, region, taking into account the relative low cost of production and favorable economies of scale. For example, the use of refined oil would not be favorable due to high production costs and low production scale, on the other hand the use of seeds, algae and fat have a low production cost and greater availability than refined oils or recycled, which is a favorable factor for the production of biodiesel from these elements. When choosing a source of biodiesel production plants, a relationship is taken into account is how much they produce and the yield of oil per hectare. Following some examples of studied seeds: soybean, Babassu(*Orbiginiasp.*), castor oil, fish oil, microalgae(*Chorellavulgaris*) (Miao & Wu, 2006), tobacco

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(Usta, 2005), *JatropaCurcas* (Berchmans & Hirata, 2008), Karanja (*Pongamiaglabra*) (Meher et al, 2006), salmon (El-Mashad et al, 2008), cooking oils, among others. All biodiesel sources are chosen according to the chemical composition of their fatty acids in relation to the size of their chains, unsaturation degree and the presence of other chemical functions, as these factors influence the biodiesel quality.

7. New advanced techniques to obtain biodiesel

In recent years soybean biodiesel has achieved a high level of advanced techniques to improve its production. Has been developed a methodology using microwave assistance to improve the esters conversion rates,, using heterogeneous catalysts, nano Cao, for example which facilitates the interaction between the molecules (Hsiao et al, 2011). Dr Hsiao and his research group has proved that by this methodology, is possible to obtain a higher biodiesel yield in less time. There are two factors that influence this reaction type. The use of nanocompounds facilitates the interaction between the molecules, nanocompounds possibility a high contact surface between the molecules. The microwave methodology reduces even the reaction time due to changing the electrical field activates the smallest variance degree of ions and molecules leading to molecular friction, enabling the initiation of molecule, chemical reaction. This methodology also provides an easier access to susceptible bonds, so, increases the chemical interaction, been obtained products in less time and higher yields. Microwave methodologies has proved to be part of desirable green chemistry, cause it is a safe, comfortable and clean way of working with chemical reactions. Microwave flow system assistance through homogeneous catalysis is another example which has improved the biodiesel production in less time, depending of some factors as reaction residence time, catalyst amount and temperature at the exit point (Encinar et al, 2012). In attempt to improve the microwave assisted methodology to obtain biodiesel another technique was added, used, the ultrasound. Microwave and ultrasound developed methodology has proved to be very efficient when used together. In this process, the first step used is ultrasound, cause ultrasonic field induced an effective emulsification and mass transfer that increases the rate of ester formation due to ultrasonic mixing causes cavitations of bubble near the phase boundary between the methanol and seeds oil, facilitating the thoroughly mixing, interaction between the oil and the reactant, methanol (Hsiao et al, 2010).Another technique has been also developed using ultrasonic irradiation with vibration ultrasonic. Instead of using heterogeneous or homogeneous transesterification catalyst, was used the enzyme methodology, through the application of Novozym 435. This methodology has proved to be efficient in enzymatic reaction to obtain biodiesel. Was observed that the use of ultrasonic added to vibration is a further factor to obtain higher values of biodiesel, cause the movement increase might facilitate the interaction between the substrate and the active site (Yu et al, 2010).Transesterification of soybean oil was achieved using ultrasonic water bath and two different commercial lipases in organic solvents (*n*-hexane) for