Franciele Bonatto
Jair de Oliveira
João Dallamuta
(Organizadores)

Ciência, Tecnologia e Inovação

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APRESENTAÇÃO

Há quase quarenta anos, Alvim Toffler em seu Best Seller, The Third Wave, profetizou; “Pode-se criar mais valor com uma ideia em dez segundos do que com dez mil horas em uma linha de produção”. Esta talvez seja a melhor definição de inovação, não exatamente do conceito, mas do que ela efetivamente gera como efeito nas organizações e na sociedade.

Ciência, tecnologia e ambiente, considerando neste último fatores econômicos, sociais e legais, são base para a inovação. No que no que concerne a nossos pesquisadores, eles tem feito a parte deles, produzido ciência e tecnologia a despeito das dificuldades econômicas e culturais no Brasil. Há muito que melhorar sim, mas também a muito há se reconhecer.

Esse livro apresenta dois pilares de inovação, ciência e tecnologia, em uma reunião de vinte e quatro artigos, que são o resultado de pesquisas realizadas nos mais diversos setores com uma riqueza de metodologias e resultados.

Nesta obra, temos a oportunidade de leitura é fruto de trabalhos científicos de diversos pesquisadores. Aos pesquisadores, editores e aos leitores para quem em última análise todo o trabalho é realizado, agradecemos imensamente pela oportunidade de organizar tal obra.

Boa leitura!

Franciele Bonatto

Jair de Oliveira

João Dallamuta

SUMÁRIO

CAPÍTULO 21

EVALUATION OF HETEROGENEOUS CATALYSTS DERIVED FROM WHITE AND BROWN CHICKEN EGGSHELL FOR SOYBEAN BIODIESEL SYNTHESIS

Diego Oliveira Cordeiro
Federal University of Rio Grande do Norte (UFRN), Department of Chemistry Engineering, Campus I, Natal – RN

Mário Hermes Moura Neto
Federal University of Rio Grande do Norte (UFRN), Department of Chemistry Engineering, Campus I, Natal – RN

Marta Maria da Conceição
Federal University of Paraíba (UFPB), Center for Technology and Regional Development, João Pessoa - PB

Luis Ferreira de Lima
Federal University of Rio Grande do Norte (UFRN), Department of Chemistry Engineering, Campus I, Natal – RN

Janduir Egito da Silva
Federal University of Rio Grande do Norte (UFRN), Department of Chemistry Engineering, Campus I, Natal – RN

Eduardo Lins Barros Neto
Federal University of Rio Grande do Norte (UFRN), Department of Chemistry Engineering, Campus I, Natal – RN

SUMMARY: Calcium oxide may be considered as a very promising heterogeneous catalyst for the biodiesel production, for it has high efficiency and it is environmentally friendly. CaO can be obtained in a sustainable manner by the calcination of the chicken eggshell, since this material is rich in calcium carbonate. Although there are clear differences between types of chicken eggs, published research on the subject does not distinguish between white and brown eggshells. Thus, the objective of this work was to analyze and compare the properties and characteristics of the heterogeneous catalysts derived from the white and brown eggshell obtained in different calcination conditions, as well as to evaluate the catalytic capacity of these catalysts to produce soybean biodiesel. The different raw materials were calcined by varying the time parameters: 80, 120, 160 minutes, and temperature 800, 900 and 1000 °C. The analysis techniques were DRX, FRX, BET and MEV granulometry. Thermal analysis (TGA/DTA) was also used to determine the conversion to biodiesel. Among the catalysts derived from the shell of the chicken egg, the white shell calcined at 800 °C in 160 minutes showed a higher catalytic potential.

KEYWORDS: Biodiesel, Heterogeneous catalysis, eggshell, thermogravimetric analysis.

1 | INTRODUCTION

Over the last few years, environmental pollution and fossil fuel scarcity have been widely reported, and research on alternative fuels has received much attention (Qu et al.,

2017). Biodiesel is one of these alternative fuels, which due to its physical and chemical similarity with diesel can replace it in diesel cycle engines (Winden et al., 2015). It can be defined as fuel alkyl esters of simple fatty acids, usually methyl or ethyl (Kok e Topa, 2015). This biofuel is usually obtained by the transesterification reaction of vegetable or animal oil using a short chain alcohol in the presence of an acid, base or enzymatic catalyst (Escorsim et al., 2015). Brazil has been highlighted in the world scenario as a potential biodiesel producer, due to its diversity of oilseeds (Silva et al., 2015). One of the main oilseeds used in the production of biodiesel is soybeans, which covers about 50% of the biodiesel produced in the world (Park et al., 2016).

