

Chapter 2 Bifunctional catalysts applied to produce biodiesel from waste cooking oil

Capítulo 2 Catalizadores bifuncionales aplicados a la producción de biodiésel a partir de aceite de cocina usado

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Abstract

This work aims to present the analysis of the catalytic performance of $\text{Fe}_2\text{O}_3/\text{CaO}$ as a bifunctional catalyst in the production of biodiesel from waste cooking oil. The clamshell was used as a source of calcium oxide by calcination. The catalyst was characterized by Thermogravimetric analysis and Differential scanning calorimetry (TGA-DSC), X-ray diffraction (XRD) and Inductively coupled plasma atomic emission spectroscopy (ICP-AES). The catalytic tests were conducted at 55 °C, the methanol:oil ratio was 12:1, amount of catalyst of 6%wt and reaction time of 5 h. The content of methyl esters in the produced biodiesel was >98% and was found to fulfill the specifications of European Norm UNE-EN 14214.

Biodiesel, Waste cooking oil, Clamshell, Bifunctional, Transesterification

Resumen

El objetivo del presente proyecto fue evaluar el comportamiento catalítico del catalizador bifuncional $\text{Fe}_2\text{O}_3/\text{CaO}$ en la obtención de biodiesel a partir de aceite de cocina usado. La concha de mar se utilizó como fuente alternativa de óxido de calcio por medio de la calcinación de la misma. El catalizador fue caracterizado por medio del análisis termogravimétrico y calorimetría diferencial de barrido (TGA-DSC), difracción de rayos X (DRX) y espectroscopia de emisión atómica de plasma acoplado por inducción (ICP-AES). Las pruebas catalíticas se realizaron a las siguientes condiciones de reacción: 55°C, relación metanol:aceite de 12:1, cantidad de catalizador de 6% en peso y tiempo de reacción de 5h. El biodiesel producido obtuvo un contenido de ésteres metílicos superior al 98%, además de que el mismo cumple con las especificaciones de la Norma Europea UNE-EN 14214.

Biodiesel, Aceite de reúso, Concha de almeja, Bifuncional, Transesterificación

1. Introduction

It is well known that the current energy sector depends mainly on the use of fossil fuels and together with globalization, has led to an increase in greenhouse gas emissions (Hafeez *et al.*, 2020). Also, since it is a non-renewable energy source, the price of fossil fuels has been increasing, while their reserves have been decreasing. This has motivated the search for less polluting alternatives, such as biodiesel.

Biodiesel is currently considered one of the most viable options coming from a renewable and clean energy source, since it can be synthesized from various vegetable and / or animal fats (Borah *et al.*, 2019). In addition, it can be used in diesel engines, because biodiesel has physicochemical properties similar to petroleum diesel (Lv *et al.*, 2020). However, the main challenge to face in the biodiesel synthesis, lies in the decrease of its production cost, as well as looking for alternatives to replace edible oils as a raw lipid source (Khan *et al.*, 2019). Derived from the above, reuse cooking oils have been used as raw material for obtaining biodiesel. However, most of the current heterogeneous catalysts are not capable of handling the high content of free fatty acids (FFA) that this type of lipid raw material has, which makes it necessary to carry out the process of obtaining biodiesel in two separate reactions: esterification and transesterification, thus increasing biodiesel production costs.

Nowadays, studies referring to heterogeneous catalysis have focused on the search for bifunctional catalysts, which can handle lipid raw materials such as used cooking oils, due to the fact that they have two different active sites, one acidic, capable of esterifying free fatty acids and a basic site, which allows the transesterification of triglycerides, in the same stage. For this, the present work proposes the use of a bifunctional catalyst based on clam shell waste from restaurants, impregnated with iron.

The originality of this work lies in the identification of the catalytically active iron crystalline phase for the production of biodiesel, using the reuse cooking oil transesterification reaction, where the calcination temperature of the catalyst is a determining variable for the identification of said complex, within which are those corresponding to the system $\text{Ca}_n\text{Fe}_n\text{O}_{2n+1}$ ($1 \leq n \leq 2$) and are directly related to oxygen vacancies. The combination of CaO and Fe salt, at the appropriate calcination temperature, will allow to obtain a bifunctional catalyst.

The foregoing has aroused great interest, because:

1. You can give a second use to a waste such as used cooking oils.
2. Decrease in production costs (approximately 60-70% for raw material only).
3. It involves the principles of "Green Chemistry" (Pájaro & Verbel, 2011) such as:
 - The use of processes that use substances with the least possible toxicity.
 - Put the use of renewable raw materials first.
 - The process must be completed in the minimum number of steps, avoiding extra steps.
 - Prioritize the use of catalyzed reactions over non-catalyzed ones.

2. Environmental problem

Nowadays, the energy supply is mainly based on the use of fossil fuels, because at least 60% of the total energy used worldwide is obtained from their use (Mansir *et al.*, 2018a). This is mainly attributed to the fact that it was adapted to various sectors such as agriculture, transport and industry (Ogunkunle & Ahmed, 2019).

In recent years, one of the main objectives that various investigations have had is to reduce greenhouse gas emissions such as CO₂, of which approximately 25% correspond to emissions related to the use of fossil fuel for transportation (Hafeez *et al.*, 2020; Llanes Cedeño, 2017). In this sense, biodiesel has become one of the most used options to reduce the use of fossil fuels, by having a cleaner combustion, it can help to reduce CO emissions, which is a product of incomplete combustion and that can be transformed in CO₂ in the presence of an atmosphere with a sufficient amount of oxygen (Llanes Cedeño, 2017). However, the commercialization of biodiesel has not spread, because it has a high production cost compared to a diesel of fossil origin (Mansir *et al.*, 2018b).

The above problem has led to various investigations that aim to use lower-cost raw materials, such as waste cooking oils, since their use as lipid raw material allows a double benefit by significantly reducing production costs (Mahmood Khan *et al.*, 2020) and by reducing contamination to soils and water bodies, which can be generated by improper disposal (Lee *et al.*, 2014).

