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Study of Eggshell as Precursor of a Heterogeneous Catalyst in One Step Neutralization and Transesterification Reactions of Acid Macauba and Soybean Oil

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Abstract Biodiesel is an important biofuel used worldwide as a total or partial substitute for fossil diesel. Many studies have been developed to reduce their costs, specially using acid oils as waste oil and inexpensive heterogeneous catalysts. CaO obtained from calcinated waste eggshells has been the object of study of this work to produce biodiesel using neutral soybean oil (<1.0 mg KOH/g) and high-acidity soybean oil (9.5 mg KOH/g) and macauba oil (20.0 mg KOH/g). A preliminary study of transesterification of neutral soybean oil with methanol in a molar ratio of oil:alcohol 1:12 in 3% of CaO-egg reached conversion 95% of FAME after 4 h of reflux. The progress of the reaction was analyzed both quantitatively by ^{1}H NMR, as qualitatively by HPLC. The resultant biodiesel has met the international specifications as the kinematic viscosity and density, with values 4.37 mm^2/s and 885.8 kg/m^3, respectively. The study of breakthrough of the reaction between the doped acid soybean oil in the presence of methanol in a molar ratio of oil:alcohol 1:18, using 3% (w/w) CaO-egg indicated that the oil triglyceride only begins to be transesterified after all the neutralization of FFA. After 6 h of reflux the FAME conversion was of 96%. Using the same reaction conditions, while using the acid macauba oil, the FAME content was of 94%. The results showed the efficiency of CaO-egg for simultaneous neutralization/transesterification reaction for high-acidity oil, in only one step reaction.

Keywords: *eggshell, biodiesel, high-acidity oil, heterogeneous catalyst, macauba oil*

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1. Introduction

The eggshell is a waste generated in large quantities, especially for companies that produce powdered eggs, liquid eggs, biscuits industries, pasta, cakes and breads. Up to now there is no well-established use for this waste, often for the trash, without taking advantage of its mineral wealth. Knowing that the shell is 10% of the egg weight, the residue generated corresponds to around 5.92 million tons per year worldwide [1]. The calcareous layer of the egg is composed mainly of calcium carbonate (85-95%), magnesium carbonate (1.4%), phosphate (0.76%) and 4% organic matter [2]. As a proposal of a socio-economic-financial-environmentally suitable destination for the waste egg shells, the use of this waste in the biodiesel sector is proposed, allowing a green route from the reuse of natural wealth and adding gains economic and environmental.

According to the American Society for Testing and Materials (ASTM D6751), biodiesel is defined as mono-alkyl ester derived from lipid feedstocks, such as vegetable oils or animal fats. The most common method for obtaining it is the transesterification. In this process, the triglyceride (TG) is reacted with methanol in the presence of a catalyst to produce a mixture of fatty acid methyl esters (FAME) and glycerol [3]. The FAME are separated and purified before to be used as biodiesel, in substitution of diesel. Among the parameters that influence the transesterification reaction highlights the type of catalyst used, which may be homogeneous or heterogeneous, bifunctional or acid or alkali.

The conventional catalytic process consists in alkali homogeneous catalysis [3]. However, this process involves technological problems resulting in higher production cost. Among these stand out: i) the need for thorough washing of the resulting FAME for the removal of the homogeneous catalyst, resulting in a massive production of waste water; ii) the impossibility of re-use the catalysts; iii) lower purity of glycerin obtained by the transesterification due to the presence of residual catalyst; iv) the production of soaps resulting in lower yield of biodiesel as well as obstruction of the process, especially when using oils with high acidity [3,4,5].

Thus, in recent years, the scientific literature has presented a lot of work to develop alternative routes of biodiesel synthesis, aiming the simplification of the transesterification process and ensuring less environmental impact. To this purpose, it is proposed supercritical reactions, microwave or ultrasound use, enzymatic catalysis and heterogeneous catalysis [5]. Among those alternatives, the heterogeneous catalysis is presented as one of the most extensively studied in recent years. Among those alternatives, the heterogeneous catalysis is presented as one of the most extensively studied in recent years. In heterogeneous catalysis, the catalytic mass is supported on solids, does not dissolve in contact with reagents, and products, and so can be filtered off after synthesis. Thus, the use of these catalysts reduces the costs associated with extensive washes and abundant generation of waste water, it may also be recycled and reused by reactivating [4].