Homogeneous catalysis, with NaOH and HCl, is widely used for biodiesel production due to its high reaction activity. However, they cause a number of problems, such as the difficulty in separating biodiesel and alcoholic phase, it needs washing and it generates effluents (Sandesh et al., 2016). In order to overcome these problems, heterogeneous catalysts have been developed, since they have an easy separation of the biodiesel after the reaction ending, besides generating biodiesel and glycerin with higher degrees of purity (Degirmenbasi et al., 2015).

Heterogeneous catalysts such as alkaline earth metal oxides, zeolites, oxides and inorganic salts, coordination compounds and ionic liquids, ion exchanging resins, organic acids, bases and lamellar materials, structured oxides originated from controlled calcination (Cordeiro et al., 2011). Have been developed. Among them, a catalyst that stands out is calcium oxide (CaO) due to its high basicity, low solubility and ease of handling (Sheng et al., 2014) Studies have been developed about the acquisition of CaO from calcination of the $CaCO_3$ present in eggshells (85-95%) for application in transesterification (Yin et al., 2016; Tan et al., 2015; Jazie et al., 2013).

Despite the large number of articles referring to heterogeneous catalysts derived from chicken eggshell, no studies were found in the literature to study the differences in the properties and characteristics of the calcined catalysts of the white and brown eggshells, thus treating the catalytic capacity of the chicken eggshell calcined generically, without distinction between white and brown shells.

Therefore, the objective of this work was to analyze and compare the properties and characteristics of the heterogeneous catalysts derived from the white and brown eggshell obtained in different calcination conditions, as well as to evaluate the catalytic capacity of these catalysts to produce soybean biodiesel.

2 I MATERIAL AND METHOD

2.1 Raw Material

For transesterification reaction Concordia ® commercial soybean oil was used, lot: LR00472, Neon brand methyl alcohol BP, lot: 17068. The brown and white eggshells

obtained from Granja Santa Clara located in the city of Cuité-PB. Also, it was used calcium oxide derived from the Vetec® brand calcium carbonate PA, lot: 1107378.

2.2 Heterogeneous Catalysts Acquisition

The eggshells of the white and brown eggs were placed separately in a vessel with distilled water for 4 hours, and then washed with running water followed by distilled water to ensure removal of any residue that did not constitute the shell of the egg. They were then placed in a greenhouse at 70 °C for a period of 12 hours and macerated to facilitate calcination.

Samples of white and brown egg shell and $CaCO_3$ were calcined under different temperature conditions (800 °C, 900 °C and 1000 °C) and time (80, 120 and 160 minutes) over a heating rate of 5 °C/min. The calcination conditions were based on review articles of CaO with catalyst for transesterification reaction (Boey et al., 2011).

To facilitate the identification of samples, a nomenclature was created in three parts, the first part being the type of calcined material, white eggshell (CB), brown egg shell (CM), Commercial $CaCO_3$ (CI). Following the indication of the calcination temperature, 800 °C (8), 900 °C (9) and 1000 °C (10), and finally the indication of the calcination time, 80 minutes (P8), 120 minutes (P12) and 160 minutes (P16) (Table 1).

	Brown eggshell			White eggshell			Commercial $CaCO_3$		
	800°C	900°C	1000°C	800°C	800°C	1000°C	800°C	800°C	1000°C
80 min.	CM8P8	CM9P8	CM10P8	CB8P8	CB9P8	CB10P8	CI8P8	CI9P8	CI10P8
120 min.	CM8P12	CM9P12	CM10P12	CB8P12	CB9P12	CB10P12	CI8P12	CI9P12	CI10P12
160 min.	CM8P16	CM9P16	CM10P16	CB8P16	CB9P16	CB10P16	CI8P16	CI9P16	CI10P16

Table 1 - Catalysts produced under different conditions.

2.3 Biodiesel synthesis

The biodiesel synthesis was carried out through the methyl route at 1:12 molar ratio, oil/methanol and 6% heterogeneous catalyst (CaO). 1.2 grams of CaO and 12.2 mL of methanol were added to the batch reactor, subjected to 300 rpm stirring for a period of 20 minutes at room temperature. Then, 22.2 mL of soybean oil was added to the mixture, adjusting the stirring to 600 rpm and the thermostated bath at 65 °C. The system was subjected to reflux condensation to ensure that no evaporation of the alcohol occurred during the process. The reaction was controlled for a period of 3 hours (Chen et at., 2015).