3. Biodiesel

Biodiesel is defined by the American Society for Testing and Materials (ASTM) as a mixture of long chain fatty acid monoalkyl esters, which can be derived from lipids coming from vegetable or animal fats. In recent decades, biodiesel has become a viable alternative fuel, mainly due to its physicochemical characteristics and its renewable character, since it is possible to obtain it from vegetable oils (refined, inedible or reused), as well as animal fats (Bhavani & Sharma, 2018). Some of the advantages and disadvantages of using biodiesel versus petroleum diesel are summarized in Figure 2.1.

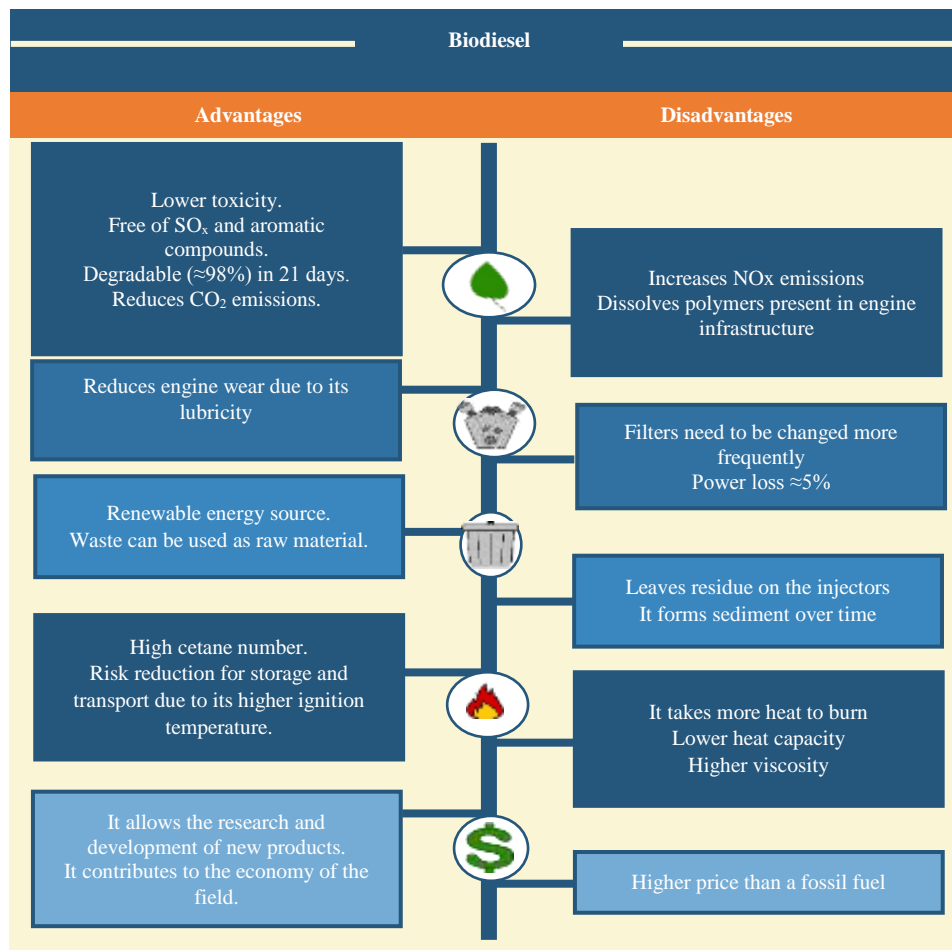
3.1 Lipid raw material

To obtain a biodiesel with the quality to accomplish with different regulations, it is necessary to have a refined lipid raw material, or as clean as possible, because most catalysts cannot handle the presence of free fatty acids (FFA) in percentages greater than 2%.

Currently, there is a great controversy about the use of vegetable oils with nutritional value as lipid raw material for the biodiesel production, due to the enormous demand that exist (Lv *et al.*, 2020), for which, various studies have been oriented to the search for lipid raw materials that do not have a nutritional value, as is the case of used cooking oil, which is a highly polluting waste and available in large quantities (Khodadadi *et al.*, 2020). Cooking oil changes its chemical composition when subjected to high temperatures and when it comes into contact with moisture and other substances from food. This results in a large amount of impurities, which greatly affect the performance of the transesterification reaction and the purity of the final product.

The use of used cooking oils allows a double benefit, since by using them as lipid raw material, the costs of manufacturing biodiesel can be significantly reduced, and also it reduces the environmental pollution caused by the discharge of this residue in the water bodies and soils (Lee *et al.*, 2014). When a waste cooking oil (WCO) is used as a lipid raw material, this must undergo through a cleaning process. This consists of three main steps: 1) filtration, where the solid contaminants are separated, 2) degumming, to separate the water-soluble phospholipids, and 3) drying, where the water residues are removed.

Figure 2.1. Advantages and disadvantages of using biodiesel



4. Synthesis methods

In this section the main methods to produce biodiesel, are summarized.

4.1 Transesterification

The transesterification reaction is one of the most widely used methods in the synthesis of biodiesel. In this reaction, a triglyceride molecule, from the lipid raw material, and three molecules of an alcohol (mainly methanol) interact, thus obtaining three molecules of methyl esters and one of glycerol. However, this reaction has two main disadvantages, the slow reaction rate and the sensitivity of the reaction to the amount of free fatty acids present in the lipid raw material. In this reaction, it is possible to use both acid catalysts and basic catalysts, in order to improve reaction times and thus increase biodiesel production.

To avoid the environmental and corrosion problems derived from the use of an acid catalyst, this process is commonly catalyzed with a basic catalyst, however, if the lipid raw material has a content greater than 1% by weight of FFA, this reaction will tend to saponify, which leads to a reduction in obtaining biodiesel and hinders the removal of the catalyst at the end of the reaction (Guo *et al.*, 2021). Therefore, it is required to carry out a previous esterification process, or the presence of an appropriate catalyst that can carry out both reactions simultaneously.