Despite the numerous advantages of heterogeneous catalysis in relation to homogeneous, it is worth mentioning that the activity of heterogeneous catalysts is depended on their nature, active sites, structural morphology, porosity, and thermal stability [6]. Heterogeneous catalysts represent slower reaction rate but this limitation can be balanced by elevating the reaction temperature, pressure, amount of reactants molar ratios oil:alcohol, catalyst content and reaction time, in order to have the same conversion achieved with homogeneous catalysis [5,7,8,9]. Furthermore, these catalysts are thermally activated and deactivated for the transesterification reaction at temperatures close to the boiling point of methanol and most of the proposed catalysts are expensive and their use implies operational change processing, which has hindered its industrial application [4].

Among the heterogeneous catalysts used in the production of biodiesel through transesterification reaction, metal oxides stand out, such as CaO, MgO, SrO, BaO, aluminas, and mixtures of these [5,10]. The CaO has been more studied by having a better catalytic performance due to its larger number of basic sites per unit mass and for presenting a better activity in re-use, since the other oxides showed high efficiency loss from the second use [5,11]. The CaO also has economic advantages, high alkalinity, lower solubility and easy handling [4,11,12,13].

Although be easily extracted in large quantities from limestone and therefore possess low cost, CaO can also be effectively obtained from calcination of $CaCO_3$ residues such as eggshells [14], bones [15], oyster shells [16] and shellfish [17], to be used in biodiesel synthesis. The use of recycled materials is not only effective in reducing the production costs, but also in the preservation of natural resources mineral [4]. Otherwise, it is noteworthy that are few and recent studies in the literature on this catalyst in the production of biodiesel, especially while using high-acidity oil.

Considering that approximately 70 to 95% of the cost of biodiesel belongs to the price of the oil [18], it is evident that the use of lower-priced oil has great positive impact on the energy sector, which includes non-edible oils and the ones with higher acidity. However, the use of oil with the presence of free fatty acids (FFA) greater than 3%, is presented as a limiting factor in the production of biodiesel through alkaline homogeneous catalysis promote soaps formation, which can damage the engines of cars if not removed, and difficult the separation stages in the production process [19,20]. An alternative route for the use of these oils is to divide the process into two steps, the first in an acid esterification, wherein the FFA are converted into esters and, in a second stage, alkaline transesterification occurs to the remaining triglycerides [6,19,20]. Sharma et al used the CaO obtained from the eggshell in the transesterification of oil *Pongamiapinnata* high acidity (19.88 mg KOH/g), however, they first proceed the oil esterification with H_2SO_4 acid [2].

The *Acrocomia aculeata*, known as Macauba is a palmaceae found in tropical and subtropical America from southern Mexico and the Antilles to the southern regions of Brazil, reaching Argentina and Paraguay. Targeting the cultivation of Macauba as an energy crop for the energy sector is attractive because it does not compete with food. It is pest resistant, perennial and can be planted in consortium with agricultural activities. It can produce about 6.2 tons of oil/ha, of which about 718 kg is derived from its almond that is rich in lauric acid [21]. This oilseed has the disadvantage that, just like the palm, it has increased acidity in a short time of storage. Due to its high acidity and not being used as a human food, its oil can generate what is called biodiesel of second generation.

Develop heterogeneous catalysts of low cost and high efficiency and develop appropriate processes for the production of biodiesel from lower cost of high-acidity oils using green and innovative technologies, are some of the important challenges that are still posts for the biodiesel industry. In this work, a study of the progress of neutralization and transesterification of acid Macauba oil (20.0 mg KOH/g) and soybean oil doped oleic acid (9.5 mg of KOH/g) was done with the catalyst CaO obtained by calcining residues of chicken eggshells, used as catalyst. The transesterification process was compared with low acidity soybean oil (<1.0 mg KOH/g). The results confirmed the efficiency of eggshell catalyst and its excellent performance for neutralization/transesterification in one step reaction. This can be an important contribution for biodiesel industry.

2. Materials and Methods

2.1. Materials

Methanol (99.8%, Dinâmica ®, São Paulo, Brazil), $CDCl_3$ (99.0%, Synth$^{®}$, São Paulo, Brazil), Na_2SO_4 (99.0%, Vetec$^{®}$, São Paulo, Brazil), CaO (99%, Vetec$^{®}$, São Paulo, Brazil) commercial refined soybean oil were used without further purification. Comparative reactions occurred with the commercial refined soybean oil and its respective doped oil with oleic acid (99.0%, Dinâmica$^{®}$, Sao Paulo, Brazil), in a ratio of 150 g soybean oil 20 g of oleic acid resulting in an acid oil 9.5 mg of KOH/g (4.8 wt% of FFA). The crude macauba oil used in this work was obtained in a Brazilian plant extraction cooperative. A blend of this macauba oil was made by mixing 20% of the pulp oil (71.0 mg KOH/g) with 80% of almond oil (8.2 mg KOH/g), resulting in a high acidity oil (20.0 mg KOH/g).

