INFLUENCE OF CARBONATION AND REHYDRATION ON CAO DERIVED FROM CALCINING CHICKEN EGGSHELLS IN THE CATALYTIC PROCESS OF SOYBEAN OIL TRANSESTERIFICATION

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ABSTRACT

CaO is the most used heterogeneous catalyst in transesterification reactions due to its high catalytic activity, low solubility in methanol, non-toxicity, and low cost. One of the greatest disadvantages of using CaO is its predisposition to react with H₂O and CO₂ present in the atmosphere forming Ca(OH)₂ and CaCO₃, respectively. Therefore, the objective of this study is to investigate the catalytic capacity of the catalyst derived from calcined chicken eggshells on different days after calcination. The catalyst used was produced under a temperature of 800 °C during a period of 160 minutes. The catalytic solid was characterized on days 1, 2, 3, 4, and 15 after calcination by X-ray fluorescence (XRF), X-ray diffraction (XRD); thermogravimetric analysis (TGA); transmission electron microscopy (TEM); Brunauer, Emmett, and Teller isotherm (BET); and Hammett analysis techniques. The reaction occurred at a temperature of 65 °C, had a molar ratio of 12:1 alcohol/oil, used 6% catalyst, and was carried over a period of 3 hours. The results showed that the rehydration and carbonation processes did not significantly affect the CaO.

KEYWORDS

biodiesel; heterogeneous catalysts; calcium oxide; rehydration; carbonation

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1. INTRODUCTION

The use of energy is an important aspect of every society's way of life, and plays a necessary role in its development. The demand for energy has been increasing since the establishment of human society due to population growth and industrial development. Most of the world's current energy demand is derived from conventional energy sources such as coal, oil, and natural gas (Thapa et al., 2018).

The transportation sector contributed with 64.5% of the world's total oil consumption in 2014 (Sakthivel et al., 2018). In addition, the World Energy Council (WEC) indicates that the proportion of diesel to gasoline demand will increase from 1.5 today to 3.8 by 2040. Diesel engines will suffer a more serious fuel supply crisis if new alternative diesel fuels are not explored (Liu et al., 2017).

Biodiesel has been the major substitute for petroleum-derived diesel fuel. This is due to some factors such as having similar properties to diesel, high combustion efficiency, lower sulfur content, excellent lubricity, and high cetane number (Fazal et al., 2018; Ventura et al., 2018). Biodiesel can be defined as a mixture of mono-alkyl esters, usually methyl or ethyl, of long chain fatty acids from C₁₄ to C₂₂ (FAME) obtained by esterification and transesterification processes, with the second process being derived from renewable lipids such as animal and vegetable fats (Santos et al., 2018; Hernández-Montelongo et al., 2018).

The development of catalysts has been highlighted in producing biodiesel through the transesterification reaction. Therefore, extensive research has been conducted to improve the activity, stability, and economic benefits of the catalysts (Yan et al., 2016).

Homogeneous catalysts, such as NaOH and KOH, have a great impact on the transesterification reaction because of their very high catalytic activity and their low cost. However, the use of homogeneous catalysis processes have several disadvantages, such as the difficulty of separation, reuse of the catalyst, occurrence of saponification, corrosion of the reactor, and the generation of large quantities of waste water. Due to problems associated with the use of homogeneous catalysis,

numerous studies have been carried out to investigate the application of heterogeneous catalysis. With new promising technologies that employ heterogeneous catalysts, a reaction can occur with a satisfactory high rate under simple reaction conditions, and without the typical problems associated to homogeneous catalysis (Shan et al., 2015; Marinkovic et al., 2017).

Among heterogeneous catalysts, CaO is the most used due to its high catalytic activity, low solubility in methanol, non-toxicity, and low cost. Another advantage is the possibility of obtaining it through natural and residual raw materials such as shells, bones, rocks, ash, and eggshells derived from calcium carbonate (CaCO₃). Residual chicken eggshell, for example, contains more than 95% CaCO₃, and is considered a good source of CaO from biomass (Marinkovic et al., 2017; Mansir et al., 2018).

An activated CaO catalyst can be prepared by calcination at high temperatures. However, it has the disadvantage of easily reacting with H₂O (water) present in the atmosphere, forming Ca(OH)₂, as well as being easy to react with CO₂ to form CaCO₃. These processes are called rehydration and carbonation, respectively (Kouzu et al., 2017; Antzara et al., 2015).