example (Batistella et al, 2012). Dimethyl carbonate is a useful alternative to obtain biodiesel, this one is nontoxic, cheapness product and the reaction obtained product, glycerol carbonate is a value added substance with various useful applications. This can be obtained through enzymatic transesterification of soybean oil in organic solvents in mild conditions (Seong et al, 2011).The products, biodiesel are obtained in more time, but by other side this methodology has many advantages: It is an easy to use methodology, the enzyme can be reusable and the reaction work up is chemically friendly, cause it's not necessary the treatment of water used to purify biodiesel by the traditional, usual transesterification by homogeneous basic catalyst and is obtained an added value product, the glycerol carbonates. Heterogeneous catalysis using subcritical methanol is an advance in the soybean biodiesel obtaining methodology. By this technique is possible to use less amount of catalyst and have as main advantages the catalyst reusable and the separation, obtaining from reaction medium through centrifugation. The use of small amount of a catalyst, K_3PO_4, 0.1%wt, insoluble in methanol has transformed the reaction in subcritical methanol more available, cause has reduced the temperatures from 350ºC to 160ºC and the methanol molar ratio from 42 to 24, for example. The catalyst can be reusable at least three times. (Yin et al, 2012). KF Modified calcium magnesium oxide catalyst is an example of heterogeneous catalysis to obtain soybean biodiesel and even to recycle the catalysts due to be easily removed from the reaction through centrifugation and the use of a reaction under atmosphere pressure and 65ºC of temperature. This new catalyst has even improved the ester methyl yield from 63.6% (CaO-MgO catalyst) to 97.9% (KF-MgO-CaO) (Fan et al, 2012). Response surface methodology is an applicable technique to improve the results in obtaining soybean biodiesel. This methodology verifies the main parameters to optimize the biodiesel production process (Silva et al, 2011).The use of a process entirely independent from petroleum has been reached by the use of ethanol, obtained from a renewable source, sugar cane and seed oil. Gomes and his research group has developed a methodology to obtain ethyl biodiesel and even has developed a methodology to simplify the work-up process. In order to optimize the separation step of glycerol from biodiesel, many techniques have been studied. The microfiltration through ceramic membrane has demonstrated to be a useful technique to obtain biodiesel. This methodology is environmentally friendly cause reduces the amount of used water to purify the biodiesel. This technique simplify the entire purification process, the biodiesel is obtained by transesterification, after the end of reaction is added acidified water, this process facilitates the separation in two phases, the organic one, rich in oil and the aqueous, which posses the soaps converted in water soluble salts, catalysts, glycerol and other water soluble substances (Gomes et al, 2011). In water, glycerol forms greater droplets that are retained during the microfiltration step, been the biodiesel obtained by this way with glycerol content lower than 0.02% wt, the limit of free glycerol specified by Brazilian regulation. Mesoporous silica catalyst was used in a heterogeneous catalysis of soybean transesterification with methanol. La_{50}SBA-15 is used to obtain an ethyl biodiesel in mild conditions after 6 hours. The main advantage of this technique is the use of a heterogeneous catalysis to obtain ethyl biodiesel in mild conditions, don't use the usual high temperatures 473K and lower amounts of the ratio Oil/ Alcohol, from 36 to 20. This lower amount of alcohol facilitates the phase separation organic/ water, less amount of alcohol causes an easier purification process, because diminishes the possibility of emulsion formation (Quintela et al, 2012). The heterogeneous catalysis of biodiesel has reached an advance with the development of methodologies using membranes.

