

BIODIESEL PRODUCTION OVER FLY ASH-BASED CATALYSTS

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ABSTRACT

One of the major challenges for the current generation is to be capable of efficiently combine human development and advance with the support and protection of the environment. Many call this sustainability, which is based on three pillars: social, environmental and economic, and can be applied in different segments. This work is dedicated to propose a novel economic and efficient coprecipitation-based methodology for heterogeneous catalyst synthesis focused in biodiesel production via transesterification. The major idea is to produce catalysts based on reduction of expensive reagents and valorizing residues, namely, coal fly ash (CFA) and chicken egg shells (CES). Several FAES catalysts were synthesized via the same methodology (with slight variations) to evaluate the suitability of the crystalline material precipitated for biodiesel production from soybean-sunflower and WFO oils. In terms of characterization, ATR-FTIR, XRD and SEM-EDS analysis were carried with all the catalysts. Data analyzed shows that FAES N° 6 and N° 7 calcined at 800 °C were the most efficient catalysts synthesized, reaching an average biodiesel conversion – measured via an ATR-FTIR methodology – of 80.59 % and 81.30 % respectively. This is a behavior superior even to traditional catalysts, such as NaOH, 77.60 %, and CaO, 80.60 %. These two FAES catalysts contain within their crystalline structure several minerals beyond just CaO, such as brownmillerite, andradite, mayenite, wadalite and periclase. All of which, after calcination, become mixed mineral oxides that are recognized as efficient biodiesel catalysts and can hold different active sites, alkaline or acidic.

Keywords: *Biodiesel; Fly ash; Chicken egg shell; Residue valorization; Catalyst; Coprecipitation*

1 INTRODUCTION – CONNECTING EDGES

Undoubtedly, the traditional methods of producing energy were under questioning due to its side effects, much of those supported with concrete data and arguments. A biofuel front also

prospered recently. In Brazil, for instance a program to turn biodiesel a state policy and, parallelly, strengthen social support was conceived in 2004 and named National Biodiesel Production and Use Program (PNPB). In European Union (EU), following the Renewable

Energy Directive (RED) issued by (EU, 2009), it is a mandatory target by 2020 to reach 10 % of renewable energy in the transport sector and 20 % for an overall share for renewable energy in the energy matrix. The RED II directive issued by (EU, 2018) envisions to reach a minimum of 14 % of renewable energy in the transport sector and 32 % for an overall share for renewable energy in the matrix. Besides, it brought new requirements for Greenhouse Gases (GHG) emissions and sustainability criteria for biofuels used in transport to be eligible for government support and financing. Also, it also presented new conceptualizations and definitions like the Indirect Land Use Change (ILUC) concept, that relates to the use of agricultural areas for biofuels instead of food production.

2 THE BIODIESEL

At present, significant participation in the world matrix is associated to the growth of the renewable energies in general. The world's Total Primary Energy Supply (TPES) is a manner of attesting and sensing this behavior. In 2016, around 14 % of the total energy available in the world came from renewable sources of Primary Energy (PE). The data indicates that liquid biofuels, as yet, do not, significantly, contribute to the worldwide TPES to the same extent as solid biofuels/ charcoal, which are responsible for 62.4 % of the total of renewable energies. Contrastingly, that the annual growth rate of the use liquid biofuels was ca. 10 %.

2.1 Initial Definitions and Basis

The EU Commission states in its regulation the definition of biofuel as liquid or gaseous fuel intended to be used for

transportation and with an origin from biomass (EU, 2003). (EIA, 2019) characterize biofuels as being any kind of liquid fuel or blending products derived from biomass and intended to be used firstly as transportation fuel. Biodiesel is defined by Krawczyk (1996) and Ma & Hanna (1999) as being produced from biologic materials, such as vegetable oils and animal fat that can be applied as a fossil diesel substitute.

