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Soybean Oil Transesterification for Biodiesel Production with Micro-Structured Calcium Oxide (CaO) from Natural Waste Materials as a Heterogeneous Catalyst

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Abstract: In this study, micro-structured calcium oxide obtained from the calcination (850 °C for 3 h) of *Gallus gallus domesticus* (chicken) eggshells was used as a catalyst in the transesterification of soybean oil. This catalyst was characterized by Scanning Electron Spectroscopy (SEM) methods. The structure of the obtained CaO showed several agglomerates of white granular solids with a non-regular and unsymmetrical shape. In terms of calcium oxide catalytic activity, three different catalyst loadings (1%wt, 3%wt, and 5%wt) were tested for the same reaction conditions, resulting in transesterification yields of 77.27%wt, 84.53%wt, and 85.83%wt respectively. The results were compared to the current literature, and whilst they were lower, they were promising, allowing us to conclude that the tendency of yield improvement for this reaction, when the size range of catalyst particles is to be reduced to a nano scale, can be verified.

Keywords: biodiesel; calcium oxide; transesterification; eggshell; solid base heterogeneous catalyst; micro- and nano-structured catalysts

1. Introduction

Currently, due to the continuous growth of the world's population, there is a high energy demand in both the industrial and domestic sectors, as well as an increase in public awareness about pollution and the overuse of fossil fuels. This has led to a rise in interest regarding research on alternative renewable energy sources [1–3].

Of the most common renewable energy sources for road transportation, i.e., hydrogen, natural gas, syngas, and biofuel, the latter is the most suitable, environmentally-friendly, and the only one which is ready to be used in vehicles equipped with internal combustion engines (ICE). Biodiesel (from the Greek, bio, life + diesel, from Rudolf Diesel) is the world's most famous biofuel. It is a preferred alternative for petrodiesel (diesel from petroleum oil) in ICE, due to its benefits, such as its availability, non-toxicity, and similar cetane-number, as well as the fact that it can be used directly or in blends with

conventional diesel without any need for revamping and even improves the diesel fuel lubrification properties [3–5].

In terms of industrial application for biodiesel production, homogeneous catalysts, such as NaOH and KOH, are usually preferred, but their removal is rather complex and sometimes polluting, bringing extra costs to the final product [6–8]. Considering heterogeneous catalysts for the transesterification reaction, calcium oxide (CaO) is a widely-used catalyst due to being cheap, non-corrosive, economically benign, and easy to handle, in addition to having a high basicity compared to homogeneous base catalysts [2]. It can be obtained from natural sources through the calcination of waste egg and oyster shells (~95% $CaCO_3$) at 850 °C for 3 h, exhibiting high activity for the transesterification of soybean oil due to its superior basic strength [9,10].

On the other hand, heterogeneous catalysts are, for the time being, somewhat time consuming, still inefficient, and still present problems related to mass transfer limitations. One solution regarding this problem might be the use of micro- or nano-structured catalysts, as new heterogeneous catalysts [1,11–14]. Using these based CaO catalysts, it would be possible to overcome some of these issues, as they present a higher surface area and catalytic activity, thus allowing a significant improvement in the transesterification efficiency to be achieved, resulting in faster reactions, i.e., shorter reaction times, low reaction temperatures, and lower catalyst loadings.

Nanocatalysts have recently become the focus of recent research. Reddy et al. (2006) [15] showed that a nanocrystalline CaO was an efficient catalyst for producing biodiesel with high yields at room temperature using soybean oil and poultry fat as raw materials. Hu et al. (2011) [16] developed a nanomagnetic solid base catalyst, KF/CaO-Fe_3O_4, based on a magnetic Fe_3O_4 core. In a reaction carried out at 65 °C with a methanol/oil molar ratio of 12:1 and a catalyst concentration of 4% weight related to oil, the biodiesel yield exceeded 95% at 3 h of reaction time. Wen et al. (2010) [17] concluded that the solid base catalysts KF/CaO can be used for biodiesel production with a yield of more than 96%. Kaur et al. (2011) [18] prepared a 1.75 Li-CaO (1.75% weight lithium impregnated CaO) catalyst, which, in the optimized conditions for the transesterification of Karanja and Jatropha oils, could achieve over a 99% conversion of oils to fatty acid methyl esters (FAME).