These membranes can be prepared in a simple way by the use of clays as hydrotalcite and poly (vinyl alcohol). The biodiesel is prepared by transesterification and can be obtained in mild conditions, 60ºC in a volume ratio oil/methanol of 5:60. The methyl biodiesel by this methodology can be obtained in 90%. The catalyst can be reused at least by 7 times (Guerreiro et al, 2010). An alternative method to obtain biodiesel is the enzymatic-catalytic way. In general this methodology has as main advantage the enzymatic selectivity, is a reusable catalytic and facilitates the separation, purification process. Methodology using a immobilized lipase onto a nanostructure has been developed due to the good transesterification activity of lipase and the use of electrospinning method to obtain nanofibrous membranes, which have larger surface area and porous structure that can lower the substrate resistance and facilitate enzyme immobilization, generating a reusable catalyst for biodiesel synthesis. The use of this methodology simplifies the separation process, where after the reaction, glycerol can be removed by centrifugation and the biodiesel obtained in the 90% range (Li et al, 2010).

Variable	Base Catalyst	Acid Catalyst	Lipase Catalyst	Supercritical Alcohol	Heterogeneous Catalyst
Reaction temperature (ºC)	60 - 70	55 - 80	30 - 40	239 - 385	180 - 220
Free fatty acid in raw material	Saponified products	Esters	Methyl esters	Esters	Non sensitive
Water in raw materials	Interfere with reaction	Interfere with reaction	No influence		Non sensitive
Yields of methyl esters	Normal	Normal	Higher	Good	Normal
Recovery of glycerol	Difficult	Difficult	Easy		Easy
Purification of methyl esters	Repeated washing	Repeated washing	None		Easy
Production cost of catalyst	Cheap	Cheap	Relatively expensive	Medium	Potentially cheaper

Table 3. Example of different technologies to produce biodiesel.

8. Non usual methods of soybean biodiesel analysis of cold properties and oxidation state

Several methods have been used to characterize biodiesel, and each methodology analyses some aspects of biodiesel as cold properties and oxidation process. Most legislation assumes a small group of tests to determination of biodiesel quality. Eighteen percents of Brazilian biodiesel production uses soybean as oil sources. Several nations have been establishing standards and legislation about biodiesel. Mainly determinations include iodine value, acid content, specific mass, esters content among others. The aim of this work are the availability of methodologies that wasn`t includes on official methodologies.

8.1. Cold properties

Official methodologies of biodiesel are: Cold Filter Plugging Point (CFPP), Cloud Point and Pour Point. Pour point indicates a moment of initial crystallization, but this methodology has low accuracy. For studies with more complexity other methodologies has better performance.

8.2. Differential scanning calorimetry

One of most usual and versatility methodology is a differential scanning calorimetry, these methodology are based on monitoring the difference in energy provided/released to/ by the sample (reagent system) in relation to a reference system (inert) as a function of temperature when both systems are subjected to a controlled temperature program. The changes in the temperature of the sample are caused by phase rearrangements, dehydration reaction, dissociation or decomposition reactions, oxidation or reduction reaction, gelatinization and other chemical reactions. DSC evaluates absorption or energy liberation to determine the initial of the reaction. A typical curve of biodiesel is presented at figure 1:

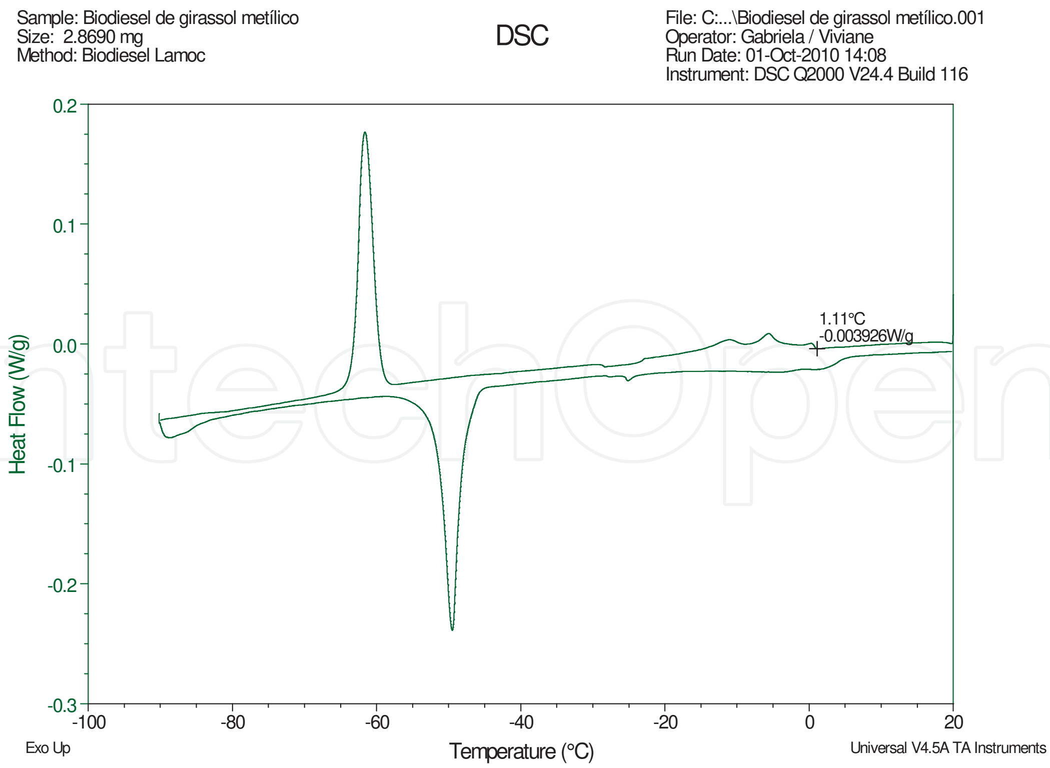

Figure 5. Differential Scanning Calorimetry of biodiesel.