2.3 Biodiesel Production Pathways

There exists different technologies to produce biodiesel from raw materials like vegetable oils and fats. The most known are direct use and/ or blending, micro-emulsion, thermal cracking or pyrolysis and esterification/ transesterification, mentioned by innumerous researchers including (Demirbaş et al., 2016; Ruhul et al., 2015; Schwab, Bagby & Freedman, 1987).

2.3.1 Esterification

Esterification is a reaction of an alcohol (mostly methanol) with a FA molecule, resulting in an ester and a water molecule. This process is mostly used as a bypass to situations the transesterification reaction does not proceeds as usually expected (*i.e.* in terms of conversion), commonly, with low quality raw materials such as animal fats and WFOs.

2.3.2 Transesterification

The reaction occur in three separated steps to produce FAME or FAEE, depending on the type of alcohol used as reagent. It is reversible, meaning it is needed a so-called "driving force" to steer it to the way desired (towards products). It requires the presence of

catalysts, either acidic or basic (also named alkaline), under either homogeneous, heterogeneous or enzymatic conditions, as massively evaluated by authors like (Demirbaş et al., 2016; Atadashi et al., 2013).

3 CATALYSIS IN BIODIESEL PRODUCTION

Catalyst is capable of providing an alternative path, with a, relatively, lower activation energy when compared to the regular one, to a certain reaction to occur. This, obviously, influence the rate of reaction. Hence, the catalyst is not part of a chemical reaction at all, not being consumed or produced during the entire process. Usually, it is said that catalysts are, at the same time, reactant and product of a chemical reaction to reinforce this concept of not being part of the reaction. Exists ample investigation streams towards developing catalysts from different natures to overcome some of the major drawbacks, as Figure 1 highlights.

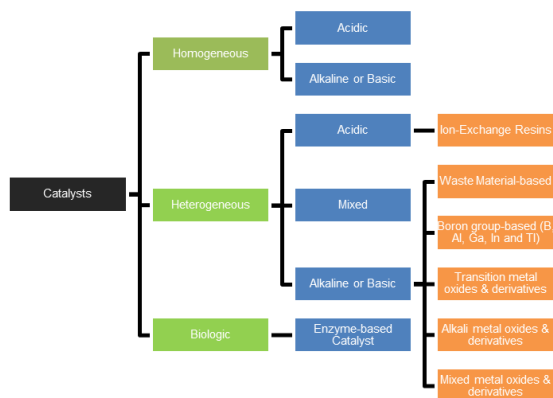


Figure 1 - Catalysts in biodiesel production.

Adapted from: (Ruhul et al., 2015).

3.1 Homogeneous Catalysts

Due to its nature, the catalyst miscibilize with the reagents forming a single phase medium, as debated by (Ruhul et al., 2015).

3.2 Heterogenous Catalysts

It is characterized by occurring in a different medium than the one where happens the main chemical reaction (e.g. transesterification or esterification). Theoretically, this catalysis is carried in the interface of the two phases such as solid-liquid, solid-gaseous or liquid-gaseous and, for that, actives sites are needed since molecules will need to adsorb on them to further on react. Some drawbacks are associated to longer reaction times, amount and a higher alcohol: oil ratio, as discussed by (Ruhul et al., 2015).

4 Coal and Fly Ash

In 2017, according to (IEA, 2019), coal solely was responsible for approximately 38 % of the total electric energy produced worldwide in TOE. Historically, coal did not lose global importance at least since 1990, varying between not more than 40 % and not less than 37 %.

4.1 Coal Fly Ash (CFA)

Its formation out of raw coal is achieved submitting the material to high temperatures near 1300 °C – 1700 °C via different types of technology like pulverized coal combustion (PCC), a subcritical steam technology, and supercritical (SC) and ultra-supercritical (USC) steam coal combustion technology. This material is currently very much relevant as it is a byproduct of a fundamental economic sector – energy industry – that is spread throughout the world and is fundamental to guarantee electric energy access.