4.2 Esterification

In this reaction, a free fatty acid molecule, which can come from a waste cooking oil, interacts with the catalytic surface and with a low molecular weight alcohol molecule, to obtain a monoalkyl ester molecule and a water molecule. This reaction is considered as a previous step in the synthesis of biodiesel from waste cooking oil, since it is capable of converting the FFA contained in the lipid raw material into monoalkyl esters, thus reducing the production of soap and increasing the quality of the biodiesel. However, its main disadvantage lies on the lack of efficient catalysts (Gnanaprakasam *et al.*, 2013).

4.3. Pyrolysis

This process consists of a heat treatment in an atmosphere lacking oxygen, because it seeks to decompose large molecules into smaller ones (Hernández N., 2011).

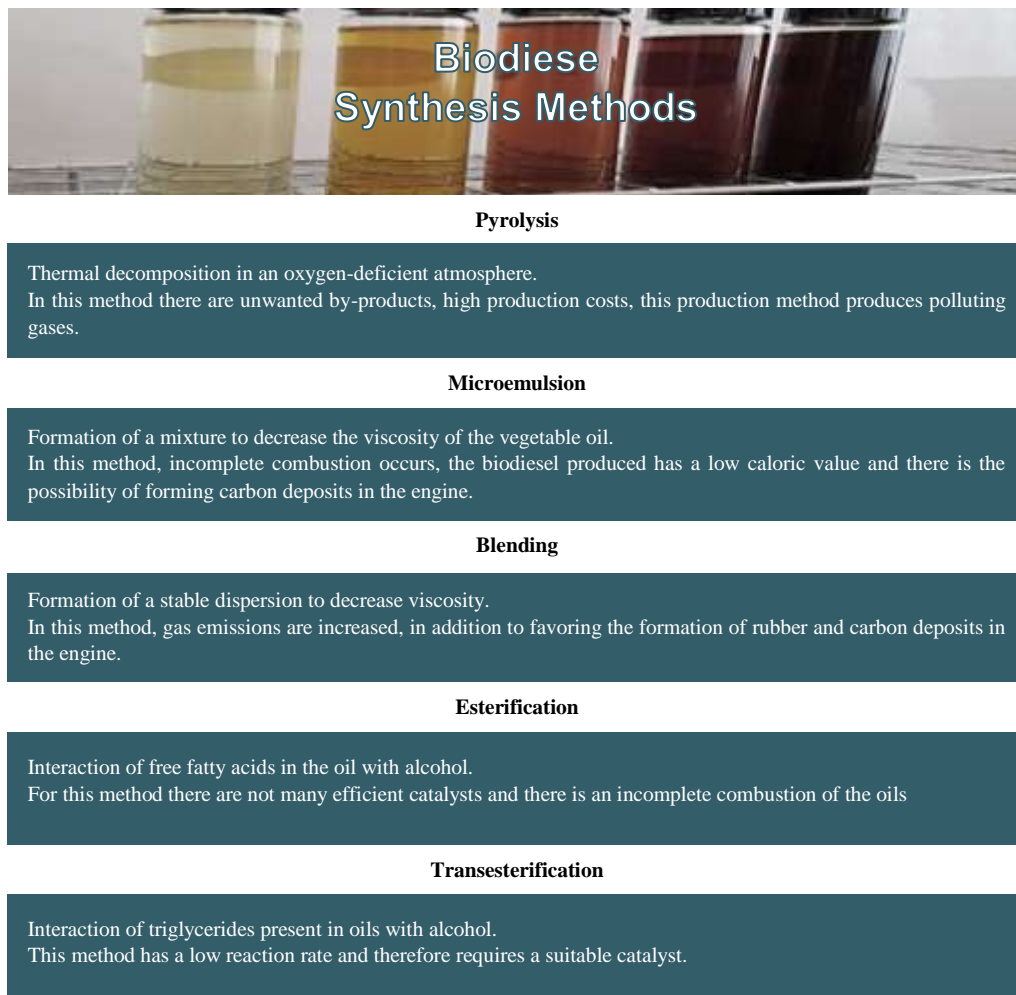
4.4. Blending

This method seeks to reduce the viscosity of an animal fat or vegetable oil by blending it in different proportions with fossil fuels (Gandure *et al.*, 2017).

4.5. Microemulsion

This method seeks to reduce the viscosity of a vegetable oil through the use of surfactants such as water or oils (Ramadhas *et al.*, 2016). Figure 2.2 summarizes some of the disadvantages of the most widely used synthesis methods for biodiesel.

Figure 2.2 Biodiesel Synthesis Methods



5. Catalysis in the transesterification reaction for the production of biodiesel

As previously mentioned, the transesterification reaction has a low reaction rate, which is why the presence of a catalyst is necessary to help the process be carried out in a faster and more efficient way. The catalysts used in the transesterification reaction can be divided into three main categories: homogeneous, heterogeneous and enzymatic catalysts.

5.1 Homogeneous catalysis

In this type of catalysis, both the reactants and the catalyst are in the same phase, which allows the reactants to mix, forming unstable intermediates that combine with more reagents to obtain the corresponding reaction products (Guo *et al.*, 2021). The main disadvantage of this type of catalysis is the loss of the catalyst at the end of the reaction, as well as the need to carry out a cleaning process at the end of the reaction. This cleaning process usually implies the use of large quantities of water and this reduces the process sustainability.

5.1.1 Homogeneous acid catalysis

Within homogeneous catalysis, we can find homogeneous acid catalysts, which are capable of handling unrefined lipid raw materials, since they can catalyze both, the esterification and transesterification reactions. Despite this, these catalysts require longer reaction times and high reaction temperatures (Lam *et al.*, 2010). In addition, there is a great risk of environmental damage due to its use, as well as corrosion in the pipes and reactors that handle it. Some of the most commonly used homogeneous acid catalysts are: HCl, CH₂O₂, CH₃COOH, HNO₃, H₂SO₄, Fe₂(SO₄)₃, H₂PO₄ (Gebremariam & Marchetti, 2018a).