The FFA profile of the neutral soybean oil and the acid macauba oil blend was determined using gas chromatography with flame ionization detector (GC-FID). For that TG was converted into FAME with one hydrolysis step and one methylation step using the methodology already established in the literature [21].

2.1.1. CaO-egg and CaO-com Preparation and Characterization

The white chicken eggshells were cleansed with tap water and distilled water and dried in an oven at 105 °C for 12 h. After drying, the shells were ground in a mill, resulting in a thin powder, and maintained in a desiccator. This sample was coded as Eggshell. Immediately before its use as a catalyst, the Eggshell was calcined in a muffle oven at 900 °C for 3 h and coded as CaO-egg. For comparison, the commercial CaO was also calcined at 900 °C in air for 3 h immediately before its use, and it was coded as CaO-com.

The catalysts were initially characterized by thermogravimetry to evaluate the presence of different phases and the temperatures of the phase transition. The thermogravimetric curves were obtained using a Shimadzu model TGA50H thermobalance at a heating ratio of 10°C/min, from 25 to 900°C, in air atmosphere with a gas flow of 50 mL/min. The structural analysis was performed by X-ray diffraction (XRD). The X-ray diffractograms were obtained using a Shimadzu diffractometer model 6000, Cu tube, 30 kV voltage, 30 mA current, and screening velocity of 1°/min, at a 2θ interval from 5 to 80°. The isotherms were obtained using the NOVA-2200 equipment, version 6.11, and nitrogen as the adsorbent. Before the adsorption, the CaO catalysts were degassed at 180 °C for 8 h. The specific surface areas were calculated according to the BET (Brauner, Emmett, Teller) methodology. The catalyst micrographs were obtained by scanning electron microscopy (SEM) after metallization with gold using a BAL-TEC model MED 020. A Quanta 3D, FEI microscope was utilized.

2.1.2. Synthesis and Characterization of the Biodiesel

The vegetable oil (100 g) was mixed with methanol at molar ratios of 1:12 of oil:alcohol for refined soybean, and 1:18 of oil:alcohol for acid soybean and macauba oil. The catalysts CaO (CaO-com or CaO-egg) were added with variable amounts: 1, 3 and 5% (w/w). The mixture was kept under mechanical stirring at 600 rpm and reflux (65 °C) for 4 h. During the reactions, 2 mL aliquots were taken every 20 or 30 min to permit tracking of the transesterification reaction. These aliquots were centrifuged and analyzed by ^{1}H NMR for the quantification of FAME by monitoring the signals of the methoxyl and the α-CH_2 groups [22]. At the end of this reaction, the catalyst was removed through vacuum filtration and the glycerin was separated through decantation. The excess methanol was removed in a rotary evaporator at a reduced pressure.

The aliquots collected during the transesterification reaction and the final FAME were dissolved in $CDCl_3$ and characterized by hydrogen nuclear magnetic resonance (^{1}H NMR), with TMS used as the reference, using a Bruker AVANCE DPX200 spectrometer with the TOPSPIN1.3™ program – actualization level 10 – for quantification of the FAME. High performance liquid chromatography (HPLC) was used to detect the presence of the FFA, monoacylglycerides (MG), diacylglycerides (DG), triacylglycerides (TG), and FAME also following the same conditions described for Bejan et al [23]. The acidity of the of the doped soybean oil and its respective ester was measured by acid number (ASTM D664).

The kinetic calculus, used the analyze the behavior of reaction under different conditions, was performed using the approximation of pseudo-first order equation, as presented by Sousa et al [24]. The values of apparent rate constants were calculated and were related to the slope of the lines obtained in the ln(1-x) versus time graphs. For neutral soybean oil, it was calculated the initial, k'_i, between 1 and 2 h, and intermediate, k'_m, between 2 and 3.5 h, apparent rate constants. For high acidity soybean oil, the k' was calculated between 2 and 6 h.

The final biodiesel was also characterized by kinematic viscosity at 40 °C (ASTM D445) and density (ASTM D4052). Atomic absorption spectroscopy (ABNT NBR 15553) with a Perkin Elmer Analyst 400, was used in order to quantify the calcium content that leached to the liquid phase. The calcium content data were quantified according to a calibration curve with seven points and an $R^2 = 0.993$. The content of FAME at the final biodiesel was also determined by GC-FID, according to EN 14103:2011, and was adapted for the use of methyl heptadecanoate as internal standard, using a Shimadzu GC-2010 gas chromatograph with an AOC-5000 auto injector and a DB-Wax (30 m × 0.32 mm × 0.250) mm capillary column. Helium was used as the carrier gas (2 mL/min).