5. EXPERIMENTAL PROCEDURES

The practical part of this entire work it is, essentially, divided in two major sections: Heterogeneous Catalyst Development, Synthetization and Improvement, and Biodiesel Production.

5.1 Heterogeneous Catalyst Development, Synthetization and Improvement

The first phase requires the production of two source solutions, hereafter named 1st Source Solution (FSS) and 2nd Source Solution (SSS), composed, respectively, of metallic cationic species and alkaline active species. The major role of FSS is to supply the metallic species needed, while the one of SSS is to enrich the medium with Ca and nitrate (NO_3^{2-}) ions.

The FSS is produced from CFA residues from bituminous coal collected from the Skawina power plant, located in the municipality of the same name in southern Poland and owned by the Czech electricity conglomerate ČEZ Group ®. This procedure is done by contacting 20 grams of raw and *in natura* FA with 400 ml of a 3 M solution of HCl for 2 hours. This solution was made by adding 99.3712 milliliters of reagent-grade HCl from Panreac AppliChem ® 37 % in 400 milliliters of distilled water.

The SSS is made of another waste, chicken egg shells (ES) that is mostly composed of calcium carbonate (CaCO_3). It was collected from a local restaurant near the IST Alameda campus in Lisbon, Portugal and, to become a suitable raw material for the source solution, is required a pre-processing stage. ES were thoroughly washed to remove dust and residues, dried at 60 °C in a laboratory oven for 24 hours and manually milled in a ceramic mortar with

pestle until becoming a white-like fine powder. Finally, 10 g of the powdered ES were added to 200 milliliters of a ≈ 0.7 M solution of HNO_3 . This solution was made by adding 10 milliliters of reagent-grade HNO_3 from Honeywell Fluka ® ≥ 65 % of purity in 190 milliliters of distilled water. The second phase of the methodology is the precipitation step, which is focused on associating the previously prepared source solutions and conditioning for the nucleation of crystals and precipitation of a solid phase, further base for the heterogeneous catalyst. The Figure 2, as follows, summarizes the whole procedure. It consists of combining 200 milliliters of each source solution prepared – FSS and SSS – in a beaker at 50 °C with vigorous agitation. Further, an alkaline species is added to the aqueous medium dropwise together with a pH controlling measure via stripes – Hydrion® papers from Micro Essential Laboratory ® until reaching the value of 10.0 (± 1.0).

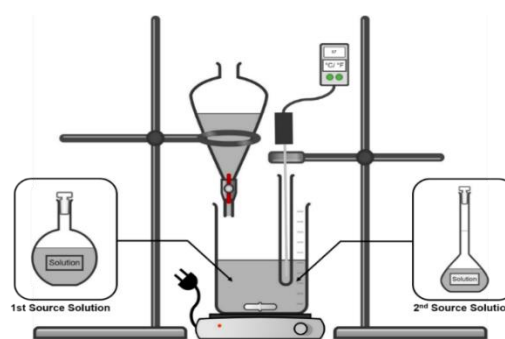


Figure 2 – Heterogeneous catalyst synthesis.
Source: Author and Chemix Lab Diagrams.

Depending on the catalyst preparation sample, different alkaline species were chosen to be added to the aqueous medium. Namely, they are the following ones: KOH, $((\text{NH}_4)_2\text{CO}_3$ and $\text{Ca}(\text{OH})_2$. This final powdered material, CaO, was used to make the alkaline suspension used to

raise the pH during the precipitation phase of the methodology. It was made by, straightforwardly, mixing 10 g of CaO in 270 milliliters of distilled water. Thus, containing ≈ 3.6 % wt. (3.5714 %) of Ca(OH)_2 in suspension. The third and last phase of the methodology is the aging/ crystallization step. It consists, basically, of allowing the final aqueous medium, obtained after adding the alkaline species, crystallize under a vigorous agitation at 50 °C for 6 hours in the same beaker. The main objective is to allow the recently nucleated crystals to combine between themselves and grow the crystals as to form the solid minerals. This is a very complex process which can involve agglomeration of particles, crystal growth, deconstruction of crystallites, redissolution and even Ostwald ripening process. After that, the agitation is ended and the whole recipient is moved to a laboratory oven at 60 °C for 24 hours to promote aging and precipitation.