After the reaction was completed, the mixture was placed in test tubes and

centrifuged at 1500 rpm for 20 minutes to ensure separation of the catalyst from the liquid phases. The process was completed in the decanting funnel for a period of 24 hours, with the biodiesel being the supernatant phase and the glycerin-decanted phase.

After separation of the glycerin and biodiesel phases, the latter still underwent a quantitative filter vacuum filtration to ensure that no catalyst residue interfered with the biodiesel analysis.

2.4 Characterizations

The basic composition of the catalysts was determined by FRX using a Shimadzu apparatus, model EDX-700. FRX analyzes were performed using 300 mg of samples CM8P12, CB8P12 and CI8P12.

The granulometric analysis was performed in a sieve model 920, of the Cilas brand without the use of dispersants. The surface area of the catalysts were measured by N2 adsorption performed by the Micromeritics brand equipment, at the temperature of the analysis bath of -194.30 °C, at an equilibrium interval of 30 seconds. The heat treatment took place in a heating stage under a ramp of 10 °C/min, up to 300 °C for a period of 480 min.

X-ray diffraction analyzes were performed using a Bruker ADVANCE eco D8 device, copper anode and nickel detector filter. Measurements were completed in the 2θ range from 10 ° to 90 ° with a scan rate of 0.2 °/s.

SEM images were obtained from the Hitachi Microscope, Model Tabletop Microscope TM-3000, Accelerating voltage: 5kV and 15kV, using a zoom of 4000 thousand times for each sample.

Ester determination was performed by gas chromatography on a Shimadzu GCM-QP2010 chromatograph, Durabond DB-23 column (30 m x 0.25 mm x 0.25 lm). The temperature of the injector and the detector, 230 °C and the column, 90 °C. Elution gradients were 90 °C to 150 °C (10 °C/min); 150-200 °C (2 °C/min); and 200-230°C (10 °C/min) at a time of 0.65 h. The carrier gas was helium. The external calibration curve was performed with the chromatographic patterns of fatty acid monoesters. Quantification was obtained by calibration curves with methyl esters standards (adapted ABNT NBR 15764).

The thermogravimetric analyzes of the biodiesel and soybean oil samples was performed using the Shimadzu brand DTG-60 thermal analyzer, with a heating rate of 10 ºC/min, in the ambient temperature range up to 550 ºC in a nitrogen atmosphere with a flow of 100 mL/min, alumina crucible. Analyzes were performed using an average of 5 mg of the sample. Thermogravimetric analyzes of the white eggshell, brown eggshell and commercial $CaCO_3$ were performed, under a heating rate of 5 °C/min, in the temperature range of 100 °C to 900 °C. The concentration of $CaCO_3$ in the sample analyzed in thermogravimetry, C_{CaCO3}, can be determined by the mass loss,

Δm, of CO_2 measured in the last thermal decomposition event and the relationship between the molecular masses of calcium carbonate, MM_{CaCO3}, and carbon dioxide, MM_{CO2}, through Equation 1:

$$C_{CaCO3} = \square m \frac{MM_{CaCO3}}{MM_{CO2}} \qquad \text{Equation (1)}$$

Only the thermogravimetric analyzes (TGA and DTG) were performed with all 27 biodiesel samples characterized by the different types of catalysts. CM8P12, CI8P12 and CB8P12 samples were selected for the remainder analyzes, since they presented the same characteristics in the calcination (temperature of 800°C and temp of 120 minute). The sample CB8P16, because it has the highest conversion among biodiesel catalyzed by a material obtained through eggshell, CI10P12, because it has the highest conversion rate among all of the biodiesel samples, and CM8P8 because it has as characteristic being the catalyzed biodiesel obtained in the shortest calcination time.

3 I RESULTS AND DISCUSSIONS

3.1 Catalyst Analyses

3.1.1 Thermogravimetry

The thermal analysis curves TGA (figure 1) indicate the thermal stability of the three raw materials used in calcination. Commercial calcium carbonate ($CaCO_3$) was the only raw material that presented only a single thermal decomposition event in a defined way, between the temperature ranges 552-738 °C, with mass loss Δm = 43.68%, due to the release of carbon dioxide. Thus, according to equation 1, the amount of calcium carbonate present in the sample is 99.32%.