In the present work, the use of CaO from natural sources, in this case, chicken eggshells, which were then grinded, as a catalyst in the transesterification of soybean oil was studied. The obtained particles from the calcination of the calcium carbonate present in the shells were converted into calcium oxide and then analyzed by Scanning Electron Microscopy (SEM) to assess their structure and particle size. This is an intermediate study regarding the use of nano-structured heterogeneous catalysts for the improved obtention of biodiesel. The results for the soybean oil transesterification will be, in the future, used as a benchmark for a comparison with nanocrystalline CaO catalysts that are currently being studied and prepared by this research team using the Supercritical Anti-Solvent (SAS) method [19–23]. This technique consists of solubilizing CaO into conventional liquid solvents. These solvents are then saturated by supercritical CO_2, resulting in the controlled precipitation of nanocrystalline CaO by the anti-solvent effect [24,25]. Therefore, it will be possible to optimize the nanoparticle size by tuning the operational conditions.

2. Materials and Methods

2.1. Materials

Soybean oil was purchased from a local supermarket in Lisbon, Portugal. Methanol was used in the form of laboratory grade (MeOH; >99% pure). *Gallus gallus domesticus* (chicken) eggshells were collected from several households.

2.2. Preparation of the CaO Catalyst

The eggshells were washed several times with boiling water and then left to dry overnight at 100 °C. After that, the shells were grinded and the obtained solids were sieved into a fine powder using a 30 Mesh (<500 μm) strainer.

For benchmark tests, the calcination was performed for 3 h at 850 °C, with a heating rate of 5 °C/min. The calcium carbonate present in these shells was converted into calcium oxide (CaO), as shown in the equation below:

$$CaCO_3(s) \overset{850\ ^\circ C}{\rightarrow} CaO(s) + CO_2(g). \quad (1)$$

The obtained calcium oxide was then used as a solid base heterogeneous catalyst for the soybean oil transesterification reaction.

2.3. Catalyst Characterization

Scanning Electron Microscopy images were obtained (JEOL 7100F with an Oxford light elements Energy-dispersive spectroscopy (EDS) detector and Electron backscatter diffraction (EBSD) detector) in order to characterize the produced calcium oxide's morphology and particle size.

Dynamic light scattering graphics were also obtained (Microtrac NANO-flex 180° DLS size) to characterize the calcium oxide's particle size distribution.

2.4. Soybean Oil Transesterification

The transesterification of soybean oil was performed using the CaO resulting from the eggshell calcination and further grinding as the catalyst.

The transesterification reaction took place in a 25 mL flask. In total, 5 g of soybean oil was weighted and heated in a water bath to achieve the reaction temperature of methanol reflux (65 °C). Then, 2.24 g of methanol was weighted and placed inside the reaction flask. The amount of methanol used corresponded to a methanol/oil molar ratio of 12:1. These conditions resulted from work previously developed within this research group on the transesterification of triglycerides using calcium-rich heterogeneous catalysts and the optimization studies then performed [26–29].

Three different catalyst loadings were tested: 1%, 3%, and 5% (*w*/*w*, oil basis). The catalysts were added to the methanol, and the mixture was stirred at a high velocity rate. When the methanol reflux temperature was reached, the soybean oil was slowly added to the previous mixture.

Tests with different reaction times were also performed, ranging from one to five hours. Then, the mixture was filtered and placed inside a separation funnel to allow separation of the FAME phase from the glycerol phase.

The yield of the transesterification reaction was calculated using the following equation:

$$\text{Biodiesel yield } (\%) = \frac{\text{Measured weight of FAME}}{\text{Theoretical weight of FAME}} \times 100. \quad (2)$$

The theoretical weight of FAME was calculated using the stoichiometry of the transesterification reaction, as shown in Figure 1.