Nevertheless, contamination by atmospheric CO₂ and H₂O results in a major disadvantage in the application of CaO to biodiesel catalysis. There are very few studies addressing this problem in the literature. Even with the large number of articles published regarding the use of CaO as a catalyst in transesterification reactions. Nothing on this topic is addressed in the main review articles (Kouzu & Hidaka, 2012; Mansir et al., 2018; Boey et al., 2011; Catarino et al., 2017).

Reyero et al. (2014) were the first to study the stability of CaO in catalytic performance in the transesterification reaction. In their research, they used four commercial CaO samples to investigate activation and stability under reaction conditions.

Sánchez (2015) used calcined *Mytilus Galloprovincialis* shells as a catalyst to investigate the stability of CaO. The transesterification reaction occurred using 10% catalyst with a reaction time of 0 to 600 minutes. The first reaction was carried out

with the newly calcined catalyst, the second reaction was conducted with the same catalyst 4 days after calcination, and, finally, the third and last reaction was performed 21 days after calcination with the same catalyst.

On the following year, **Reyero (2015)** published a paper on the subject, this time using calcined eggshells as the catalyst and sunflower oil as raw material. The stability study was carried out in the periods 0, 7, and 30 days after calcination. Therefore, the focus of the research was only the carbonation process, since rehydration occurs in the first days after CaCO_3 calcination. Although these studies are very relevant, to our knowledge there are no published articles continuing the work by implementing different parameters such as: calcination conditions, CaCO_3 raw material, transesterification reaction condition, and type of oilseed used. A continuation study is necessary for a deeper understanding of the subject, especially in the early days of CaO aging after calcination.

Based on what has been reported, this article aims to investigate the catalytic capacity of the catalyst derived from calcining white chicken eggshells on different days after calcination. The oil used for transesterification reaction was derived from recycled soybean.

2. MATERIALS AND METHODS

2.1 Feedstock

This work used recycled soybean oil, Neon brand methyl alcohol, and calcium oxide as feedstock. Recycled soybean oil was acquired from a diner in the city of Cuité-PB, Brazil. Calcium oxide was derived from calcining eggshells from white chickens. These eggs were obtained from a commercial establishment located in the city of Cuité-PB, Brazil.

2.2 Obtaining and characterizing the heterogeneous catalyst

The eggshells were individually washed in tap water to remove the coarser dirt. Then, they were soaked in distilled water for a period of 2 hours. Following, the eggshells were rinsed with distilled water.

After washing, the eggshells were dried in an oven for 8 hours at $105\text{ }^{\circ}\text{C}$, then, they were ground, macerated, and sifted in a 150-mesh sieve. Thereafter, the eggshell powder was calcined at a temperature of $800\text{ }^{\circ}\text{C}$ for a period of 160 minutes under a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$. The sample was removed from the flask at $150\text{ }^{\circ}\text{C}$ and quickly placed in a desiccator. Following, we used a vacuum pump to remove as much air as possible from the glasswork, to prevent a reaction between catalyst, H_2O , and CO_2 present in the atmosphere.

The next day, the sample was removed from the desiccator to be analyzed under Basic Force, BET, SEM, XRD, XRF, and TGA techniques. The remainder of the catalyst was divided into two parts. The first part was placed in a shallow beaker, distributed as uniformly as possible at the bottom of the glass, to react with H_2O and CO_2 present in the atmosphere. The catalyst was again characterized on the 2nd, 3rd, 4th, and 15th day to analyze the changes in catalyst properties and characteristics caused by rehydration and carbonation. These eggshell samples were aged 1, 2, 3, 4, and 15 days after calcination and named CD1, CD2, CD3, CD4 and CD15, respectively. The second part was placed in another beaker with the purpose of monitoring daily the mass gain of the sample caused by rehydration and carbonation reactions.

The daily record of CaO mass increase was studied in order to monitor the periodical changes in sample characteristics caused by rehydration and carbonation. The study was initiated after the calcination of the chicken eggshells. After the calcination, the eggshells were cooled off in a desiccator. Shortly after, a small amount of sample (0.4208 g) was placed in a glass container (measuring 2 cm in diameter and 2.5 cm in height). The sample amount was enough to cover the surface of the glass. The container was opened for the oxide formed in the calcination to absorb the H_2O and the CO_2 present in the atmosphere.

The basic force of the catalyst was determined by the Hammett indicator method. The indicators used were phenolphthalein ($\text{H}_+ = 9.8$), indigo carmine ($\text{H}_+ = 12.2$), and 4-nitroaniline ($\text{H}_+ = 18.4$). Basicity of the catalyst was measured by the Hammett indicator–benzene carboxylic acid (0.02 mol L^{-1} anhydrous methanol solution) titration method.