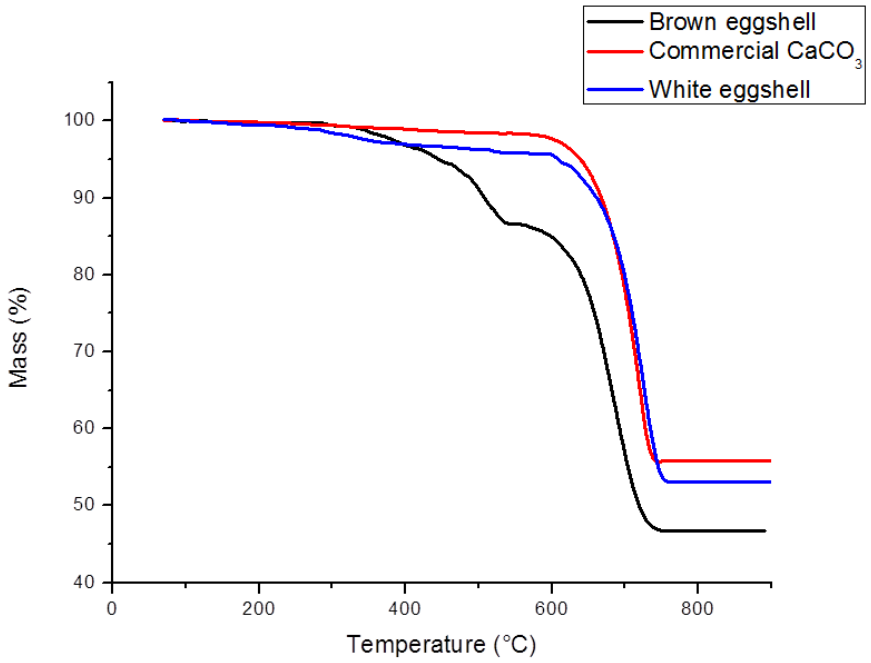

Figure 1 - Thermogravimetric curve derived from the decomposition: Brown and white eggshells and $CaCO_3$.

The TGA curves of the white and brown eggshells presented two thermal decomposition events. As for the white egg shell the temperature ranges are 233-534 °C with Δm_1 = 3.83% due to the decomposition of organic materials (Pereira et al., 2009) and 534-757 °C with Δm_2 = 43.20% corresponding to the release of carbon dioxide, resulting in 98.23% of calcium carbonate. In the case of brown eggshell, the first thermal decomposition event is 221-540 °C with Δm_1 = 16.29%, showing a more significant content of organic material, such as protoporphyrin, a compound responsible for the brown pigmentation of eggshell (Pandit et al., 2017). The second thermal decomposition event occurred between 534-757 °C with Δm_2= 39,81%, corresponding to 90,53% calcium carbonate, 7,8% less than the amount of $CaCO_3$ present in the white eggshell.

3.2 X-Ray Fluorescence (XRF)

The results of the X-ray fluorescence spectra are shown in Table 2, where the calcium oxide has a 99.9% degree of purity, when obtained from the calcination of calcium carbonate. The white eggshell presented 99.57% calcium oxide, with presence of 0.2% of strontium oxide and magnesium. In the case of the brown eggshell, the determined CaO content reaches 97.15%, containing a much more significant percentage of strontium oxide, 1.23%, besides containing magnesium oxide (MgO) and silicon dioxide (SiO_2) and sulfur trioxide (SO_3). A similar result was presented by Boronat et al (2015) in which they obtained 97.68% of CaO in the total composition, having magnesium oxide as the secondary composition. Similar results were also

obtained by Kamkum et al (2015).

Oxides	Brown egg-shell	White egg-shell	Commercial $CaCO_3$
CaO	97.148 %	99.573 %	99.901 %
SO_3	0.194 %	-	0.099 %
MgO	1.248 %	0.236 %	-
SrO	1.227 %	0.191 %	-
SiO_2	0.83 %	-	-

Table 2 - Chemical composition of the oxides formed by the calcination of the white eggshell, brown eggshell and commercial $CaCO_3$.

3.1.3 Granulometry and BET

According to the table 3, we can affirm that there is a tendency of increase in the average grain size of the catalyst with the increase of the temperature and the calcination time. The CB8P12 sample was produced with the calcination time 40 minutes lower than the CB8P16 sample. On the other hand, in the production of the CI8P12 sample, the calcination occurred at the same time as the CI10P12 sample (120 minutes), but with a temperature of 200 ° C less. This increase in the mean particle size, in relation to the increase in time and temperature in the calcination, was expected because, according to the literature, granulometry is strongly influenced by the calcination temperature (Goivêa et al., 2017).