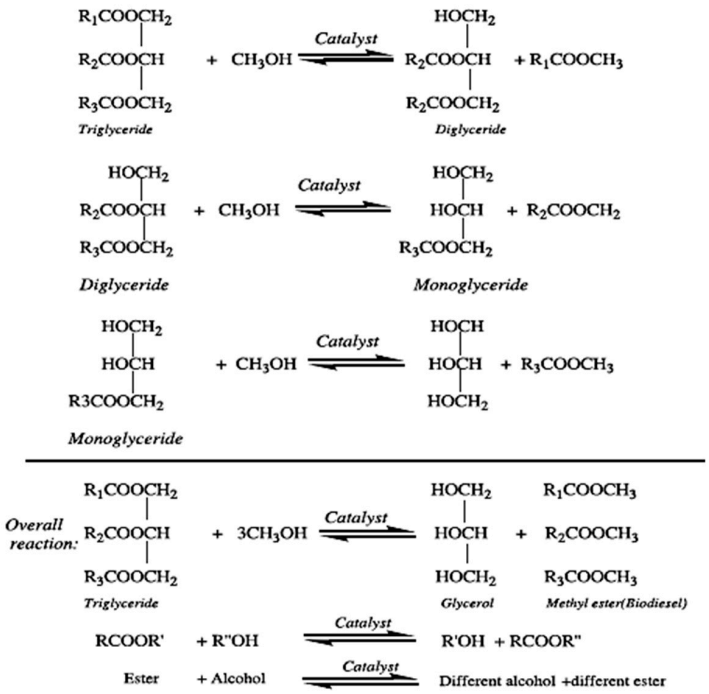

Figure 1. The transesterification of triglycerides and the three steps followed to obtain fatty acid methyl esters (FAME) [4].

3. Results

3.1. Characterization of the Catalyst

3.1.1. SEM Analysis

SEM micrographs of the CaO obtained from the calcination of *Gallus gallus domesticus* (chicken) eggshells were used to identify the morphology of the resulting white powder, as shown in Figure 2.

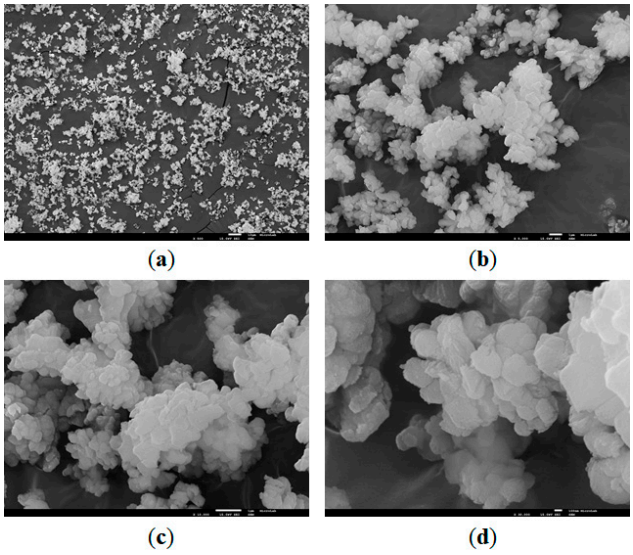

Figure 2. Scanning Electron Spectroscopy (SEM) microstructures of the CaO obtained from the calcination of eggshells. Eggshells were washed and left to dry overnight at 100 °C, crushed by mortar, and calcined at 850 °C for 3 h. Magnification and bars: (**a**) 500×, 10 μm; (**b**) 5000×, 1 μm; (**c**) 10,000×, 1 μm; (**d**) 30,000×, 100 nm.

3.1.2. Dynamic Light Scattering (DLS) Analysis

The characterization of calcium oxide obtained from the calcination of chicken eggshells was also performed by analyzing the size distribution for the particles. Dynamic light scattering allowed us to assess the size distribution range, which is shown in Figure 3.

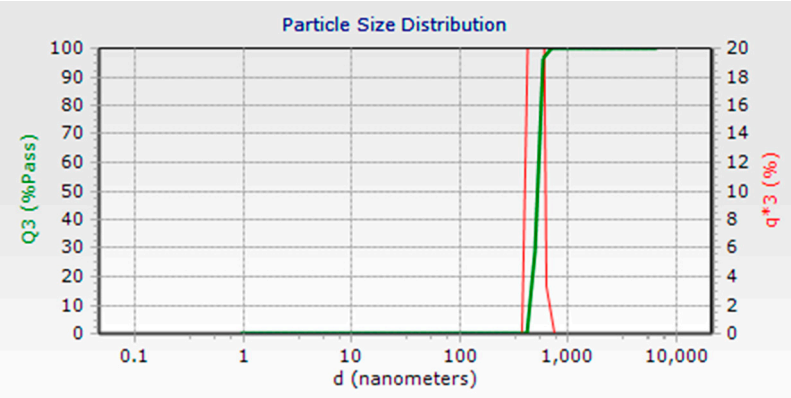

Figure 3. Dynamic light scattering analysis of calcium oxide obtained from eggshells, showing the size range of calcium oxide particles.