Small signal at temperature of -1.1ºC is due a crystallization of saturated ester notably palmitic and stearic methyl esters, shaped signal of -60ºC is caused by crystallization of unsaturated esters (oleic, linoleic and linolenic methyl esters). These temperatures can change by cooling rate, so is important promoting standardization for independent analysis.

DSC trying to be associates with pour point results, because, a priori, both methods analyze a formation of firsts crystals, Formation of crystals initiate with nucleation of crystals that precedes crystallization is dependent on the formation and growth of aggregates or clusters of molecules. These aggregates must overcome a critical size in order to keep a steady growth and become a crystal of detectable dimensions [Avrami, 1940; Avrami, 1941]. At the stage of crystal growth, molecules of solute adsorb on the crystal surface and the process depends on the diffusion of material from the liquid phase to the solid phase which is being formed. Any of these stages can control crystal growth. The added substance must be capable to interfere with one of these stages: either avoiding or delaying the growing of aggregates to a critical size or reducing crystal growth rate [Mullin,2001].

In this point it's crucial to understand the difference of results obtained by pour point analyses and DSC. Calorimetric method is very sensible and detect energy associate of crystallization phenomena under of critical crystal size. While pour point detection occur only when crystal reached a minimum size.

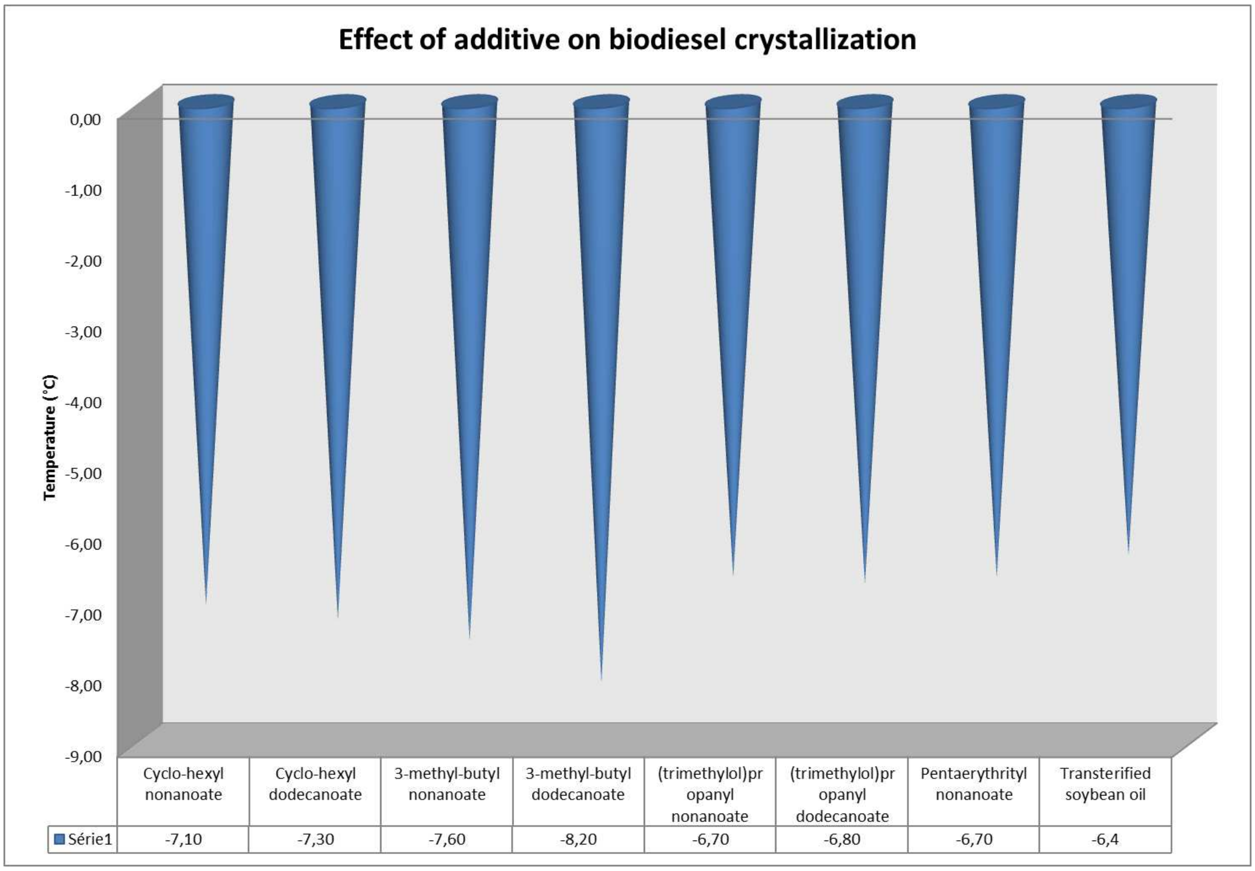

Figure 6. Impact of additives into onset temperature of biodiesel crystallization based on Soares et al, 2009

Soares et al (2009) present a work in which several esters derived from branched chain, cyclic monohydroxylated alcohols or polyhydroxylated alcohols were added to methyl transesterified soybean oil (biodiesel like) to investigate their effect on the transesterified soybean oil crystallization. In this work were added kinetic studies, were conducted in order to detect differences in crystallization mechanisms due to differences in additive structures.

They obtained a depression of onset crystallization point about 2ºC when used an additive (0,08mol/100g of transesterifed soybean oil)

Still about this work were determined induction times of crystallization. Induction time indicates how many time initiate crystallization at determined temperature. This time tends to reduce while temperature decreases. This information is important because permitted association with limit time to storage before crystallization.