Sample	Average diameter (µm)	Surface area BET (m^2/g)	Pore volume (mm^3/g)	Average pore size (nm)
CB8P12	17.03	21.9148	62.222	11.38
CB8P16	21.03	30.7005	78.665	10.24
CM8P8	13.55	4.4996	21.679	19.28
CM8P12	21.24	14.3713	46.430	12.79
CI8P12	9.13	23.9475	79.177	13.26
CI10P12	17.84	52.7150	108.801	8.361

Table 3 - Average diameter and surface area BET of the attained catalyzers.

The surface area of the CaO samples was determined by the Brunauer-Emmett-Teller (BET) method. The catalysts present similar isothermal forms, classified as type IV, with an H3 hysteresis loop, typical of mesopore-containing solids (2-50 nm) (Sing et al., 1985). Table 3 shows a significant variation between the surface area results,

mainly between samples CM8P8 and CI10P12, which presented the surface area value of 4.4996 m²/g and 52.7150 m²/g respectively. The greater the surface area of a catalytic solid, the greater the dispersion of the active sites, thus promoting a more efficient transesterification (Sudsakorn et al., 2017). Therefore, according to the result of the BET surface area, the catalyst CI10P12 has a higher catalytic potential in relation to the other samples. For the samples obtained from the eggshell, the CB8P16 catalyst presented the best result.

3.1.4 X-ray Diffraction

X-ray diffraction analyzes (Figure 2) showed that the patterns of the six catalyst samples analyzed showed little variation between their crystalline structures. Despite the low variation, the results of the calcined samples of white eggshell presented more similarities with calcined $CaCO_3$ than the samples derived from brown eggshell.

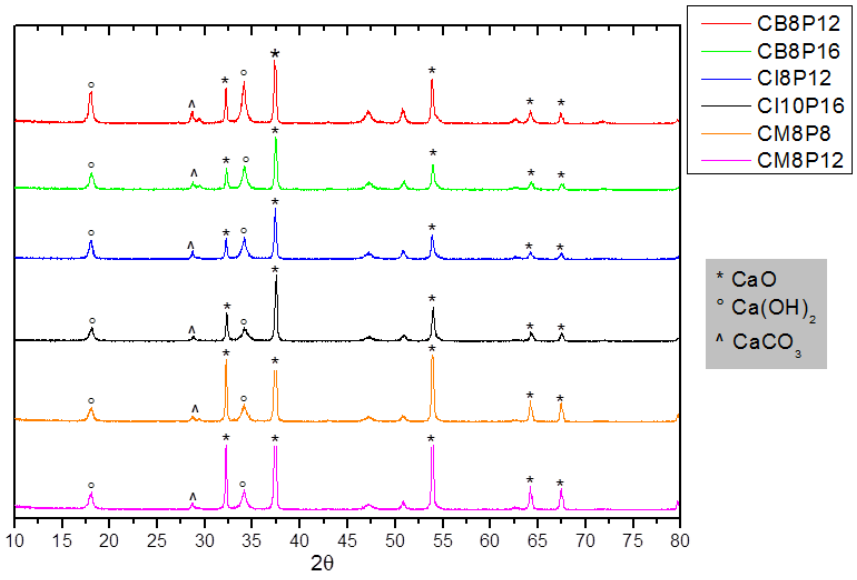

Figure 2 - XRD analysis of the samples: CB8P12, CB8P16, CI8P12, CI10P12, CM8P8 and CM8P12.

The XRD patterns show diffraction peaks at 32.19 °, 37.35 °, 53.84 °, 67.34 °, 67.55 ° and 80.88 ° corresponds to face-centered cubic phase calcium oxide (JCPDS : 4-777) with space group *Fm*-3 *m* .Showing that the calcination was successful for CaO formation. Also two less intense peaks at 17.93 ° and 34.12 ° correspond to the calcium hydroxide ($Ca(OH)_2$) of the hexagonal phase (JCPDS: 01-086-0174), attributed to the absorption of moisture from the air.And the diffraction peaks at 29,39 ° that characterize the calcium carbonate ($CaCO_3$) belongs to the rhombohedral phase (JCPDS nº 01-086-0174), and can be attributed to carbonation through the absorption of the CO_2 present in the atmosphere or calcination incomplete (Nagbhushana et al., 2017).

3.1.5 Scanning electron microscopy

As shown in figure 3, samples CB8P12, CB8P16 and CM8P12, presented an aggregate of nanoparticles in size and shape irregular. Being the predominant spheroid oval shape. It was also possible to observe similar results in the mean granulometry for these samples (table 3). However, the two samples of CaO obtained by industrial calcium carbonate presented a different morphology of the catalysts derived from chicken eggs.