3.2. Catalytic Activity

The catalytic activity of the obtained CaO was tested in a bench scale setup at methanol's reflux temperature. The purpose of this experimental work was to assess the optimal reaction conditions for the transesterification of the soybean oil, more specifically, considering the reaction time and catalyst loading. The catalyst loading of 5% and the molar ratio of methanol/oil were previously tested within this research group [26–29]. This was considered a good starting point regarding the evaluation of using calcined eggshells as a heterogeneous catalyst for the transesterification of soybean oil. Additionally, an excess of methanol was necessary, in order to guarantee that the equilibrium shifted towards the products, due to the fact that the transesterification of fatty acids is a reversible reaction, as shown in Figure 3 [5,30].

As shown in Figure 4, for the same molar ratio of methanol/oil (12:1), a catalyst loading of 5% presents the best result in terms of the fatty acid conversion yield, reaching a maximum of 85.83% conversion in only three hours of reaction.

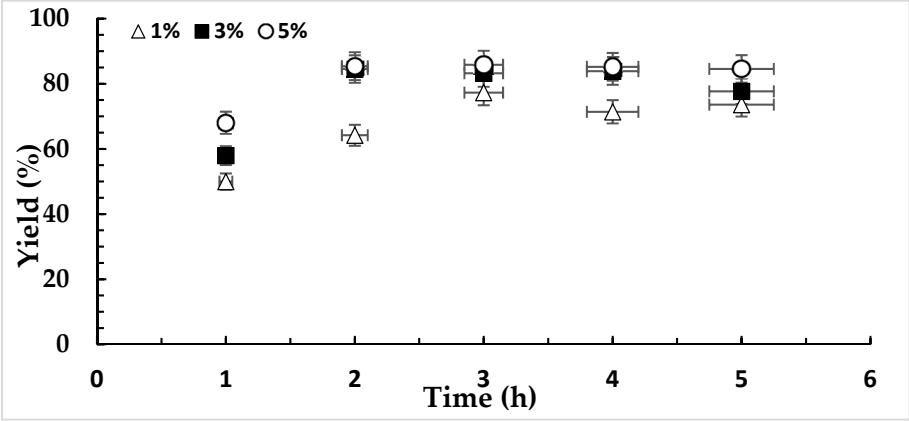

Figure 4. Effect of the reaction time on the FAME yield for three different catalyst loadings.

For the other two catalyst loadings, although the obtained yields are not as high as for the 5% loading, the results for the catalyst loading of 3% exhibit conversion yields in the same range.

A maximum of 84.53% was obtained, for this loading, when the reaction had been running for two hours.

As for the lowest catalyst loading (1%), the highest achievable yield was 77.27%. It is expected that the micronization of this catalyst into nano-structured CaO will result in an increase of its activity, meaning that, possibly, lower amounts will be needed to obtain at least similar FAME yields. In fact, it is expected that FAME yields could be even higher.

4. Discussion

4.1. SEM Analysis

The morphology of the CaO obtained from the calcination of chicken eggshells showed well-developed and defined particles. The structure of the obtained CaO showed several agglomerates of white granular solids, which displayed a non-regular and unsymmetrical shape.

Comparing the obtained morphology with several other studies, it was possible to notice that the observed structure was quite similar. All the micrographs exhibited white non-regular solids where the only noticeable divergence between the various micrographs was the general particle size [31–36].

By analyzing the SEM micrographs for the obtained CaO, it is possible to assume a general particle size smaller than one micron (<1 μm), which, for CaO obtained from calcined eggshells, is the most common size range. Although the particles are smaller than 1 μm, they are not yet in the nano particle range. According to IUPAC (International Union of Pure and Applied Chemistry) the particle's dimensions have to be within the 1–100 nm range in order to be classified as nano [37].