3. Resultas and Discussions

3.1. Synthesis and Characterization of the Catalyst

In order to choose the best temperature to process the Eggshell, aiming at convert all $CaCO_3$ into CaO, a derivative thermogravimetric analysis (DTGA) was done (Figure 1A). Its curve shows two steps of weight loss, the first one (ca. 8.25%) was centered at the 437 °C, due to the decomposition of $Ca(OH)_2$, releasing H_2O and CO_2 [14]. The second and the most dominant step of weight loss (ca. 47.12%), is centered in 807 °C, corresponds to the $CaCO_3$ decomposition into CaO, relearning CO_2 [14]. Through these results, 900 °C was the temperature chosen for the Eggshell calcination, resulting in 42% (w/w) of CaO-egg catalyst as a fine white powder.

Although the CaO-egg used at the transesterification reactions was the one obtained immediately after calcination of the Eggshell, a thermogravimetric study of CaO-egg after exposure to ambient conditions for several days (Figure 1B) was performed aiming to evaluate the catalyst stability. This curve presented a main event (c.a. 24.28%) around 448 °C, indicating the presence of $Ca(OH)_2$, certainly formed from the hydration of CaO with H_2O present in ambient conditions [4,25]. The absence of another event during calcination of CaO-egg-hydrate from 650°C highlights the absence of $CaCO_3$, previously present in its starting material. This result shows the importance of Eggshell heat treatment at 900 °C just before the transesterification reactions.

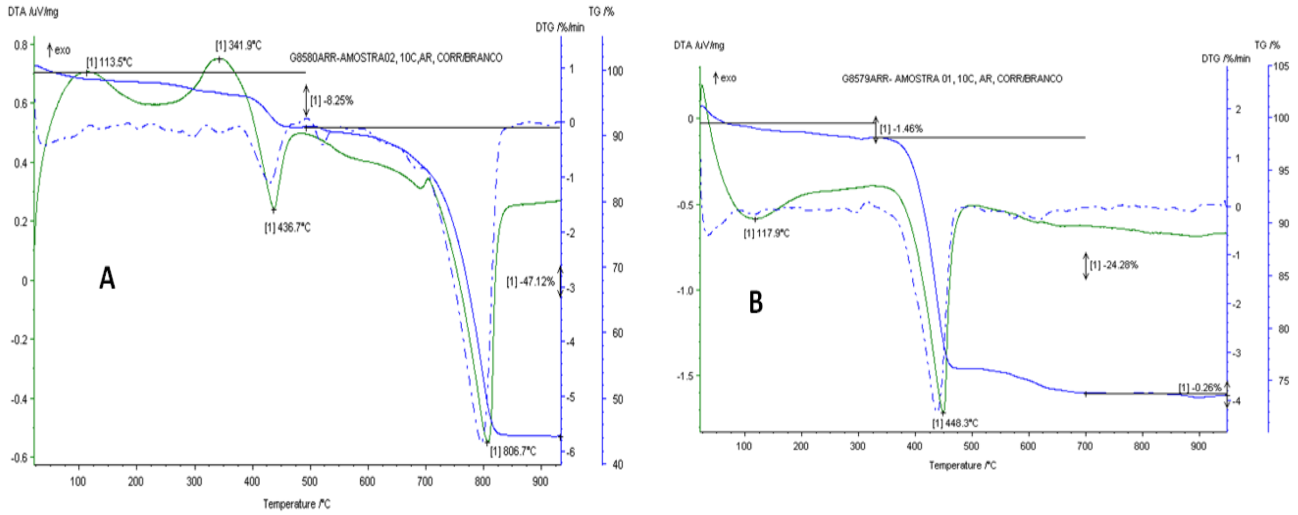

Figure 1. TGA and DTGA curves of the (A) Eggshell and (B) of the CaO-egg exposed to ambient conditions

The CaO-egg and CaO-com diffractograms (Figure 2) correspond to the JCDPS 77-2376 standard. The high intensity of the peaks of CaO-egg XRD, indicated by the small width at the half-height, shows the formation of a compound with excellent structural organization and phase purity. This analysis also confirms the absence of the characteristic peaks of $CaCO_3$ on CaO-egg and confirms its dominance in the precursor Eggshell.