5.1.2 Basic homogeneous catalysis

Basic homogeneous catalysis is preferred at an industrial level, due to the fact that it is friendly to the environment and has higher reaction rates than acid catalysis, in addition to requiring lower reaction temperatures that can range from room temperature to 70 ° C (Guczi & Erdöhelyi, 2011; Lam *et al.*, 2010; Tariq *et al.*, 2012). However, this type of catalysis gives low reaction yields with unrefined lipid raw materials, due to the presence of FFA (Guo *et al.*, 2021; Lam op. Cit.). Some of the most commonly used basic homogeneous catalyst are: NaOH (Guo op. Cit.), KOH, KOCH (Molina, 2013), NaOCH₃ (Guo op. Cit.; Mosali Raj and Bobbili Sharath, 2011; Talha & Sulaiman, 2016)

5.2 Enzyme catalysis

Currently, this type of catalyst has caught attention because this type of catalysis is capable of reducing the number of impurities of the final product and facilitates the work of removing the catalyst at the end of the reaction. However, its main disadvantage is related to the high price of this type of catalyst (Molina, 2013).

Lipases are usually the most used as catalysts, due to their high tolerance to the content of free fatty acids and to obtain yields close to 100%. Some of the most commonly used are: *Pseudomonas cepacia*, *Rhizomucor miehei*, *Rhizopus orizae*, *Candida antarctica*, among others (Guncheva & Zhiryakova, 2011).

5.3 Heterogeneous catalysis

In this type of catalysis, the reagents and the catalyst are in the different phase. These types of catalysts provide a surface on which the reaction will take place. (Aguilar R., 2003).

The main advantages of this type of catalysis are the ease of recovery of the catalyst at the end of the reaction, the possibility of using the catalyst in more than one reaction cycle and also the fact that they can be designed with greater selectivity for the process. However, this type of catalyst also has some important disadvantages, such as the decrease in its catalytic activity due to the deactivation of the catalyst after the reaction cycle.

5.3.1 Heterogeneous acid catalysis

In heterogeneous catalysis, we can find heterogeneous acid catalysis, which is capable of handling unrefined lipid raw materials, since it can esterify and transesterify, as well as not being sensitive to the moisture present in the lipid raw material. However, the most relevant disadvantages of these catalysts lie in the need for longer reaction times and reaction temperatures ranging between 120-200 °C (Faruque *et al.*, 2020; Helwani *et al.*, 2009; Lam *et al.*, 2010); in addition to the environmental and corrosion damages mentioned. Among the most commonly used heterogeneous acid catalysts are: sulfonic resins, zeolites, carbon-based catalysts (Lam *et al.*, 2010).

5.3.2 Basic heterogeneous catalysis

On the other hand, basic heterogeneous catalysis has been widely studied due to the high availability of catalysts, as well as the simplicity of recovering such catalysts at the end of the process (Lam *et al.*, 2010; Talha & Sulaiman, 2016). However, for this type of catalyst, to obtain good reaction yields, refined lipid raw materials or with low FFA contents (<2%) are required. (Guo *et al.*, 2021; Lam *et al.*, 2010).

Examples of the most commonly used basic heterogeneous catalysts are: alkaline earth metal oxides (CaO, SnO, MgO), some metal mixtures (Ca / Mg, Mg / Al), zeolites, hydrotalcites, among others (Adepoju *et al.*, 2020; Helwani *et al.*, 2009; Lam *et al.*, 2010; Mansir *et al.*, 2018b).

CaO is one of the heterogeneous catalysts most used to obtain biodiesel, due to its low cost, lower toxicity, as well as its great abundance, among other advantages (Borah *et al.*, 2019). This compound is found in many varieties, from quicklime, to the shells of some animals, including mollusks (Borah *et al.*, 2019; Mahmood Khan *et al.*, 2020; Yuliana *et al.*, 2020). Based on this, researchers have tested mollusk waste as a source of CaO.

5.3.3. Bifunctional catalysis

Bifunctional catalysts are those that have two types of active sites, one acidic and one basic, that allow to carry out two processes simultaneously. In the synthesis of biodiesel, these catalysts can work with unrefined lipid raw materials, because they are capable of esterifying the FFAs and transesterifying the triglycerides present (Foldvari, 2011). In recent years, various investigations have been carried out to evaluate various bifunctional catalysts in the transesterification reaction. Table 2.1 shows some of the examples of bifunctional catalysts used, as well as their reaction conditions and yields.

Table 2.1 Bifunctional catalysts for the biodiesel synthesis

Catalyst	Reaction condition			Reaction time [h]	Methyl Esters [%]	References
	T [°C]	Molar ratio methanol:oil	Catalyst weight [%wt]			
TiO ₂ -MgO	160.0	50:1	10.0	6.0	92.3	(Mohammed & Bandari, 2020)
CaO/MgO	69.4	16.7:1	4.6	7.1	98.4	(Foroutan <i>et al.</i> , 2020)
CaO/γ-Fe ₂ O ₃	70.0	15:1	2.0	3.0	98.8	(Shi <i>et al.</i> , 2017)
K ₂ O/CaO-ZnO	60.0	15:1	2.0	4.0	81.0	(Mohammed & Bandari, 2020)
CaO-Ca ₃ Al ₂ O ₆	65.0	12:1	10.0	2.0	97.0	(Papargyriou <i>et al.</i> , 2019)
Mn ₂ ZnO ₄	80.0	12:1	6.0	4.0	72.3	(Sivaprakash <i>et al.</i> , 2019)
La ³⁺ /ZnO-TiO ₂	35.0	12:1	4.0	3.0	>87	(Guo <i>et al.</i> , 2021)
CaO/SnO ₂	54.1	10:1	6.0	2.0	89.6	(Solis <i>et al.</i> , 2016)
ClSO ₃ H	60.0	10:1	2.0	5.0	98.6	(Hamza <i>et al.</i> , 2021)
Ca/ZM-U	70.0	9:1	5.0	6.0	88.5	(Gaur <i>et al.</i> , 2020)
CaO/Al ₂ O ₃	50.0	3.2:10	1.6	2.1	88.9	(Narula <i>et al.</i> , 2017)

6. Methodology

6.1. Materials

The oil used as lipid raw material for this research was collected in a place dedicated to food preparation, located in Toluca, State of Mexico. In order to be able to use it as a lipid raw material in the transesterification reaction, it was necessary to remove impurities by a previous cleaning treatment.