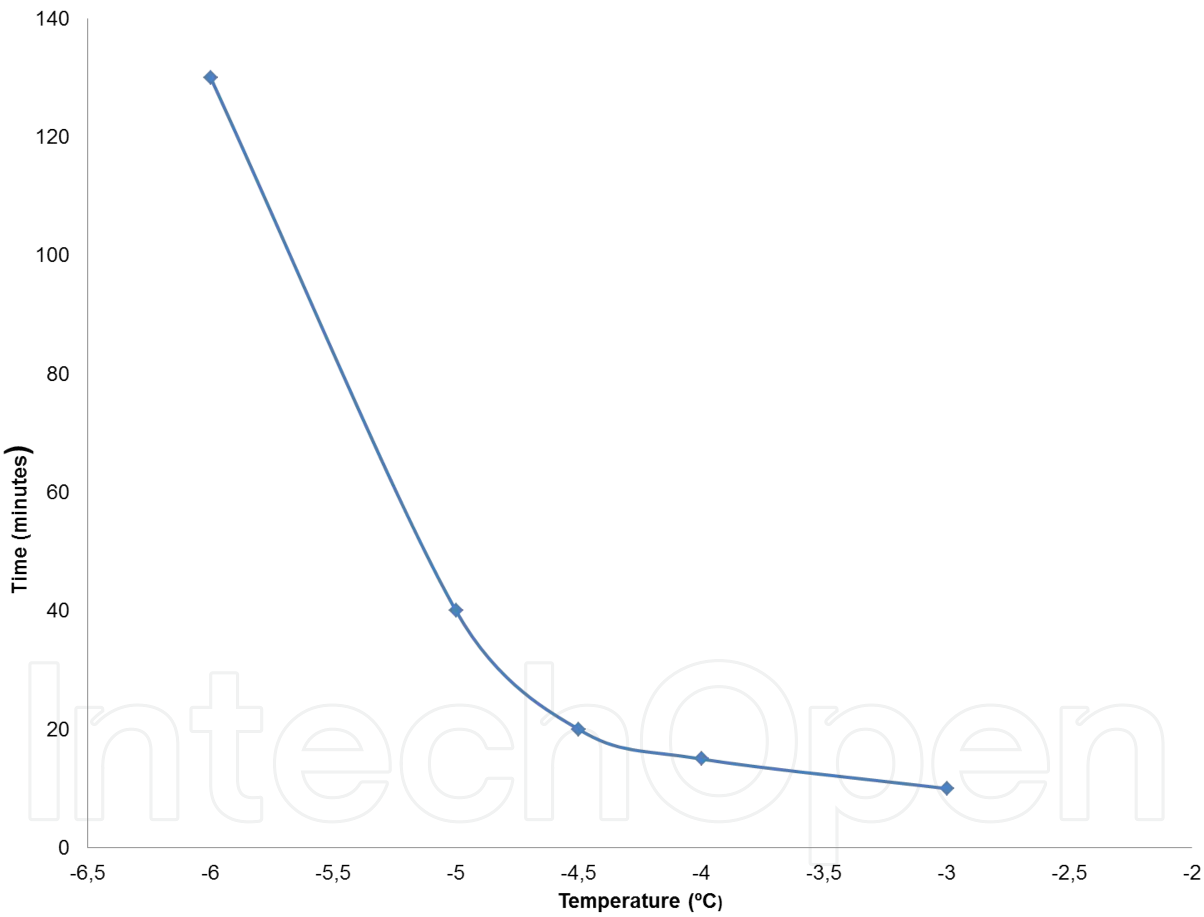

Figure 7. Induction time of crystallization based on Soares et al (2009)

These kinetic models describe how the extension of the phase transformation of a given material occurs as a function of time and temperature. Their equation is based on the suppositions of isothermal condition of crystallization, aleatory homogeneous or heterogeneous nucleation and that the new phase growth rate is temperature dependent. Avrami admitted that a number of tiny nuclei (aggregates of subcritical size) are already present in the phase to be transformed and that these aggregates must grow to a critical size to start a steady growth. By simplifying his statistical treatment presented in the calculation of transformed matter, he came to the generalized expression:

$$\alpha=1\text{-exp}\ (\text{-}kt^{n}) \tag{1}$$

Where α is the volume fraction transformed (crystallized mass); k is dependent on a shape factor, on nucleation probability, on nucleation and growth rates and on the dimensionality of crystal growth while n reflects the mechanism of nucleation and growth and the crystal morphology [Avrami, 1940; Avrami, 1941]. Several works has been using DSC as assessment cold properties (ref), with better accuracy and precision.

8.3. Oxidative properties

Oxidative properties of biodiesel commonly assessment by EN 14112 called rancimat and Iodine value, but several methods have been used by analysis of oxidation state of oil and biodiesel. Oxidation products from these compounds as Petrooxy, differential scanning calorimetry (DSC), Pressure Differential Scanning Calorimetry (PDSC) (Dufaure et al, 1999) iodine value (IV) and mainly Rancimat Method. Each method is based at one step, intermediate compounds or reactants of biodiesel oxidation.

At the PetroOxy, the sample is inducted to oxidation through an intense oxygen flow, manipulating by this way the stability conditions through a specific apparatus. The analysis time is recorded as the required time to the sample absorbs 10% of oxygen pressure. Analysis is based on oxygen consumption (reactant) but not detect products.

The differential scanning calorimetry (DSC) monitors the difference in energy provided/ released between the sample (reagent system) and the reference system (inert) as a function of temperature when both, the system are subjected to a controlled temperature program. Changes in temperature sample are caused by rearrangements of induced phase changes, dehydration reaction, dissociation or decomposition reactions, oxidation or reduction reaction, gelatinization and other chemical reactions. DSC evaluated absorption or energy liberation for determining initial reaction. This process can present some problems because of formation of lipid alkyl radical is an endotermic process and others reactions are exotermic (Santos et al, 2011). The time for secondary product formation from the primary oxidation product, hydroperoxide, varies with different oils. Secondary oxidation products are formed immediately after hydroperoxide formation in olive and rapeseed oils. However, in sunflower and safflower oils, secondary oxidation products are formed when the concentration of hydroperoxides is appreciable (Guillen and Cabo 2002).