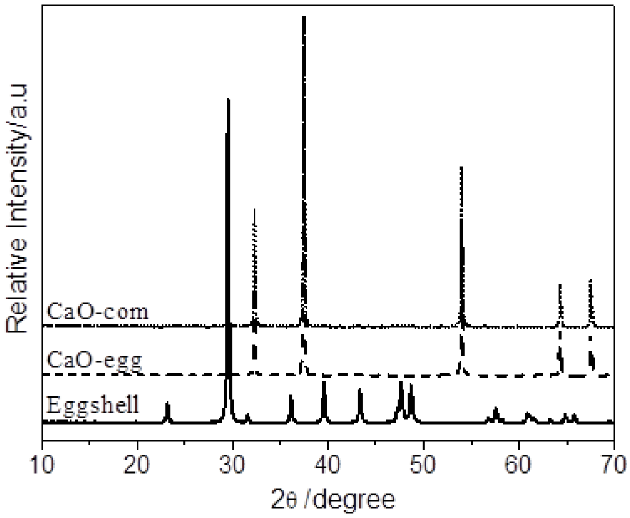

Figure 2. TGA and DTGA curves of the CaO-egg exposed to ambient conditions.

Comparative images obtained by SEM between Eggshell and CaO-egg (Figure 3), demonstrate the sintering of metal oxide from its most agglomerated particles [26]. Textural properties obtained by the BET technique indicate that the CaO-egg has a low specific area 4.33 m²/g and small average pore diameter of 12.38 nm. The respective values for CaO-com sample were of 0.93 m²/g and 10.88 nm. These results suggest a low to moderate CaO activity as a heterogeneous catalyst for both CaO-egg and CaO-com. Despite having unpromising texture properties, the CaO-egg has as great advantage compared to CaO-com due to its low cost and the fact that it can be obtained from waste, which leaves the process green and sustainable.

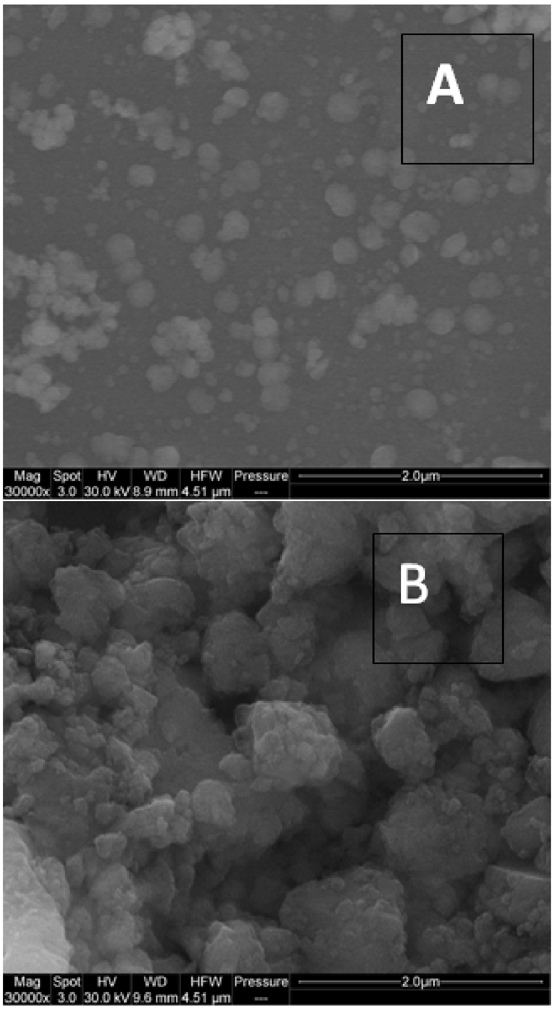

Figure 3. SEM imagens of (a) Eggshell and (b) CaO-egg

3.2. Characterization of the Soybean and Macauba Oil

Table 1 shows the FFA profile of neutral soybean oil and the blend of macauba oil (20.0 mg KOH/g) used in this work. The soybean oil composition corroborates with the data found in the literature [27], with the predominance of linoleic acid with 50.7% and oleic acid with 25.7%. Meanwhile, the macauba oil is mostly composed by 35.8% of oleic acid and 29.4% of laurate acid.

Table 1. Oils composition and their acidity and density values

	Sample	
	Soybean acid oil	**Macauba acid oil**
Composition	FFA%	FFA%
C8:0	0.31	4.17
C10:0	0.35	3.11
C12:0	0.23	29.41
C14:0	0.34	7.72
C16:0	10.67	10.46
C16:1	0.91	1.13
C18:0	4.14	2.95
C18:1	25.70	35.08
C18:2	50.72	5.98
C18:3	5.72	-
C20:0	0.24	-
Molecular weight (g/mol)	1288.24	763.58
Acidity (mg KOH/g)	<1.0	20.9
Density (kg/m^3)	920.3	918.6

3.3. Study of the Transesterification of the Neutral Soybean Oil

In order to study the CaO-egg efficiency in milder conditions, an initial study was done to choose the best conditions for transesterification of neutral soybean oil with methanol ranging its percentage amount in 1, 3 and 5% (w/w). For this purpose, a study was performed aiming to follow the progress of the reaction the conversion of TG to FAME are presented as function of reaction time (Figure 4). For this purpose, at each 20 or 30 min aliquots were collected and the product ester content was determined by ^{1}H NMR, as described in the literature [28].