X-ray diffraction analyses were performed on a Bruker ADVANCE eco D8 apparatus. A copper anode with corresponding wavelength $\lambda = 1.5418 \text{ \AA}$ was used by means of a graphite monochromator, slit (1.00 mm), nickel detector filter. Measurements were completed in the 2θ range from 10° to 90° with a scan rate of $0.2^\circ/\text{s}$.

Scanning electron microscopy analysis was performed on a Shimadzu microscope model SSX 550 SuperScan. The samples were deposited on carbon tape and, then, mineralized with gold to obtain enough electrical conductivity to avoid electrons accumulating on the sample surface. Finally, the samples were analyzed using an electron beam obtained from a tungsten filament using a zoom of 1000 to 3000 thousand times for each sample.

Subsequently, the catalyst was subjected to X-ray fluorescence (XRF) analysis by dispersive energy in Shimadzu EDX-820 equipment for determining the metal content in the sample. About 300 mg of sample were used for this analysis.

The BET surface area was measured by N_2 adsorption carried out by Micromeritics equipment. The bath temperature was of -194.30°C in a 30second equilibrium range. The heat treatment took place in a heating stage under a ramp of $10^\circ\text{C}/\text{min}$, up to 300°C for a period of 480 min.

Thermogravimetric analyses of the sample were performed using a Shimadzu DTG-60 thermal analyzer with a heating rate of $10^\circ\text{C min}^{-1}$, from room temperature up to 900°C in a nitrogen atmosphere with a flow of 100 mL min^{-1} , alumina crucible. The analyses were performed using an average of 5 mg of each sample.

Ca(OH)_2 ($C_{\text{Ca(OH)}_2}$) concentrations in the different days of sample observation were analyzed by thermogravimetry. Concentrations were determined by weight loss of H_2O measured at the first thermal decomposition event, Δm_1 , through the relationship between the molecular masses of calcium hydroxide ($\text{MM}_{\text{Ca(OH)}_2}$) and water ($\text{MM}_{\text{H}_2\text{O}}$), according to Equation 1:

$$C_{\text{Ca(OH)}_2} = \Delta m_1 \times \frac{\text{MM}_{\text{Ca(OH)}_2}}{\text{MM}_{\text{H}_2\text{O}}} \quad (1)$$

CaCO_3 (C_{CaCO_3}) concentrations in the samples

studied by thermogravimetry were determined by CO_2 loss measured in the last thermal decomposition event, Δm_2 , through the relationship between the molecular weight of calcium carbonate ($\text{MM}_{\text{CaCO}_3}$) and carbon dioxide (MM_{CO_2}), using Equation 2:

$$C_{\text{CaCO}_3} = \Delta m_2 \times \frac{\text{MM}_{\text{CaCO}_3}}{\text{MM}_{\text{CO}_2}} \quad (2)$$

2.3 Transesterification reaction and characterizations

The catalyst activity was evaluated in terms of fatty acid methyl ester (FAME) conversion during soybean transesterification. The biodiesel synthesis was performed through the methyl route in the molar ratio of 1:12 oil/methanol and 6% of heterogeneous catalyst (CaO). To initiate the synthesis, 1.2 grams of CaO and 12.2 mL of methanol were first placed in the reactor equilibrium cell, which were subjected to magnetic stirring under 300 RPM for a period of 20 minutes at room temperature. Then, 22.2 mL of soy oil was added into the mixture. The stirring was adjusted to 600 rpm and the temperature of the thermostatic bath to 65°C . The system was subjected to condensation with reflux to ensure that no evaporation would take place during the process. The reaction was controlled for a period of 3 hours.

After completing the reaction, the mixture was centrifuged to separate the liquid phase (biodiesel and glycerin) from the solid phase (CaO). The liquid phase was placed in the settling funnel for 24 hours. After separating glycerin and biodiesel phases, the latter underwent a vacuum filtration in a quantitative filter to ensure that no catalyst residue interfered with the biodiesel analyses.

Five transesterification reactions were performed. Each reaction was carried out using a heterogeneous catalyst obtained by calcining chicken eggshells aged on different days. Based on the days of aging, samples were denominated CD1, CD2, CD3 CD4, and CD15. Biodiesel samples catalyzed by these solids were named BCD1, BCD2, BCD3 BCD4 and BCD15, respectively.

The amount of FAME obtained through transesterification was analyzed by gas chromatography on a Shimadzu GCM-QP2010 chromatograph, Durabond DB-23 column (30m x

Figure 1. Percentage change of eggshell mass calcined per day.