Anhydrous methanol (99.9%) was supplied by Productos Químicos Monterrey (Fermont). For gas chromatography, methyl heptadecanoate ($\geq 99\%$) was supplied by Sigma Aldrich, which was used to quantify methyl esters. The clam shells, used as a source of CaO and as a support for the catalyst, were collected from restaurants dedicated to the sale of seafood, located in San Luis Mextepec, State of Mexico.

6.2. Catalyst preparation

The clam shell was subjected to a cleaning process and later, it was ground and sieved (0.42 mm) to homogenize the particle size. In order to obtain CaO, from the CaCO₃ present in the shell as the majority component, it was necessary to subject the seashell to a heat treatment (900 ° C) for 6 h.

Once the calcium oxide was obtained, the impregnation of the Fe in the support was carried out, starting from Fe(NO₃)₃*9H₂O (>99.5%) as precursor salt. In order to verify the effect of the iron load on the transesterification reaction, three different percentages by weight of iron precursor salt were tested (0%, 5% and 7%). Finally, the catalytic sites were activated by means of another thermal treatment at 500 ° C for 6 h.

6.3. Catalyst characterization

The clam shell was analyzed by a simultaneous thermal analysis (SDT Q600 simultaneous TGA / DSC, TA Instruments) under nitrogen flow conditions with a heating rate of 10 ° C / min. The X-ray diffraction analysis technique was used, in order to identify the crystalline species present in the bifunctional catalyst, as well as to determine the crystalline structure of calcium oxide before iron impregnation. These tests were carried out in a Bruker X-ray diffractometer, Advanced 8 model with Cu K α radiation of 30KV and 35 mA. The data were collected at the scan angle (2θ) from 5° to 80°, with a step time of 56.7s and a step size of 0.029 °.

6.4. Pretreatment of used cooking oil

Due to the fact that the type of oil used in the present work presents impurities derived from the heat treatment to which it was subjected during food preparation, it was necessary to carry out a previous treatment. First, the used cooking oil was filtered with the help of a fine mesh cloth to remove all the larger solid impurities. Subsequently, the oil was centrifuged at 600 rpm for 10 min to separate the smaller impurities. Next, the oil was heated to 80 ° C and was placed in a decanting funnel, it was washed with water (10% of the volume of the oil) at 80 ° C. Finally, the water residues were removed from the oil, placing the organic phase in a glass container under vacuum conditions and heated at 80 ° C for 30 minutes.

6.5. Catalytic evaluation

The catalytic activity of the bifunctional catalyst was evaluated by the waste cooking oil transesterification reaction with methanol, using a 250 mL capacity batch reactor, connected to a reflux system. The experiments were carried out with a constant methanol: oil molar ratio (12: 1). And the amount of catalyst used was 6% by weight of the oil. The reaction temperature (55 ° C) was kept constant with a heating rack throughout the reaction time (5 h). At the end of the reaction, the catalyst was separated from the products (methyl esters and glycerol) by centrifugation. The remaining methanol was separated from the biodiesel by evaporation under vacuum conditions.

6.6. Biodiesel characterization

The determination of the amount of methyl esters was carried out according to the UNE-EN14103 biodiesel test, using a Scion 456-GC gas chromatograph equipped with a flame ionization detector and CPwax capillary column with a length of 30 m, thickness of 0.25 μ m film and 0.32 mm internal diameter. The determination of the kinematic viscosity was carried out according to the European standard EN ISO 3104, with the help of a Canon-Fenske capillary viscometer immersed in a bath at constant temperature (40°C). The acid number was determined with the test of the European standard EN 14104, with the help of a potentiometric titrator (877 Titrino Plus-Metrohm) using potassium biphthalate as the primary standard to evaluate the concentration of the titration solution (KOH)

7. Results

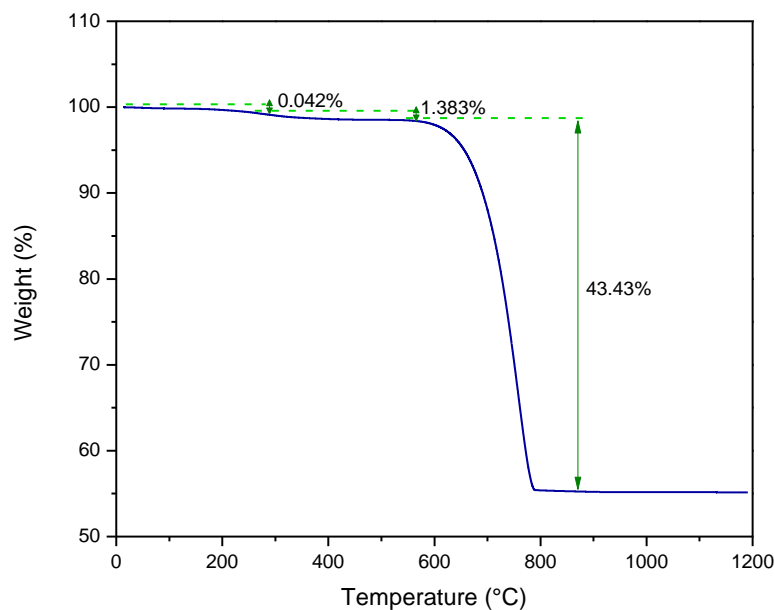
7.1. Catalyst characterization

7.1.1 Thermogravimetric analysis and differential scanning calorimetry

During the synthesis of a catalyst, different variables must be taken into account, such as the calcination temperature, the calcination time and the heating ramp, which can affect the formation of the chemical species that will grant the catalytic activity. In the case of clam shell, it is necessary to transform CaCO_3 into CaO , otherwise, there is a risk of significantly reducing the activity of the catalyst due to insufficient CaO production, or else, due to the absorption of moisture and CO_2 in the environment.