The present work prepared the following catalysts samples via the above described methodology, henceforth, named Fly Ash – Egg Shell (FAES) catalysts:

- ❖ FAES N° 1 – FA and ES added directly to the HNO_3 solution, without preparation of FSS and SSS. Alkaline species used: $(\text{NH}_4)_2\text{CO}_3$. pH final: 10.0 (± 1.0). Crystallization time: 6 hours.
- ❖ FAES N° 2 – Alkaline species used: Ca(OH)_2 . pH final: 5.0 (± 1.0). Crystallization time: 6 hours.
- ❖ FAES N° 3 – Alkaline species used: KOH. pH final: 10.0 (± 1.0). Crystallization time: 6 hours.

- ❖ FAES N° 4 – Alkaline species used: $(\text{NH}_4)_2\text{CO}_3$. pH final: 10.0 (± 1.0). Crystallization time: 6 hours.
- ❖ FAES N° 5 – Alkaline species used: KOH. pH final: 10.0 (± 1.0). Crystallization time: 168 hours.
- ❖ FAES N° 6 – Alkaline species used: Ca(OH)_2 . pH final: 10.0 (± 1.0). Crystallization time: 6 hours.
- ❖ FAES N° 7 – Alkaline species used: Ca(OH)_2 . pH final: 10.0 (± 1.0). Crystallization time: 6 hours.
- ❖ FAES N° 8 – FA added directly to FSS and 10 ml of $\text{HNO}_3 \geq 65$ % of purity. Alkaline species used: Ca(OH)_2 . pH final: 10.0 (± 1.0). Crystallization time: 6 hours.

The last requirement to arrange the synthesized catalysts for the second section of this work is to submit each sample to a calcination step at 800 °C in a laboratory muffle furnace Nabertherm ® L9/ 12 at 800 °C. It was prepared other catalysts, namely, CaO, calcined at 800 °C and 900 °C (like FAES N° 1), *in natura* FA and NaOH, to serve as a comparison parameter with the FAES synthesized catalysts.

5.2 Catalytic Tests

The biodiesel production was done with a soybean – sunflower mixed vegetable oil from Manuel Serra S.A. ® (Serrata ® brand) and WFO collected from one canteen at IST. Both raw materials were used for a transesterification

methodology in a laboratory scale scheme, as described in Figure 3.

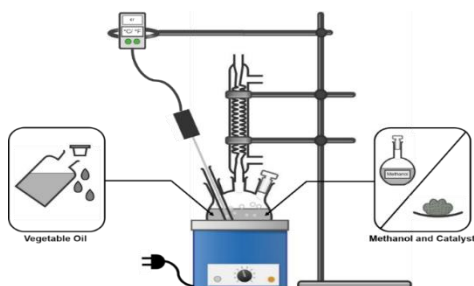


Figure 3 – Biodiesel production setup.

Source: Author and Chemix Lab

The reactional parameters and conditions were defined and standardized throughout the whole experiments. It was defined a pre-conditioning step for the raw material of 1 hour at 100 °C and a reactional temperature at 67 °C – methanol total reflux condition – under vigorous mixing. The methanol: oil molar ratio is 12:1 (excess of 300 %), the catalyst amount in % wt. is 2.5 and the reactional time is 6 hours. When NaOH and CaO were used, a preconditioning step (also named contact step) at 65 °C for 1 hour between methanol and the catalyst was required. Each experiment was repeated three (3) times, meaning four records for each catalyst. A mean molar mass for stoichiometric calculations was obtained using data from (Kincs, 1985) and an equation proposed by (Pighinelli, 2007).