0.25mm x 0.25 mm). The temperature of the injector and detector was 230 °C and the column temperature was 90 °C. The elution gradient was 90 to 150 °C (10 °C min⁻¹); 150-200 °C (2 °C min⁻¹); and 200-230 °C (10 °C min⁻¹), at a time of 0.65 h. Helium was used as carrier gas. Quantification was obtained by calibration curves with methyl ester standards (adapted ABNT NBR 15764). The biodiesel yield was calculated by the following expression: Yield = (biodiesel weight × FAME %)/(weight of oil). FAME % is the FAME concentration obtained by GC analysis.

Thermogravimetric analyses of biodiesel and soybean oil samples were performed using a Shimadzu DTG-60 thermal analyzer with a heating rate of 10 °C min⁻¹ at temperatures that ranged from room temperature to 600 °C, in a nitrogen atmosphere with flow of 100 mL min⁻¹, using 5 mg of each sample in an alumina crucible.

3. RESULTS E DISCUSSIONS

3.1 Mass increase

Sample mass, which was initially 0.4208 g, increased to 0.5208 g on the second day of

analysis, 24 hours after the first weighing, constituting a 23.74% mass increase. This mass gain is associated to rehydration and carbonation process of CaO, since CaO absorbs H₂O and CO₂ over time in the atmosphere, becoming Ca(OH)₂ and CaCO₃. Thus, the CaO concentration decreased and, consequently, the amount of H₂O and CO₂ absorbed by the sample also decreased, resulting in a continuous mass gain until the 15th day (CD15), when no mass gain was registered.

From Figure 1, it is possible to observe that the mass increase of the solid by days did not occur in a polynomial function of the first degree. This is due to two factors: first, the variation in air humidity and air pollution between the analyzed days; second, the distinct absorption of H₂O and CO₂ by calcium oxide. As characterized in TG and XRD analyses, the formation of Ca(OH)₂ occurs more rapidly than the formation of CaCO₃. On the fourth day of analysis, Ca(OH)₂ ceased to be formed, while the CaCO₃ concentration continued to form. Furthermore, one could observe that the Ca(OH)₂ concentration decreased on the 15th day of analysis with respect to the 4th day.

3.2 X - Ray fluorescence

The X-ray fluorescence spectrum analysis was

Table 1. Percentage of oxides present in the calcined chicken eggshell sample.

Raw material	CaO (%)	MgO (%)	SiO ₂ (%)
Chicken eggshells	99.042	0.499	0.459

Figure 2. X-ray diffraction of chicken eggshell samples at 1, 2, 3, 4, and 15 day periods after calcination.

performed in the sample after calcination to identify metal oxides in the chicken eggshell (Table 1). It was possible to observe the presence of three oxides: CaO, MgO, and SiO₂, with calcium oxide being the major substance, with 99.042%. In many studies published in the literature, the CaO concentration in chicken eggshells varies by up to approximately 97%, and by less than 1% of other oxides (SrO, Na₂O, Al₂O₃, Fe₂O₃ and P₂O₅) in composition (Eletta et al., 2016; Boronat et al., 2015).

3.3 Ray diffraction

CD1, CD2, CD3, CD4, and CD15 samples were submitted to X-ray diffraction to evaluate rehydration and carbonation of CaO (the predominantly formed oxide), according to Figure 2.

The XRD standard for CD1 shows diffraction peaks at 32.19°, 37.35°, 53.84°, 67.34°, 67.55°, and 80.88°, which corresponds to the calcium oxide of the cubic phase (JCPDS: 4-777) with *FM-3 m* space group.

In the XRD standard for CD2, two less intense peaks are observed at 17.93° and 34.1°, corresponding to the calcium hydroxide (Ca(OH)₂) of the hexagonal phase (JCPDS: 01-086-0174),

attributed to the absorption of the air moisture (Nagabhushana et al., 2017).

In the analysis corresponding to CD3, the appearance of the diffraction peak at 29.39°, that characterizes the calcium carbonate (CaCO₃) belonging to the rhombohedral phase (JCPDS nº 01-086-0174), can be attributed to the carbonation through the absorption of CO₂ present in the atmosphere.

There was no continuation in the increase of the peaks corresponding to Ca(OH)₂ in the XRD standard for CD4 when compared to the 3rd day. However, it was observed that there was a significant decrease in the intensity of CaO peaks.

In the analysis corresponding to CD15, it was possible to observe peaks only for Ca(OH) and CaCO₃, with these being of low intensity if compared to CaO peaks presented by CD1. It is possible to affirm that much of the CaO structure ceases to be crystalline and becomes amorphous when it undergoes rehydration and carbonation.