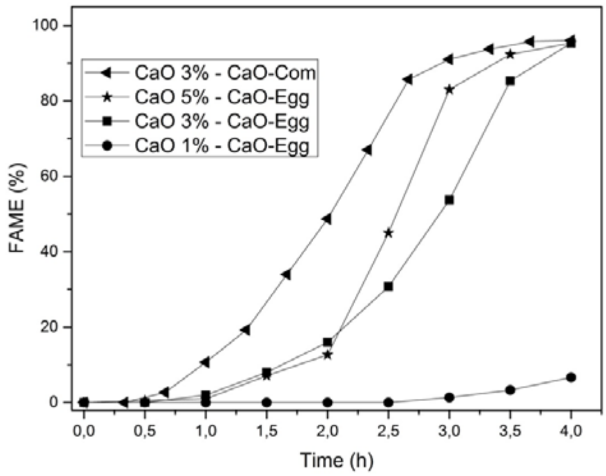

Figure 4. Advance of transesterification of the neutral soybean oil using CaO-com and CaO-egg in different concentrations

It is noteworthy that the GC-FID method proposed by international specifications EN 14214 and CNS 15072 is a globally used technique for the quantification of FAME with high purity. However, this technique has limitations when using a sample with high level of intermediate and non-volatile contaminants within the analysis parameters used in determining esters, causing plugging problems in the column [29]. Above all, this technique has a high cost by the need for specific standards, columns and high-value gases. For all these reasons, the ^{1}H NMR technique was chosen in this study to quantify the relationship between FAME and their TG along the reaction and the final product.

From the curves shown in Figure 4, the apparent rate constants, k', for each reaction were obtained according Sousa et al [24], being the initial apparent rate constants, k'$_i$, calculated between 1 and 2 h and intermediate apparent rate constants, k'$_m$, calculated between 2 and 3.5 h (Table 2). Analyzing those value (Table 2), concomitant with the advance of the reaction (Figure 4), it can be clearly concluded that the catalyst content of 1% CaO-egg is not suitable for the synthesis of FAME. Despite the transesterification rate constant initial (k'$_i$) using CaO-com (3% w/w) be significantly higher than that using CaO-egg in every content (Table 2), the intermediate rate constants, k'$_m$, are equivalent for CaO-com and CaO-egg at 5% w/w. Although increasing CaO-egg content of 3 to 5% has caused a slight increase in the rate of transesterification, both the conditions convergence to the same values of FAME content after 4 h of reaction, while using CaO-com 3%. Regarding these observations, all of the following reactions were performed with 3% CaO-egg for 4 h of reflux.

Table 2. Values initial, k'$_i$, and intermediate, k'$_m$, of the apparent rate for the reactions studied

Catalyst	**Content (%)**	**k'$_i$ (min^{-1})**	**k'$_m$ (min^{-1})**
CaO-com	3	0.0093 ± 0.0012	0.025 ± 0.003
CaO-egg	1	0.000 ± 0.000	0.0013 ± 0.0002
CaO-egg	3	0.00209 ± 0.00002	0.021 ±0.003
CaO-egg	5	0,00212 ± 0.00002	0,023 ±0.003

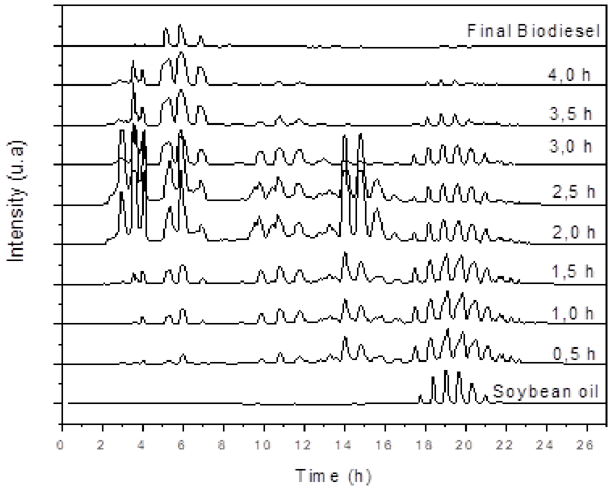

Figure 5. Overlapping HPLC chromatograms of products of the transesterification of refined soybean oil with CaO-egg 3% over 4 h of reaction