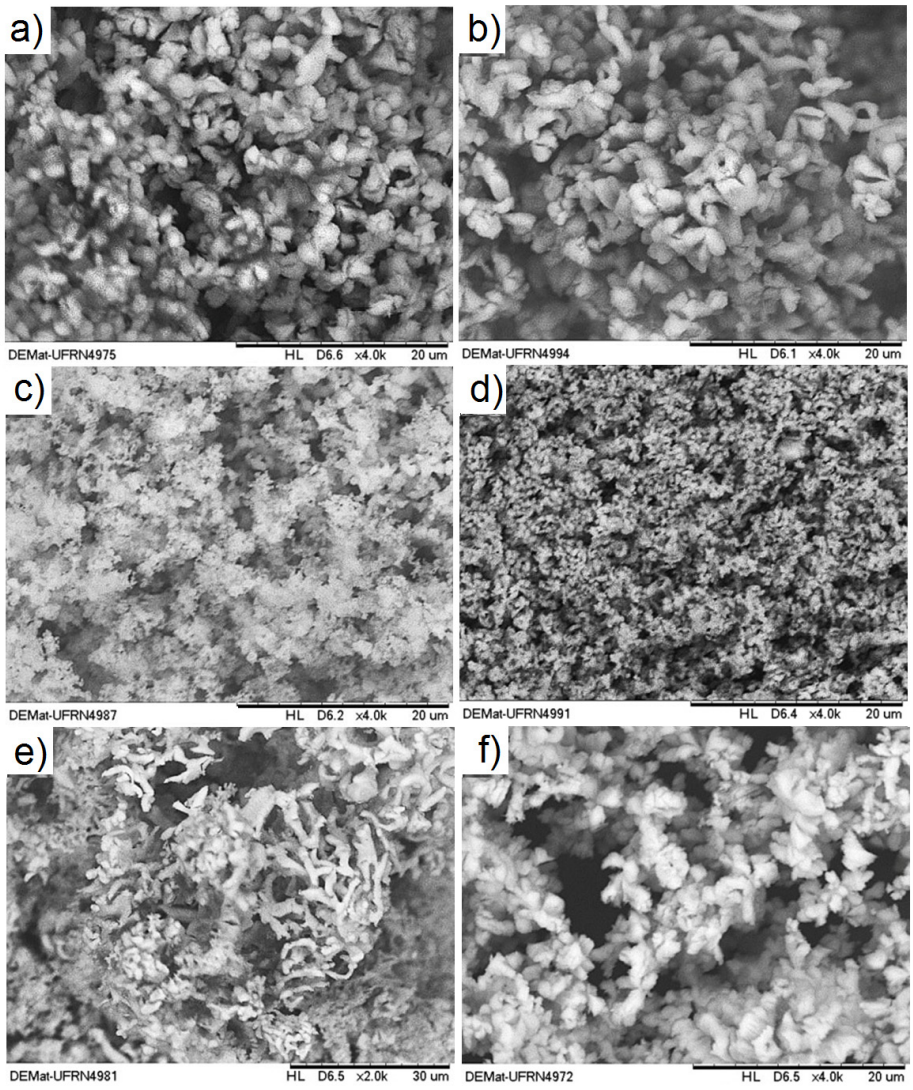

Figure 3 - Calcined catalyzers' image: a) CB8P12, b) CB8P16, c) CI8P12, d) CI10P12, e) CM8P8 e f) CM8P12.

3.3 Biodiesel Analyses

3.3.1 Gas Chromatography

The results of gas chromatography (Table 4) indicate that the soybean oil used to make the transesterification reaction are predominant constituted unsaturated fatty

acids (oleic, linoleic and linolenic) These types of fatty acids are quite susceptible to oxidation, since instauration acts as an entry point for oxygen action (Farias et al., 2016). Linoleic acid is the most abundant of the five different types of fatty acids present in the composition of soybean biodiesel, ranging from 47.39% to 39.54% depending on the conversion of the oil to biodiesel.

Ethyl esters	CB8P12 (%)	CB8P16 (%)	CM8P16 (%)	CI8P12 (%)	CI10P12 (%)
Palmitic acid	23.92	24.53	23.91	21.73	27.00
Stearic acid	43.77	47.39	46.04	42.22	39.54
Oleic acid	3.66	3.90	3.59	3.09	2.17
Linoleic acid	16.14	16.90	16.31	13.44	24.17
Linolenic acid	3.18	3.08	3.06	2.85	4.06
Total	91.67	96.80	93.91	84.33	97.94

Table 4 - Composition of the fatty acids present in biodiesel from soybean oil, obtained with the catalysts studied in this work.