In order to know and establish an adequate calcination temperature, the clam shell was analyzed, using the TGA and DSC technique; The results obtained by both methods, when analyzing clam shell, are shown in Graphic 2.1.

Graphic 2.1 Results of the TGA-DSC performed on the clam shell

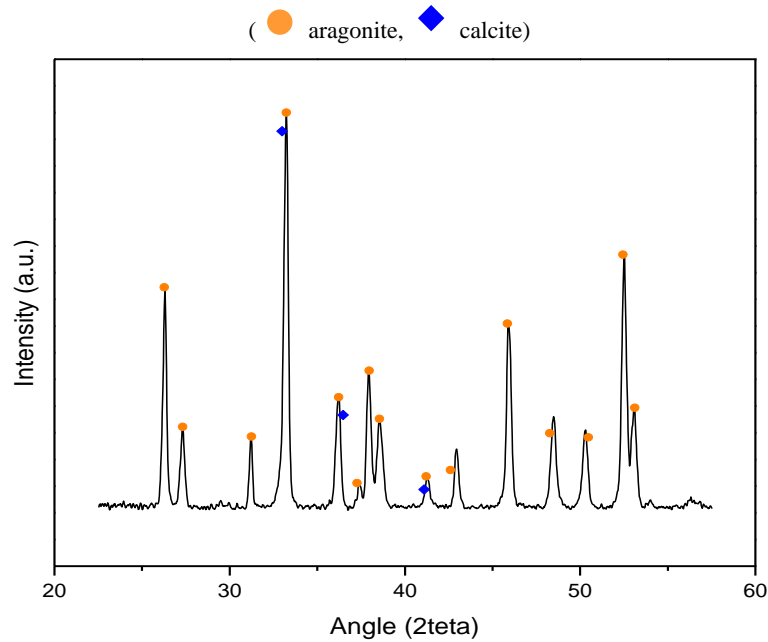


In Graphic 2.2 it is possible to clearly observe three significant weight losses. The first one occurs before 200°C and corresponds to the loss of the physisorbed water on the surface of the sample.

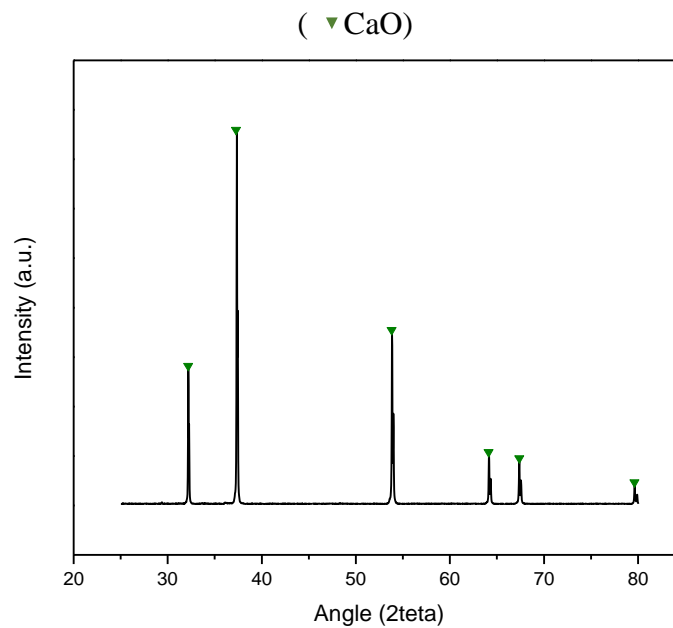
The second stage, between 250°C and 550°C , is explained by Yoshioka as the chemical transformation of the aragonite phase to the calcite phase (Yoshioka, 1985). Finally, in the third stage, the most important weight loss is observed, which is associated with the decomposition of CaCO_3 into CaO and CO_2 , which occurs between 550°C and 900°C (Foldvari, 2011). As a result of the previous analysis, it was possible to determine that the optimal calcination temperature to fully convert the CaCO_3 present into CaO is greater than 800°C , the above is consistent with reports of other investigations (Mansir et al., 2018a).

7.1.2. X-ray diffraction (XRD)

In order to know the crystalline phases in the samples, the X-ray diffraction technique was used. It is well known that the shells of different clams are largely constituted by CaCO_3 (Dey et al., 2021; Zhang et al., 2019), (Dey et al., 2021; Zhang et al., 2019), which makes them an ideal raw material for obtaining CaO . To corroborate the presence of CaCO_3 , an X-ray diffraction analysis was performed on the uncalcined clam shell and on the calcined clam shell at 900°C for 6h. The results can be seen in Figures 7.2 and 7.3, respectively. In the case of the uncalcined clam shell (Graphic 2.2), it was possible to identify that the main component of the clam shell is CaCO_3 , which is also present in the crystalline phases aragonite (JCPDS #760606) and calcite (JCPDS #240027).

Graphic 2.2 Uncalcined clam shell diffractogram

In the shell sample calcined for 6 h at 900°C (Graphic 2.3) it was possible to identify the complete transformation of CaCO_3 into CaO (JCPDS #371497). Similar results were observed in calcium oxide catalysts from natural materials such as eggshell and sea snail shell (Krishnamurthy *et al.*, 2020).

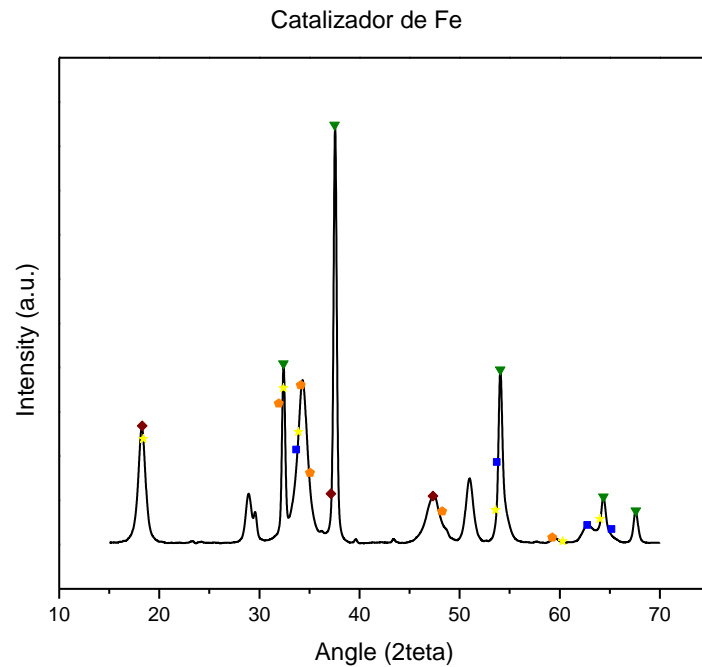
Graphic 2.3: Calcined clam shell diffractogram

According to the previous diffractograms, all the CaCO_3 has been transformed into CaO after subjecting the sample to a calcination of 900°C, which agrees with the results of the TGA analysis.