3.4 Thermogravimetric study (TGA) of the catalyst

The TGA curves (Figure 3) indicate the thermal stability of the catalytic solids derived from the

Figure 3. Thermogravimetric curves of samples CD1, CD2, CD3, CD4, and CD15.

eggshells on different days after calcination.

Weight losses, which occur at temperatures around 400°C and 650°C, can be associated with the formation of Ca(OH)_2 and CaCO_3 , respectively (Bang et al., 2017). The thermal decomposition of CaO occurs at temperatures above 2800 °C (Landolt-Börnstein, 1999), far above the maximum temperature analyzed by the apparatus. The DC1 sample practically did not have any thermal decomposition events, meaning little formation of Ca(OH)_2 and CaCO_3 in the sample. In CD2, it was possible to observe the formation of two thermal decomposition events. First, between the temperatures 398.5 °C and 459.8 °C, with $\Delta m_1 = 14.8\%$, characterizing the release of H_2O from the sample. The second event happened between temperatures 557.1 °C and 676.9 °C, with $\Delta m_2 = 8.1\%$, characterizing the release of CO_2 from the sample.

Comparing the first thermal decomposition events between the analyzed samples CD2 to CD4

(Figure 3), it was possible to observe that there was almost no change in the mass variation between them, meaning that Ca(OH)_2 concentration remained practically stable. However, the thermal stability of the CD4 sample was much lower. This implies that there is a greater tendency to undergo the formation of a new compound.

The CD4 sample presented a mass loss (Δm_1) of 14.9% in the first thermal decomposition event, whereas the CD15 sample had a percentage of 6.2%. Comparing the results of the two samples, it was possible to observe that a decrease of the mass variation occurred in the first thermal decomposition event, characterizing the decrease of Ca(OH)_2 . However, there was a significant increase in mass loss between samples CD4 and CD15 ($\Delta m_2 = 13.3$ and 29.9%, respectively) in the second thermal decomposition event, characterizing a CaCO_3 increase. This behavior is attributed to the chemical reaction represented by Equation 3:

Table 2. Chemical composition of the catalytic solid sample on different days after calcination.

Analysis period	CaO	Ca(OH)_2	CaCO_3
Day 1 (CD1)	93.57%	4.157%	2.274%
Day 2 (CD2)	20.07%	61.52%	18.41%
Day 3 (CD3)	10.86%	62.77%	26.38%
Day 4 (CD4)	8.24%	61.52%	30.24%
Day 15 (CD15)	6.65%	25.36%	67.99%

The reaction shown in equation 3 is favorable thermodynamically, in the range of 25-746 °C. Its kinetics increased with high relative humidity of the air because of the catalytic effect of the water vapor (Nikulshina et al., 2006). The chemical reaction had a favorable environment to occur

since the experiments were carried out in Natal-RN Brazil, which has an average temperature of 25.8 °C and relative humidity of 80%.

The results of the chemical composition of the samples obtained from equations (3) and (4) are presented in Table 2, where it is possible to more clearly observe the percentage variation of CaO, Ca(OH)₂, and CaCO₃ concentration in each sample.

Figure 4. SEM calcined chicken eggshell a) CD1, b) CD2, c) CD3, d) CD4, and e) CD15.

Based on Table 2, one can observe that the decrease in CaO concentration occurs rapidly between samples CD1 and CD2, where much of this percentage is due to the hydroxide formation represented by the chemical equation:

However, the formation of CaCO_3 from the CO_2 absorption by CaO (carbonation) occurs more slowly.

3.5 Scanning Electron Microscopy (SEM)

SEM analyses were performed to compare the surface morphology of the calcined chicken eggshell samples on different days after calcination. The results in Figure 4a show the external structure of the chicken eggshell a few hours after calcination. The structure resembles a set of small stones of different shapes, smooth, without ends or edges as if they were embedded in each other, and organized in maze-like morphologies (Obermeier et al., 2017). According to TGA and XRD data, this structure is characteristic of CaO. But the surface structure of CaO depends on the calcination temperature of CaCO_3 (Kumagai et al., 2018). It was possible to observe the appearance of a rough-looking substance on the surface of the structure on the second day of analysis (sample CD2) (Figure 4b), which, according to the XRD and TGA data, is mostly Ca(OH)_2 obtained through moisture absorption. Figures 4c and 4d show that there is an increase in rough structure, while the catalyst sample has a completely rough structure in Figure 4e, depicting day 15. According to XRD data, the structure is formed mainly by CaCO_3 in amorphous form.