At the Rancimat technique, oxidative stability is based at the electric conductivity increase (Hadorn & Zurcher, 1974.). The biodiesel is prematurely aged by the thermal decomposition. The formed products by the decomposition are blown by an air flow (10L/ 110 ºC) into a measuring cell that contains bi-distilled, ionized water. The induction time is determined by the conductivity measure and this can be totally automatized. Rancimat is the most used technique to determine finalized biodiesel stability, under oxidative accelerated conditions, according to standard EN14112. This technique evaluated final products of thermal decomposition.

The differential scanning calorimetry (DSC) monitors the difference in energy provided/ released between the sample (reagent system) and the reference system (inert) as a function of temperature when both in the system are subjected to a controlled temperature program. Changes in temperature sample are caused by rearrangements of induced phase changes, dehydration reaction, dissociation or decomposition reactions, oxidation or reduction reaction, gelatinization and other chemical reactions. DSC evaluated consumption or energy liberation for determining initial reaction.

The Pressure Differential Scanning Calorimetry (P-DSC) is a thermo analytical technique that measures the oxidative stability using a differential heat flow between sample and reference thermocouple under variations of temperatures and pressure. This technique differs from the Rancimat for being a fast method and presents one more variable - the pressure, allowing to work at low temperatures and using a small amount of sample (Candeia, 2009). All of these methods evaluated one aspects of oxidation process. But to predict behavior or design an adequate biodiesel its necessary to associate a oxidation process with structural properties or composition.

Iodine Value (IV) has been used for a long time to quantify unsaturated bonds on vegetable oil and, actually, biodiesel. Iodine Value is considering mainly structural method to assessment oxidation stability. Although currently some authors agree that this method is not necessarily the better method to evaluate stability.

Agreement with oxidation mechanism of fatty acids its very common associated presence of unsaturated with tendency of low stability, but Jain and Sharma (2010) presents weak relationship (R^2= 0,4374) between unsaturated esters content and induction period for several biodiesels, its associate this discrepancy with differ technology productions or presence of impurities.

Knothe (2007) bring an important discussion about relevance of Iodine value, its associate iodine value with some others structural index as APE and BAPE and associate to several properties of biodiesel in his work; he gives examples of how different mixtures of methyl esters of the three most common unsaturated FA—oleic, linoleic, and linolenic—can achieve nearly identical IV just slightly below the value of 115. This is an important fact because if oxidative stability depends of how many times one biodiesel can resist to be oxidized, and Linolenic acid reacts more fast then linoleic and oleic acid, this mixtures should present a differing oxidation behavior independently to have same iodine Value.

One of innovative uses of Thermogravimetric analysis is based on gum formation during biodiesel storage. Figure 4 shows a impact of storage at high temperature storage (85°C) of biodiesel. High resistance of biodiesel after four weeks is probably due formation of polymeric species as trimmers or tetramers of unsaturation esters.