5.3 Materials and Methods

The experimental part of this work focused on carrying several characterization analysis. Namely, acidity index, X-Ray Powder Diffraction (XRD), Attenuated Total Reflectance (ATR) - Fourier Transform Infra-Red (FTIR) Spectroscopy and a Scanning Electron Microscopy (SEM) with Energy Dispersive

Spectroscopy (EDS). The FAME yield quantification was evaluated by using the infrared spectral range 1410 cm^{-1} – 1480 cm^{-1} , (Soares Dias et al., 2019). The calculation methodology is done in terms of area ratio of a specific peak at 1436 cm^{-1} limited between 1427 – 1441 cm^{-1} and the whole area of the IR range, as indicated by Figure 4. Finally, the FAME conversion was calculated by a simple line equation similarly to what was previously done by (Rosset & Perez-Lopez, 2019).

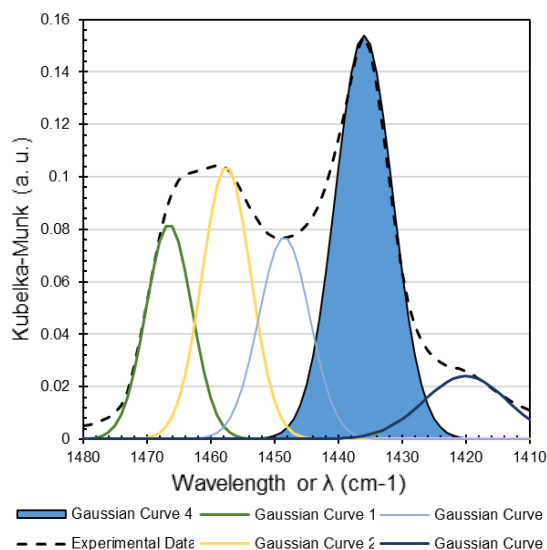


Figure 4 – FAME yield area calculation using Gaussian functions. Source: Author.

6. RESULTS AND DISCUSSIONS

The data collected for this work is presented in separated sections, specifically, focused on the raw materials, the catalysts (pre and post transesterification), and biodiesel and glycerin characterizations.

6.1.3 Vegetable Oils

It is possible to observe slight differences among the two vegetable oils, mainly related to the water content in WFO, corresponding to the

wide IR band in the range 3100-3600 cm^{-1} , as indicated by (Silverstein, Webster & Kiemle, 2005). The two oleaginous materials were submitted to and acidity index measurement to verify the level of FFA present in each. Results were, respectively, 0.09 mg KOH/ g_{oil} and 1.24 mg KOH/ g_{oil} .

6.2 Fly Ash-Egg Shells (FAES) Catalysts

Following the established experimental procedures, the 8 FAES catalysts were characterized by XRD and ATR-FTIR in two conditions. It is possible to observe that exists differences among the catalysts themselves, even more apparent when it is contrasted with the raw CFA and the CaCO_3 (PDF 5-586). It evident that the FA original structure, specifically, for FAES N° 1, since it is based on using this material directly, is not present in the XRD anymore. Mullite (16° , 33° , 35° and 41° , PDF 15-0776), hematite (33° and 50° , PDF 33-664) and quartz (21° , 27° , 50° and 61° , PDF 46-1045) also appear. Figure 5 depicts a XRD for all FAES calcined catalysts. For instance, focusing on the CaCO_3 peaks near 29° , 47° and 48° and clearly identified with the raw catalysts, they almost completely disappeared (in samples like FAES N° 2, 3, 4 and 5, the one near 29° is not existent at all), confirming the conversion to lime. Moreover, other peaks for lime standard are near 18° , 33° , 38° , 47° , 54° , 62° , 64° and 67° are identifiable. FAES N° 6 and N° 7 are composed by lime (PDF 82-1690), mayenite (PDF 9-413), brownmillerite (PDF 30-226), wadalite (PDF 81-1135) and andradite (PDF 10-288), with traces of periclase (PDF 45-0946). These two catalysts (N° 6 and N° 7) are structurally similar, sharing all

the synthesized compounds, with only one more discrepant XRD feature at 33° , absent for FAES N° 7, which is, associated to brownmillerite.