The results of the chromatographic analysis showed that the catalysts studied have reached ester contents close to the Brazilian specifications of the ANP (National Agency of Natural Gas and Biofuels) technical regulation 3/2014 the biodiesel must present a ester contents higher than 96.5%. The chromatographic analysis of the CM8P8 biodiesel was not done, because it presented low conversion visual characteristics, and the result was confirmed in TGA.

3.2.2 Thermogravimetry of biodiesel and soybean oil.

The thermogravimetry provides relevant information for the conversion of the oil to biodiesel, since the triglycerides have greater thermal stability, that is, it decomposes at temperatures higher than that of fatty acid alkyl ester (Sadrolhosseini et al., 2011). TGA analyzes of all biodiesel samples are presented in Tables 5, 6 and 7.

Sample	1st event			2nd event	
	Initial temperature/ °C	Final temperature/ °C	Mass loss (%)	Initial temperature/ °C	Final temperature/ °C
CM8P8	124.14	278.38	58.10	249.32	486.68
CM9P8	123.92	263.21	44.20	263.21	504.10
CM10P8	117.11	251.59	33.34	251.59	501.87
CM8P12	117.52	249.32	93.54	278.38	499.37
CM9P12	122.63	241.73	90.89	241.73	497.69
CM10P12	115.70	240.64	82.41	240.64	501.46
CM8P16	116.51	235.17	89.1	235.17	501.30
CM9P16	118.09	241.41	90.84	241.41	496.30
CM10P16	113.87	243.69	78.85	243.69	499.74

Table 5 - Thermogravimetric data of soybean biodiesel synthesized by heterogeneous catalysis derived from brown eggshell.

According to the thermogravimetric data of the biodiesel synthesized by the catalysts, obtained by the calcination of the brown egg shell, shown in table 5, it is possible to state that all the samples have two decomposition events. The first decomposition event occurred between temperatures ranging from 113.87 to 278.38 °C. This first thermal decomposition event corresponds to the mass of the evaporated biodiesel. In the second event, temperatures ranged from 235.17 to 504.1 °C, which corresponds to the thermal decomposition of soybean oil. This difference allows the degree of conversion of oil to biodiesel to be efficiently determined (Lizama et al., 2015). Therefore, based on Table 4, the biodiesel sample that presented the greatest conversion, for the catalysts coming from brown eggshell, was CM8P12 with 93.54 % conversion. Very close to the result given by gas chromatography 93.91% (table 4)

It can be observed in the results presented by the catalyst of the brown egg shell (table 5), that the increase of the calcination temperature worsens the conversion of the oil to biodiesel. Excessive raising of the calcination temperature during CaO production may result in a decrease in its catalytic capacity and consequently a decrease in biodiesel conversion. This may be due to gaseous diffusion of the pores during the heat treatment resulting in the limitation of the surface pores (Kouzu e Hidaka, 2012). However, there is a tendency of the greater the calcination time the greater the conversion. This trend is very evident in the results of the biodiesel samples catalyzed by the calcined eggshell in 80 minutes. All three biodiesels (CM8P8, CM9P8 and CM10P8) had conversions below 60%.

The thermogravimetric data of Table 6 show that the thermal decomposition of the synthesized biodiesel from the white eggshell also occurred in two events. The first

decomposition event occurred between temperatures of 112 to 297 °C. In the second between the temperatures of 232 and 501 °C.

Sample	1st event			2nd event	
	Initial temperature/ °C	Final temperature/ °C	Mass loss (%)	Initial temperature/ °C	Final temperature/ °C
CB8P8	112.37	249.70	31.73	249.70	500.71
CB9P8	122.28	262.18	33.02	262.18	500.94
CB10P8	125.15	258.67	14.88	258.67	494.75
CB8P12	121.91	259.62	95.35	259.62	497.55
CB9P12	119.81	251.39	89.98	251.39	500.60
CB10P12	113.21	243.63	88.91	243.63	492.60
CB8P16	120.65	232.56	97.11	232.56	497.94
CB9P16	126.58	297.13	91.72	297.13	494.49
CB10P16	118.78	252.94	85.11	252.94	498.67

Table 6 - Thermogravimetric data of soybean biodiesel synthesized by heterogeneous catalysis derived from the white eggshell.

The sample of biodiesel synthesized by the white eggshell derived catalyst, which obtained the largest mass loss in the first event and, consequently, the highest conversion in biodiesel, was CB10P8 with 97.11%. Similar conversion result obtained by gas chromatography 96.80%.