In addition to the quantitative analysis of the evolution of the formation of FAME along the transesterification of soybean oil in methanol with 3% of CaO-egg using ^{1}H NMR, a qualitative evaluation by the HPLC chromatograms (Figure 5) was also carried out. It helped to evaluate the intermediate compounds as DG and MG. It shows that the peaks scattered between 17.0 and 22.0 min are TG [23]. As the reaction proceeds, those signals are reduced and the characteristic peaks of DG arise between 8.0 and 17.0 min [23]. The peaks between 4.5 and 2.0 min refer to MG, which are in great quantity elapsed after 2.0 to 3.5 h of reaction time. These intermediaries are the last to disappear, once it is part of the slower stage of the transesterification reaction. The characteristic peaks of FAME are present between 5.0 and 8.0 min and appear only at the end of substantially pure biodiesel after 4.0 h of reaction.

Through the results presented, the transesterification of soybean oil was done with methanol in the presence of CaO-egg 3% under 4 h of reflux. The resulting biodiesel was characterized by the kinematic viscosity at 40 °C, density, FAME and calcium contents. The kinematic viscosity presented 4.37 mm^2/s which meet to the 1.9-6.0 mm^2/s viscosity limit specification of ASTM D6751 and the more restrictive EN 14214 standard (3.5-5.0 mm^2/s). The density was 885.8 kg/m^3, in accordance with the European standard that includes a density requirement in the range of 860-900 kg/m^3. Since the minimum ester content required by European specification is 96.5%, the results showed that the FAME almost met the standard specifications, with an ester content of 95% according to the GC-FID analysis.

The analysis of the Ca^{2+} concentration in the resulting biodiesel while using CaO-egg 3% was of 359.8 mg/kg, whereas using CaO-com it resulted in 545.5 mg/kg. This high leaching only reduced the induction time of the first step of transesterifiation reaction, reducing the time necessary for digliceroxide formation. It is well known that digliceroxide is the effective solid catalysts responsible for transesterification [11,24,30]. This solid is a product of calcium methoxide and glycerol formed in the beginning of the reaction. As higher Ca^{2+} leaching, as high will be the digliceroxide amount available, and quicker the reaction speed. Figure 4 showed that this induction period of time is 0.5 h for CaO-com and 1.0 h for CaO-egg using 3% of catalyst. This observation is confirmed by the high initial rate constant for the reaction using CaO-com (0.009 min^{-1}) in relation to the reaction using CaO-egg (0.002 min^{-1}) in the same condition. Therefore, is possible claim that the leached calcium does not cause important homogeneous catalysis and that CaO still acting as a heterogeneous catalyst [24]. However, for both catalysts, CaO-com and CaO-egg, the amount of Ca^{2+} in biodiesel is well above international specifications (5.0 mg/kg)

3.4. Transesterification of Acid Soybean and Macauba Oil

In order to certify the catalytic efficiency of CaO-egg while using acidic oil, the relationship between the change in acid number and FAME content was investigated. For this purpose, soybean oil doped with oleic acid (9.5 mg KOH/g) was used with 3% CaO-egg, and the oil:alcohol molar ratio was increased to 1:18 aiming to minimize the acidity interference. The acidity of the mixture was monitored during 8 h under reflux (Figure 6).

Those results show a significant reduction of the acidity of the soybean oil doped during the first 2 h of reaction. However, at this while no significant increasing of FAME content has occurred. This means that at the initial stage, the ion methoxide formed by partial dissolution of CaO in methanol, was initially neutralized by the FFA, producing calcium soap [11]. However, the produced calcium soap seems to have been scraped out from the catalyst surface into the organosol species, regenerating the much more basic sites, allowing the further transesterification to occur. This deduction stems from the fact that after the neutralization stage, the transesterification process is initiated and, as happened with the neutral soybean oil (Figure 4), after 4 h of reaction thereafter, the ester content also reaches 96% (Figure 6). Once no more FFA was convert to calcium soap, the transesterification reaction of the remaining TG occurred between methanol adsorbed on solid base active sites and glycerol from the liquid phase [28]. At this point, the active phase becomes calcium diglycinate, derived from glycerin reaction with the oxide or calcium methoxide [4,31]. The rate constant after 2 h of reaction (between 2 and 6 h) was 0.018 ± 0.002 min^{-1}, this value is close to the found for this catalyst, in the same concentration, for transesterification of the neutral oil (0.021 min^{-1}).