3.6 BET surface area

The N_2 absorption isotherms of the catalytic solid on different days after calcination are shown in Figure 5. All solid samples showed isotherms classified as type IV, with an H3 hysteresis loop, typical of mesopores containing solids (2-50 nm) (Sing et al., 1985). The presence of mesopores in the catalyst is very important when this catalyst is applied to the transesterification of triacyl glycerides. Large pores help the diffusion of the reagent into the solid to reach the active sites (Lima-Corrêa et al., 2018).

The surface area of a heterogeneous solid catalyst has a direct impact on its catalytic activity, as a larger surface area usually characterizes a larger basic region and strongly corresponds to a higher biodiesel yield (Roschat, 2008).

According to Table 3, one can observe that the surface area of the catalyst increased from the first day to the second day. However, the tendency in continuation is a reduction in the surface area from the second day after the calcination.

It is possible to affirm that, when the CaO begins to react with the humidity to form Ca(OH)_2 , the surface area and the pore volume increase. However, when the CaCO_3 formed by the reaction with CO_2 of the environment begins to become the major compound of the catalytic solid, its surface area begins to decrease. This result agrees with the work of Kouzu et al. (2017), which shows that the surface area size follows the same order: $\text{Ca(OH)}_2 > \text{CaO} > \text{CaCO}_3$.

The reduction in the surface areas of the oxide catalyst is not desired, since the catalytic process is a surface phenomenon and, in theory, the higher the surface area is, the higher the reactivity will

Table 3. Surface area and pore volume of the catalyst on different days from the calcination.

Sample	Surface Area ($\text{m}^2 \text{g}^{-1}$)	Volume of pores ($\text{m}^3 \text{g}^{-1}$)
CD1	11.08	0.0486
CD2	19.85	0.0801
CD3	11.91	0.0598
CD4	10.92	0.0528
CD15	06.08	0.0406

Figure 5. N₂ absorption isotherms of the catalyst in samples CD1, CD2, CD3, CD4, and CD15.

be. However, the activity also depends on the presence of the active sites on the surface (Lima-Corrêa et al., 2018), which can be estimated through basic force.

3.7 Basic force

The study of basicity strength in this research was performed by the Hammett method. The results obtained between samples CD1, CD2, CD3, and CD4 showed a color change in the phenolphthalein and indium carmine indicators, but did not show a color change in the 4-nitroaniline indicator showing that the basic forces of these samples are between $12.2 < H_- < 18.4$ (Table 4). The basic force for the CD15 sample was

between $9.8 < H_- < 12.2$, showing only the color change of phenolphthalein.

Thus, it is possible to affirm that the samples do not qualitatively present a significant variation of basic force, even though they lead a significant change in the chemical, morphological and structural composition of the catalytic solid. According to the definition of Tanabe (1985), these samples of solid catalysts can be considered as a strong base.

The total basicity result decreased considerably with the aging of the catalytic solid, ranging from 2.81 mmol g^{-1} on the first day to 0.86 mmol g^{-1} on the 15th day. In comparing the basicity results of the CD15 sample with other results of the

Table 4. Basic strength and total basicity after different days of calcination.

Sample	Basic strength (H_-)	Total basicity (mmol g^{-1})
CD1	$12.2 < H_- < 18.4$	2.81
CD2	$12.2 < H_- < 18.4$	2.64
CD3	$12.2 < H_- < 18.4$	2.48
CD4	$12.2 < H_- < 18.4$	2.29
CD15	$9.8 < H_- < 12.2$	0.86

Figure 6. Thermogravimetric curves of the biodiesel samples catalyzed by chicken eggshells after different days of calcination.

literature (Chen et al., 2015; Esipovicha et al., 2014), we can conclude that 0.86 mmol g^{-1} is also characteristic of a catalytic solid, which shows a good performance, with yields above 55%, depending on the applied methodology.

3.8 Thermogravimetric study (TGA) of biodiesel

The study of the biodiesel samples catalyzed by the chicken eggshell on different days after the calcination was performed from the catalyst aged at 1, 2, 3, 4, and 15 days. However, the transesterification reaction on day 3 presented errors in the experimental procedure, which led us to discard the sample even before the end of the reaction for the stipulated time. Thus, the thermal stability study of the thermogravimetric curves was performed only for BCD1, BCD2, BCD4, and BCD15 samples (Figure 6). These samples exhibited two thermal decomposition events, with the first at about 120°C to 250°C , and the second at about 250°C to 500°C . Figure 6 also shows there are no significant differences between the curves for the temperatures of thermal decomposition events.