On the other hand, for the $\text{Fe}_2\text{O}_3/\text{CaO}$ catalyst (calcined for 6 h at 600°C), the X-ray diffraction analysis managed to identify the following phases: Fe_2O_3 (JCPDS #330664), Fe_3O_4 (JCPDS #890688), $\text{Ca}_2\text{Fe}_2\text{O}_5$ (JCPDS #712264), $\text{Ca}_2\text{Fe}_{15.57}\text{O}_{25.56}$ (JCPDS #722346) y CaO (JCPDS #371497).

Graphic 2.4 Catalyst diffractogram Fe₂O₃/CaO

(■ Fe₂O₃ ◆ Fe₃O₄ ◆ Ca₂Fe₂O₅ ★ Ca₂Fe_{15.57}O_{25.56} ▼ CaO)



7.1.3 Inductively coupled plasma atomic emission spectroscopy (ICP-AES)

In order to know the composition of the bifunctional catalyst Fe₂O₃/CaO, an induction coupled plasma atomic emission spectrometry (ICP-AES) was performed.

For the synthesized sample, using 7% by weight of the precursor salt, 1.0% by weight corresponding to iron and 57.30% by weight of calcium were obtained.

7.2. Characterization of waste cooking oil

7.2.1. Acid value

To demonstrate the bifunctionality of our catalyst, it is necessary to work with a lipid raw material that has a higher amount of FFA, compared to a refined oil. This is because a conventional basic heterogeneous catalyst would saponify such FFAs.

A comparison was made between the acid value of a refined oil and the waste cooking oil that was used as raw material for the transesterification reaction. This was conducted in order to show that waste cooking oil has more free fatty acids than refined oil.

In this test it was found that the acid value of the refined oil was 0.041 mgKOH/g, in comparison with the 4 mgKOH/g (2%) present in the waste cooking oil.

7.2.2. Viscosity

Viscosity is a parameter that will allow us to know if the transesterification reaction did occur, since there is a decrease in the viscosity of the raw material after the production of methyl esters.

In order to be able to carry out a comparison before and after the transesterification reaction, the measurement of the viscosity of the waste cooking oil was used and, as a reference point, a refined oil.

The kinematic viscosity oil determination was carried out at 40 ° C by triplicate, obtaining an average value of 39.2 mm²/s for refining oil and 41.33mm²/s for waste cooking oil.

7.3. Catalytic evaluation

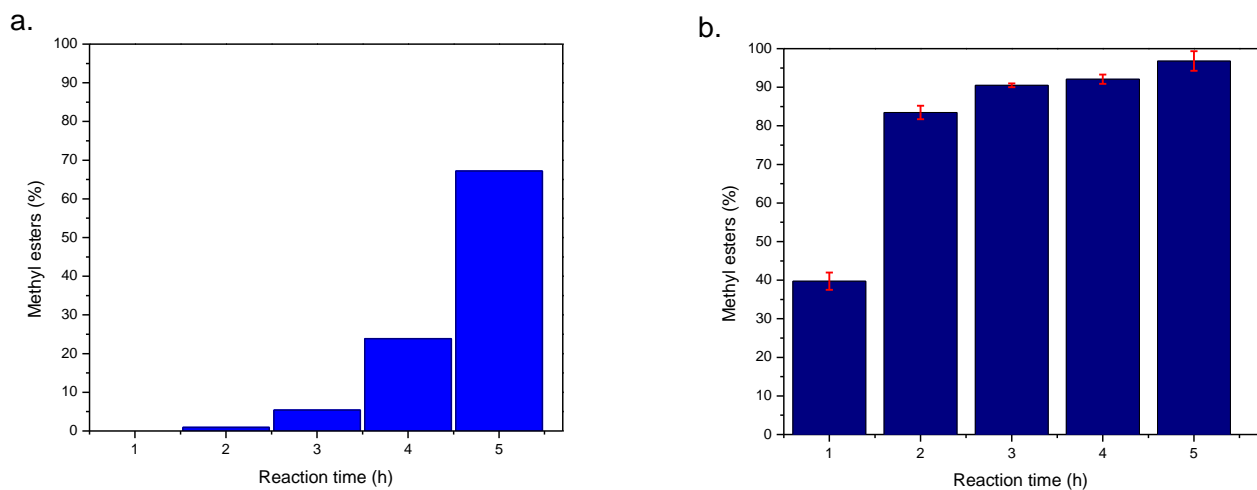
7.3.1. Influence of the type of catalyst with waste cooking oil

When waste cooking oil is used as lipid raw material, conventional basic catalysts have low reaction yields, which is attributable to the acidic character of the oil, due to the fact that it has a higher presence of FFA (Endalew *et al.*, 2011; Yuliana *et al.*, 2020).

This has been reflected in various investigations that use CaO as a heterogeneous catalyst in the production of biodiesel, obtaining low reaction yields where long reaction times are needed (Endalew *et al.*, 2011; Yuliana *et al.*, 2020). However, the presence of two different active sites in bifunctional catalysts allows them to be able to use lipid raw materials with higher FFA contents, since they can simultaneously carry out their esterification and the transesterification of triglycerides (Zhang *et al.*, 2019).