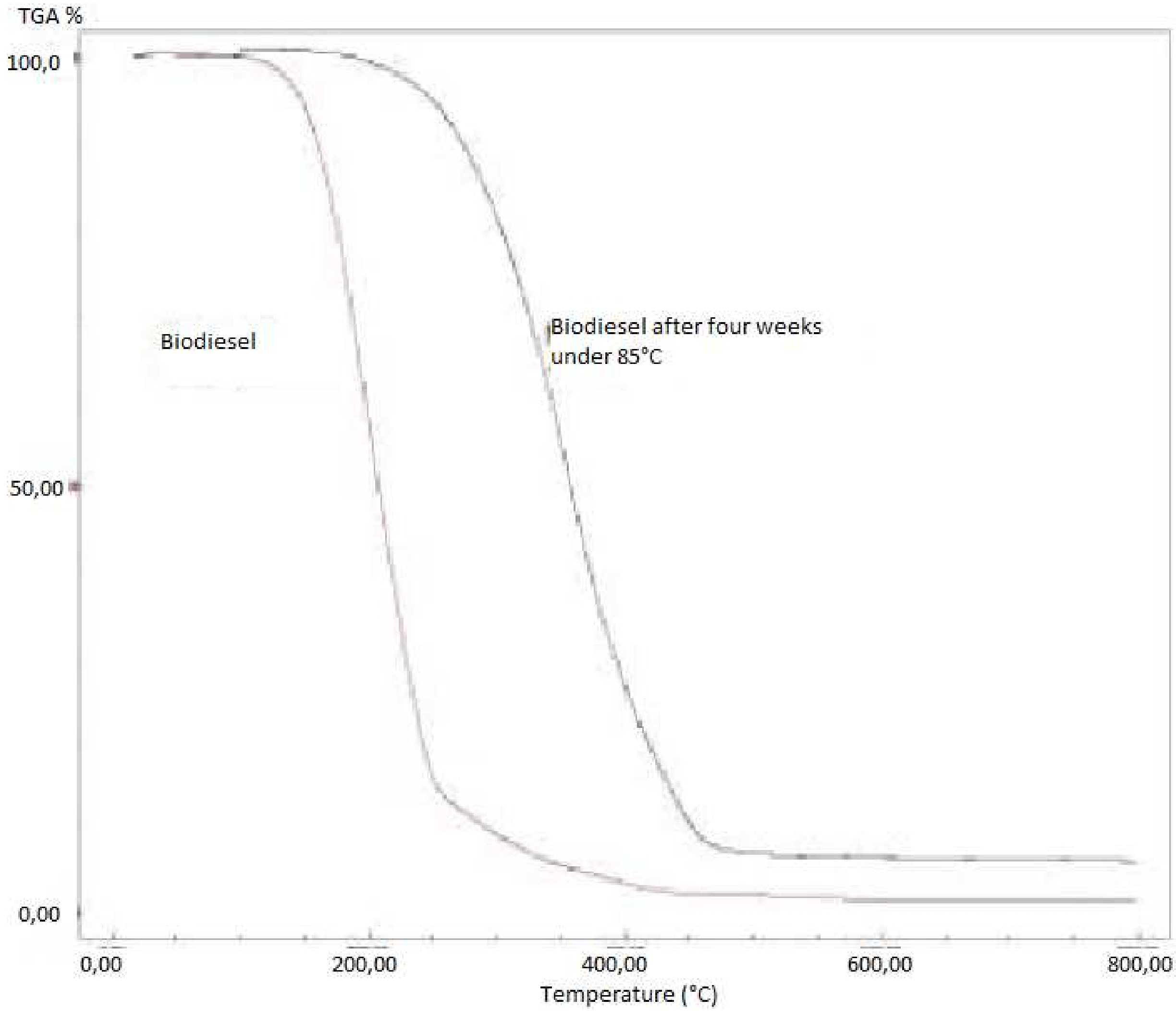

Figure 8. Formation of high molecular level species tends to increase oil viscosity

In presence of oxygen molecule polymer are forming by C-O-C linkages (Jonhson et al,1957; Wexler, 1964; Formo et al, 1979) and C-C linkages, while under an inert atmosphere only polymers with C-C linkages primordially are founded. High contents of polyunsaturated fatty acid chains enhance oxidative polymerization in fatty oils (Korus et al, 1983).Trimers and other fatty acid polymers presents higher thermal stability enhanced Termogravimetric curves of biodiesel, therefore this methodology can be used to determine biodiesel oxidation stage.

9. Conclusion

Many advanced techniques are obtained throughout the world to obtain and characterize biodiesel. To follow all these methodologies is necessary a constant research in many different science fields as chemistry, theoretical chemistry and even physics methodologies. This chapter contains only a simple updated tool to help to verify all the nowadays latest news, but never forget the most important tool to use is your brain, the determination and interest in the studied subject to unravel the science frontiers.

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