Thermogravimetry also provides relevant information for converting oil into biodiesel, since

the triacylglycerides decompose at much higher temperatures compared to fatty acid alkyl esters which tend to volatilize and decompose at lower temperatures (Sadrolhosseini et al., 2011).

The first thermal decomposition event is attributed to the biodiesel concentration present in the sample, since the concentration of the second thermal event is attributed to the remaining soybean oil in the transesterification reaction. This difference in the temperature of decomposition events occurs because the average molar mass of triacyl glyceride compounds is higher than that of the aquil ester that makes up the biodiesel, significantly increasing the forces of intermolecular interactions (Sousa et al., 2013).

By comparing thermogravimetric curves between the BCD1 and BCD15 samples, it is possible to observe that the mass variation of the first thermal decomposition event of the BCD15 sample is somewhat less than the result of the BCD1 sample, which showed temperature variations between 114.0°C and 251.6°C with $\Delta m_1 = 91.79\%$ for the BCD1 sample; and 111.1°C at 249.9°C with $\Delta m_1 = 87.62\%$ for the BCD15 sample. Thus, results indicate that the biodiesel concentration in the different samples practically

Figure 7. Chromatogram of BCD1, BCD2, BCD4, and BCD15 samples.

did not vary with the use of the calcined solid catalysts in intervals of different days with different CaO , Ca(OH)_2 , and CaCO_3 concentrations.

To confirm the results of the conversion tendency presented by thermogravimetry, it is necessary to perform a gas chromatography analysis, which is the most common technique used to analyze the alkyl ester concentration of fatty acids in a sample after transesterification.

3.9 Gas chromatography (GC)

The biodiesel obtained in the transesterification reaction has the following fatty acids: oleic, linoleic, linolenic, palmitic, and stearic (Figure 7), which are predominant in the composition of soybean oil and unsaturated fatty acids. These types of fatty acids are quite susceptible to oxidation, since unsaturation acts as an entry point for oxygen action (Farias et al., 2016).

The BCD1 sample presented the highest yield (91.89%), however, the percentage values for the yield of the BCD15 sample (85.48%) were very similar to that of BCD1, indicating that there was

no significant change in the catalytic capacity of the eggshells calcined on different days of aging, although there were significant changes in the chemical composition of this catalytic solid. According to TG results, CD1 contained a little over 2% CaCO_3 , with approximately 68% remaining on the 15th day after calcination (CD15).

The yields of the BCD1 and BCD15 samples were somewhat below the yields of calcined eggshells catalyzed biodiesel presented in the literature (Kouzu & Hidaka, 2012; Mansir et al., 2018; Boey et al., 2011; Catarino et al., 2017).

Kouzu and colleagues studied the catalytic capacity of CaO , Ca(OH)_2 , and CaCO_3 in the transesterification reaction of soybean oil with methanol. The results found by the group show that CaO yielded 93% ester yield in an hour of reaction (Figure 8). However, Ca(OH)_2 and CaCO_3 obtained only 12% and 0%, respectively (Kouzu et al., 2008). Comparing the results of Kouzu with this work, it is possible to state that the order of the catalytic capacity between the solids for the transesterification reaction are the same in both

Figure 8. Transesterification reaction kinetics of the results obtained by Kouzu et al. (2008) and Arzamendi et al. (2008) in comparison to the results obtained by BCD1 and BCD15 samples.

works ($\text{CaO} > \text{Ca(OH)}_2 > \text{CaCO}_3$). But the catalytic capacity in relation to the percentage values of ester content formed show a discrepancy with respect to Ca(OH)_2 and CaCO_3 solids. For this work, CaO absorbs moisture and CO_2 from the environment, and its chemical composition changes to Ca(OH)_2 and CaCO_3 . This change in the chemical composition of the solid leads to a small decrease in catalytic capacity, different from the results suggested in the study by Kouzu. However, it is worth mentioning that the experimental procedures employed in this work were quite different, both for obtaining the catalytic solids (CaO , Ca(OH)_2 , and CaCO_3); and for the transesterification reaction.

Arzamendi et al. (2008) also compared the catalytic activity of these solids. They achieved a yield above 60% for commercial Ca(OH)_2 using 1% of the sample with a reaction time of 24 hours. However, they were unable to obtain an ester content greater than 10% when they used reaction times equal to or less than 7 hours.