As a comparison, a reaction was carried out using only CaO as a catalyst (Graphic 2.5a), achieving 67% of methyl esters after 5 hours of reaction. On the other hand, the WCO reaction using a bifunctional iron catalyst (Graph 2.5b), managed to obtain 98.75% of methyl esters in the same reaction time.

Graphic 2.5 a. WCO and CaO reaction and b. WCO and Fe₂O₃/CaO reaction



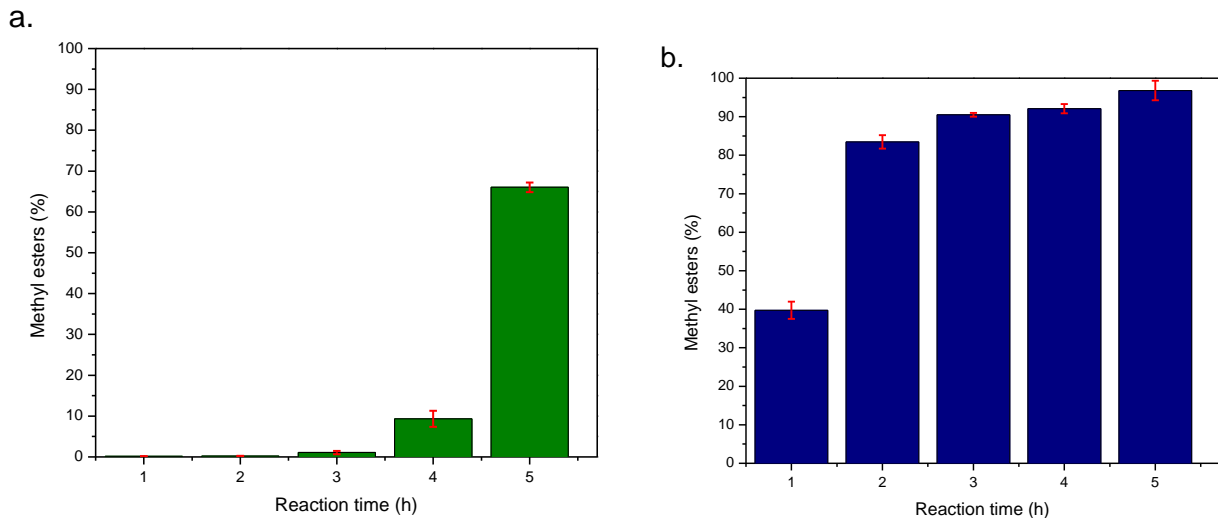
As can be seen in Figure 2.5a and Figure 2.5b, there is a significant difference in the reaction rate, since we can observe how in the fifth hour of reaction with CaO as a catalyst a lower content of methyl esters was reached, compared to the second hour of reaction with a bifunctional catalyst.

7.3.2. Effect of the amount of salt on the bifunctional catalyst (Fe₂O₃/CaO)

Another important variable to study in the use of bifunctional catalysts in the transesterification of waste cooking oil is the precursor salt load.

In order to analyze the effect of the precursor amount of iron, in this project the synthesis of the catalyst was carried out with 5% and 7% by weight of the precursor salt Fe(NO₃)₃·9H₂O. The results obtained are shown in Graphic 2.6.

Graphic 2.6 a. Catalyst 5% by weight of $\text{Fe}(\text{NO}_3)_3$ and b. Catalyst 7% by weight of $\text{Fe}(\text{NO}_3)_3$.



Comparison of the previous results shows that 7% by weight of iron precursor salt is the best amount, due to the fact that 98.8% of methyl esters were obtained after 5 hours of reaction.

The catalyst with 5% by weight managed to obtain 67.7% content of methyl esters, which is similar to the result obtained when using only CaO as a catalyst. This is attributed to the fact that there is no significant impregnation of acidic active sites (from iron), which is why it is not possible for the catalyst to carry out the esterification of the FFA from the waste cooking oil.

7.4. Biodiesel Characterization

To characterize the biodiesel obtained from the previous transesterification reactions, the content of fatty acid methyl esters (FAMES), viscosity and acid value was determined by means of the standard methods shown in UNE-EN 14103, ISO 3104 and UNE-EN 14104.

To have a point of comparison, the characterization of the biodiesel obtained from the transesterification reaction with refined oil was carried out, using $\text{Fe}_2\text{O}_3/\text{CaO}$ as catalyst, obtaining a 98.8% content of ethyl esters, a viscosity of $4.8\text{mm}^2/\text{s}$ and an acid value 0.05mgKOH/g .

On the other hand, for the biodiesel produced from waste cooking oil, an average of 98.8% of FAMES was obtained, a viscosity of $4.6\text{mm}^2/\text{s}$ and an acid value of 0.052mgKOH/g . It is very important to observe the effectiveness of the bifunctional catalyst, because this catalyst allows to obtain contents of methyl esters higher than those required by the EN-14214 standard (96.5%) and a viscosity within the range accepted by the standard ($3.5\text{-}5.0\text{mm}^2/\text{s}$).

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9. Conclusions

A bifunctional catalyst, $\text{Fe}_2\text{O}_3/\text{CaO}$, was synthesized with basic (provided by CaO) and acid active sites (provided by iron). This bifunctionality allows to process lipid raw materials with higher content of free fatty acids than those present in refined oils.

Biodiesel was obtained through a simultaneous reaction of esterification and transesterification, using 6% by weight of catalyst, a content of 1% by weight of iron, methanol: oil molar ratio of 12: 1, with a reaction time of 5h, obtaining a content of methyl esters higher than 98%.

It was determined that 7% by weight of iron precursor salt in the synthesis of the catalyst is the optimal amount of precursor salt to obtain biodiesel that complies with EN-14214 regulations.

The development of efficient heterogeneous catalysts in the use of lipid raw materials with a higher FFA content represents a significant area of opportunity in reducing the cost of biodiesel production. However, the efficiency of a heterogeneous catalyst depends on several variables, such as the type of raw material, the type of alcohol used, the molar ratio of alcohol: oil, reaction temperature, stirring speed, type of reactor, in addition to the type of catalyst used.

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