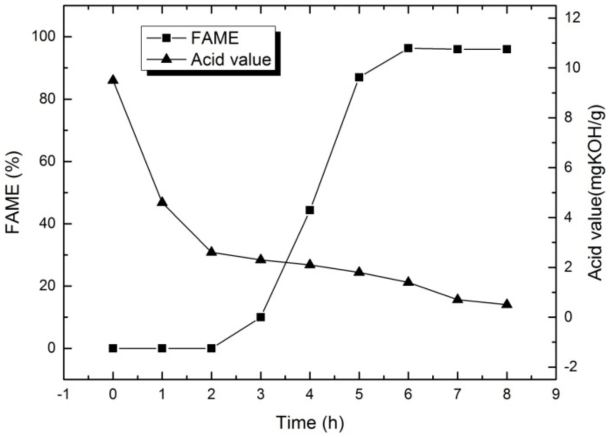

Figure 6. Relationship between FAME content and acid value of the product of transesterification of doped soybean oil, in the presence of CaO-egg 3%

The literature shows that while using an oil with FFA above 1.0 mg KOH/g, the formation of soap is promoted when the transesterification is done under homogeneous alkaline catalyst [8], as the deactivation of the catalytic sites occurs under heterogeneous catalysts, especially on the basis of CaO [11]. Meanwhile, Yan et al [32] made a study of the efficiency transesterification under several acidity of oil, varying between 1.1 and 9.2 mg KOH/g. The authors, using the CaO/MgO catalyst (16.5% of CaO), noted that increasing the acidity of the oil to 7.0 mg KOH/g, the percentage of conversion of esters also appears reasonable in the order of 90%. However, for feedstock having acidity higher than 7.0 mg KOH/g, the oil conversion rate decreased dramatically, reaching 20% for the oil with 7.8 mg KOH/g and to almost zero for 9.2 mg KOH/g [32]. This behavior is not observed in the present work, in which we obtained 96% of conversion using oil with 9.5 mg KOH/g of acidity.

Noticing the efficiency of the proposed catalyst against acid oils, an even more acidic macauba oil transesterification reaction (20 mg KOH/g) was performed with methanol in a molar ratio of oil:alcohol 1:18, in the presence of 3% of CaO-egg. After 4 h of reaction, the centrifuged product showed 94% conversion to macauba FAME. Considering that macauba oil had an initial acidity almost twice the acidity of the acid soybean oil, and that even so it was processed for a shorter period of time, it shows that the catalyst performance is very promising to process high acid macauba oil, a much cheaper raw material. The fact that macauba oil is made up of smaller triglycerides may have contributed positively to this result.

4. Conclusions

In this study CaO-egg was obtained in high purity and yield of 42% w/w from the calcination of chicken eggs. Its catalytic activity was investigated during the transesterification reaction of the neutral and acid (9.5 mg KOH/g) soybean oil and acid macauba oil (20.0 mg KOH/g).

A previous study of the transesterification condition was done using neutral soybean oil and methanol under reflux, varying the catalyst concentration of 1, 3 and 5% (w/w). The ester content formed along the reaction, measured by ^{1}H NMR showed that under 5% of its presence, a greater rate in the transesterification reaction was reached, resulting in 95% of FAME after 4 h. However, while using 3% of the same catalyst, although slower progress of the reaction, in the end of the same 4 h of reflux, the FAME content also reached the same conversion of 95%.

Through the results presented, the synthesis of the biodiesel was carried out using neutral soybean oil with methanol (molar ratio oil:alcohol of 1:12), 3% (w/w) of the catalyst, under reflux for 4 h. The resulting ester attends the international specification for biodiesel concerning its kinematic viscosity and density. Atomic absorption analysis showed a calcium leaching from the catalyst CaO, therefore this leaching is more preeminent for catalyst from commercial CaO in comparison with CaO-egg (from eggshell), making the reaction with CaO-com is initially more favored. However, after 2 h of reaction, the reaction rates are approximately the same.

When using the acid soybean oil in the presence of 3% of CaO-egg and a molar ratio oil:alcohol of 1:18, it was noticed that there was initially the calcium soap formation from FFA up to 2 h of reflux, and then immediately the transesterification process has occurred within 6 h of reaction yielding 96% of FAME. This result is very promissory because it was possible to obtain FAME by high-acidity oil using CaO-egg, an inexpensive and residual catalyst. While using the macauba oil with a high acidity of 20.0 mg KOH/g, the ester conversion reached 94% in 4 h of reaction, showing a better result than the less acidy soybean oil. It could be attributed to the lower carbon chain size of the macauba oil.

These results highlight the possibility of applying residues eggshell calcined in the presence of at least 3% as catalyst for the transesterification of non-edible oils with high acidity. For that, no multi-step reaction is necessary. This would minimize operational costs when planning its industrial application, and benefit the environment by removing both waste egg shells, and non-edible oils, affording the production of biodiesel.

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