Kouzu et al. (2008) obtained CaCO_3 from

pulverized limestone and Ca(OH)_2 was prepared by hydration of CaO in a gas flow of moist helium. As previously mentioned, these calcium solid base catalysts were used for the transesterification of edible soybean oil with methanol. Arzamendi et al. (2008) used commercial CaCO_3 and Ca(OH)_2 for the transesterification reaction of refined sunflower oil with methanol. Both studies showed low ester conversions for these catalysts. However, Reyero (2015) carried out a catalytic study with CaO aged for 30 days after calcining chicken eggshells (enough time for the CaCO_3 concentration to be higher and CaO to be lower). The author obtained a yield of 65% ester in a transesterification reaction of sunflower oil performed at 60 °C, a 12:1 molar ratio of methanol/oil, 2% catalyst, and a time of 400 minutes. These results demonstrate that the catalytic capacity of CaCO_3 and Ca(OH)_2 are significantly higher when formed from rehydration and spontaneous carbonation through the atmosphere. This assertion can be confirmed from the basic force and surface area results, which present characteristic results for good catalysts for all solid samples.

Figure 9. XRD of CD15 and CD15 mixed with methanol samples.

The second reason for the poor variation in catalytic capacity loss with aging time of the solid sample after calcination is related to the process. Before starting the transesterification reaction, initial mixture between the catalytic solid and the methanol was initially performed for a period of 20 minutes. This initial mixture before transesterification caused a reaction of the CaO with methanol, thus, forming $\text{Ca}(\text{OCH}_3)_2$, which exhibits greater catalytic activity than CaO .

$\text{Ca}(\text{OCH}_3)_2$ formation was confirmed in Figure 9, which shows XRD patterns of CD15 samples and the product of the mixture between CD15 and methanol. The mixture between CD15 and methanol was carried out under the same conditions as the experimental procedure presented in the first paragraph of section 2.3. XRD patterns of the mixture result showed diffraction peaks in 10.7° , 28.6° , and 50.9° , which correspond to $\text{Ca}(\text{OCH}_3)_2$ (JCPDS n° 00-020-1565) (Theam et al., 2015).

Comparing XRD standards of CD15 and CD15 + methanol samples, one can note that CD15 presents the compound CaCO_3 in crystalline state. By mixing the CD15 sample with methanol, the formation of the $\text{Ca}(\text{OCH}_3)_2$ compound occurred in

the crystalline phase and the characteristic peaks of $\text{Ca}(\text{OH})_2$ decreased, especially for CaCO_3 .

The $\text{Ca}(\text{OCH}_3)_2$ obtained interacted with the oil to produce esters and glycerin as by-products. Thereafter, the oil was transesterified by $\text{Ca}(\text{OCH}_3)_2$ to produce esters and glycerin as byproducts. The produced glycerin reacted with CaO to form a CaO -glycerin complex. As this CaO -glycerin complex also exhibited high catalytic activity, the reaction continued generating more glycerin. This process is called CaO activation, it repeats and accelerates the transesterification reaction even further (Kawashima et al., 2009). Another important factor is that methanol is effective in removing CaCO_3 and $\text{Ca}(\text{OH})_2$ formed on the surface of the catalyst after aging (Reyero, 2015), allowing this initial mixing process of the catalytic solid and methane to recover most of the intrinsic catalytic activity developed by the newly calcined samples.

4. CONCLUSIONS

The results of this work demonstrate that the catalytic solid employed in this research consists of

99% CaO. This solid quickly reacts with the ambient humidity forming Ca(OH)_2 , and more slowly with CO_2 forming CaCO_3 . The processes described above are referred to as rehydration and carbonation, respectively.

When the catalytic solid enters rehydration and carbonation processes, its structure changes from the crystalline phase to amorphous, but it also acquires a rough morphology. Its surface area increases in the formation of Ca(OH)_2 , and decreases as CaCO_3 becomes the major compound.

In all samples, the total basicity results were higher than 0.8 and the basic force were higher than 9.8, characterizing a strong base. The presence of active sites on the surface justifies the little decrease in catalytic activity of the solid 15 days after calcination.

Another aspect that justifies this result is the premix carried out between the methanol and the catalytic solid, which formed $\text{Ca(OCH}_3)_2$, a compound that presents more catalytic characteristics than CaO and leads to a process called CaO activation. Also, the presence of methanol promotes the removal of CaCO_3 and Ca(OH)_2 formed on the catalyst surface after aging.

Thus, it is possible to affirm that rehydration and carbonation processes alter the chemical, morphological, and structural composition of the catalytic solid, but such changes do not affect catalytic capacity as much, especially when the experimental procedure for transesterification reaction is initiated with mixture between methanol and CaO.

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