Still according to table 6, the white eggshell catalyzed samples, calcined in 80 minutes (CB8P8, CB9P8 and CB10P8), had conversions below 33%, well below the remaining samples. The result may be related to insufficient time for pore formation in the formed structure, making the surface area small, as observed in the BET result. Except for white eggshell samples calcined in 80 minutes, the influence of calcination temperature on the catalytic capacity of CaO formed was also observed. When above 800 °C, the higher the calcination temperature the lower the catalytic efficiency for the transesterification reaction of soybean oil.

Table 7 corresponds to the thermal decomposition of the biodiesel synthesized by the catalyst obtained from the $CaCO_3$ calcination, which also occurred in two events. The first decomposition event occurred between temperatures 111 to 267 °C. In the second the temperatures were between 234 and 502 °C.

Sample	1st event			2nd event	
	Initial temperature/ °C	Final temperature/ °C	Mass loss (%)	Initial temperature/ °C	Final temperatura/ °C
CI8P8	115.92	250.62	86.38	250.62	499.22
CI9P8	116.83	245.72	96.48	245.72	502.70
CI10P8	118.29	255.30	88.40	255.30	498.39
CI8P12	118.01	233.93	85.39	233.93	498.72
CI9P12	111.60	227.13	91.72	227.13	493.40
CI10P12	117.66	257.20	97.46	257.20	500.65
CI8P16	115.67	266.85	92.33	266.85	499.83
CI9P16	114.37	241.33	91.76	241.33	500.61
CI10P16	118.17	248.53	91.38	248.53	493.86

Table 7. Thermogravimetric data of soybean biodiesel synthesized by heterogeneous catalysis derived from commercial $CaCO_3$.

Based on the results presented among the biodiesel samples (present in table 7), it is possible to affirm that there was a very low variation between the values of the initial temperature and mainly percentage of loss of mass, in comparison to the samples of biodiesel obtained by the catalysis with eggshell. Demonstrating that the calcination time and temperature, have almost no influence on the catalytic activity of a catalyst derived from commercial $CaCO_3$.

Among all 27 biodiesel samples analyzed thermogravimetrically, the one with the greatest conversion was CI8P12 with 97.46%. Very similar to the result presented by gas chromatography, showing that even though the eggshell may have a great potential to obtain heterogeneous catalysts for transesterification reaction, they are much more dependent on calcination conditions than the commercial calcium carbonate itself.

4 I CONCLUSIONS

Based on the results obtained from the 27 heterogeneous catalysts derived from different raw materials, it was concluded that the catalysts obtained from the calcination of the white eggshell present a chemical composition more like the catalysts derived from the calcination of the commercial calcium carbonate than the derivatives of calcination of the brown eggshell. Regarding the morphological and structural characteristics, the catalysts derived from the calcination of the white and brown eggshells present more similar characteristics when compared to the calcination of the commercial calcium carbonate.

It was also concluded that the catalysts derived from calcined commercial calcium carbonate showed a high efficiency in the transesterification reaction in all time and temperature parameters studied.

In the reaction conditions studied (3 hours of reaction, 6% of catalyst and molar ratio of 1:12 oil and methanol), the catalysts obtained from the calcination of the chicken eggshell showed low catalytic capacity of the calcined eggshell samples in periods of 80 minutes. As well as that the calcined white eggshell has a higher catalytic capacity than the calcined brown eggshell, which CB8P16 obtained the best performance.

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SOBRE OS ORGANIZADORES

FRANCIELE BONATTO. Professora assistente da Universidade Tecnológica Federal do Paraná (UTFPR)- Campus Guarapuava. Graduação e Mestrado em Engenharia de Produção pela UTFPR. Doutorado em andamento em Engenharia de Produção pela UTFPR. Trabalha com os temas: *Supply Chain,* gestão da qualidade e gestão da produção.

JAIR DE OLIVEIRA Professor da Universidade Tecnológica Federal do Paraná (UTFPR). Administrador de empresas pela UENP. Mestre em administração pela UFPR e doutor em engenharia de produção pela EESC-USP. Trabalha com os temas: Pequena empresa e Ensino para o empreendedorismo.

JOÃO DALLAMUTA. Professora assistente da Universidade Tecnológica Federal do Paraná (UTFPR). Graduação em Engenharia de Telecomunicações pela UFPR. MBA em Gestão pela FAE Business School, Mestre pela UEL. Trabalha com os temas: Inteligência de Mercado, gestão Engenharia da Qualidade, Planejamento Estratégico, Estratégia de Marketing

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