It is expected that, with the implementation of the SAS micronization technique in the future, the CaO particles will become considerably smaller (<100 nm), presenting a regular and symmetrical shape, and thus become nanoparticles.

4.2. DLS Analysis

The size of the obtained CaO particles appears to be distributed within a small region of the nanometric scale.

By analyzing the DLS graphic, it is possible to confirm that that the obtained CaO particle size distribution lies in the narrow gap between 450 and 600 nm, so is indeed smaller than one micron (<1 μm), as mentioned before.

Moreover, it is expected that with the implementation of the SAS technique, CaO nanoparticles with a more homogeneous particle size distribution will be obtained.

4.3. Catalytic Activity

Figure 4 shows the effect of the reaction time on the FAME yields for the three studied catalyst loadings (1%, 3%, and 5%). When comparing this data with that reported from different studies using CaO waste materials as heterogeneous catalysts (Table 1), it is possible to notice that, for different fatty acid feedstocks, in similar reaction conditions, analogous types of catalysts, and catalytic treatments, the obtained results in this study show that, in terms of the transesterification yield, there is still room for improvement using this catalyst. The low yield values could be due to the existence of internal mass transfer limitations, which are related to the hindrance of triglyceride molecules in the CaO micropores and hence, the catalytic activity of the CaO particles is somewhat low. If the size of the CaO particles was reduced to nanoscale material, its surface area would be higher than before, allowing for a lessening of the effect of internal mass transfer limitations, resulting in higher catalytic activity, higher transesterification yields, and shorter reaction times.

Therefore, with the use of nanocatalysts that are currently being prepared, the obtained yields will increase and be in the same size range as that described by Wei et al. (2009).

Table 1. Comparison of yield/conversion to biodiesel using different catalysts prepared from CaO waste materials.

Feedstock	Catalyst	MeOH/Oil Molar Ratio	Catalyst Loading (%wt)	Yield (%) [1]/Conversion (%FAME) [2]	Reference
Soybean oil	Oyster shell (CaO)	6:1	20.0	99.56 [1]	[38]
Soybean oil	Chicken eggshell (CaO)	9:1	3.0	>95.00 [1]	[39]
Used cooked oil	Ostrich/chicken eggshell (CaO)	9:1	1.5	96.00 [2]	[40]
Soybean oil Deodorizer Distillate	Duck eggshell (CaO)	10:1	10.0	94.60 [1]	[41]
Waste cooking oil	Chicken eggshell (CaO) supported char	12:1	10.0	>95.00 [1]	[42]
Sunflower oil	Crab shell (CaO)/Chicken eggshell (CaO)	6:1/9:1	3.0	83.10 [2]/97.75 [2]	[43]
Palm oil	Acid-treated quail eggshell (CaO)	12:1	1.5	>98.00 [2]	[44]
Waste frying oil (WFO)				87.00 [2]	
Rapeseed oil	Commercial CaO	12:1	5.0	97.00 [2]	[29]
Soybean oil				98.00 [2]	
Low FFA (free fatty acid) WFO	Clamshell (*Meretrix meretrix*) (CaO)	12:1	4.0	83.75 [1]/90.13 [2]	[45]

[1] Yield of the transesterification (Equation (1)). [2] Conversion of fatty acid in the oil into fatty acid methyl esters (FAME).

5. Conclusions

CaO waste materials have the potential to be used as micro-structured (and possibly nano-structured) solid base catalysts in the transesterification of triglycerides for the production of biodiesel.

In terms of results for catalyst characterization, SEM micrographs showed agglomerates of granular solids with a non-regular shape, which is common for CaO originating from eggshells.

DLS analysis exhibited particle size distributions in the range of 450 to 600 nm, which means that the obtained solid did not reach a nanoscale. Therefore, there is a need for the application of a micronization technique, such as the Supercritical Anti-Solvent (SAS) method, to achieve particle size distributions below 100 nm (nanoscale).

Regarding the catalyst's activity, it showed somewhat lower transesterification yields when compared with existent literature. These results will be used as a benchmark in the near future, when the transesterification reaction of soybean oil into biodiesel using CaO nanostructured catalysts will be performed and the effect of particle size reduction on the reaction kinetics will be studied. Nevertheless, this study, as an intermediate work, clearly confirms the tendency of yield improvement when the size range of catalyst particles is to be reduced to the nano scale.

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