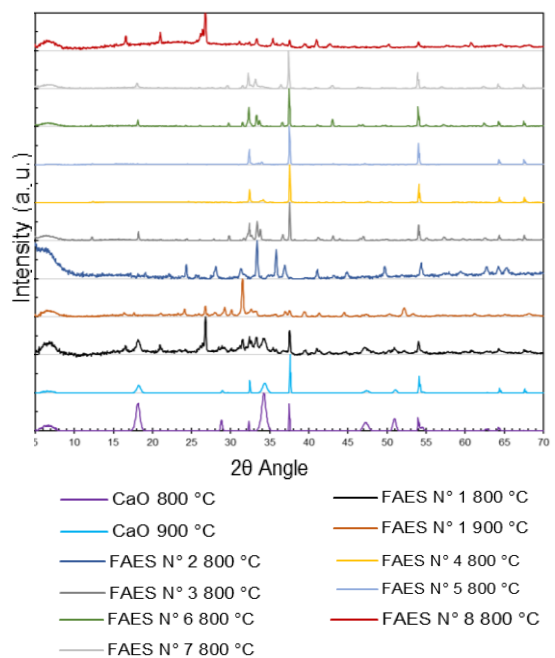


Figure 5 – XRD diffractogram for the calcined FAES catalysts. Source: Author.

The ATR-FTIR spectra of all the synthesized FAES catalysts, it is possible to observe that all the catalysts have a similar structure as compared to the CaCO_3 , with a slight difference between 900 – 1200 cm^{-1} . Figure 6 presents the FAES calcined catalysts.

To support the discussion related to the FAES catalysts, the SEM images presented in Figure 7 for all the calcined FAES catalysts synthesized. It is interesting to observe near surface variation among the different synthesized catalysts, which are very connected to the precipitated species (e.g. lime, mayenite, brownmillerite, wadalite, andradite and periclase) based on methodology variations. FAES N° 6 and

N° 7 are very similar in terms of XRD diffractograms and SEM images.

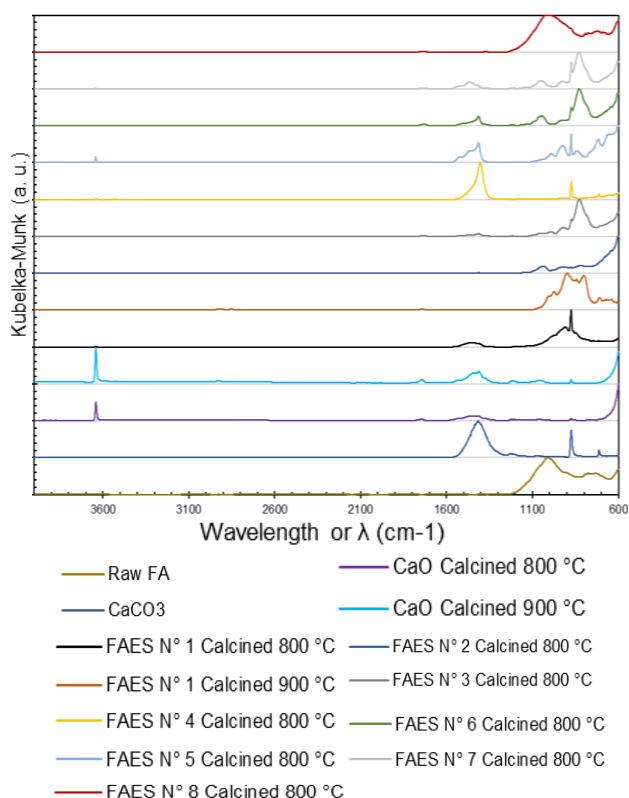


Figure 6 – FTIR of all FAES calcined catalysts. Source: Author.

Another information very much valuable obtained from SEM analysis is the EDS, showed in Table 1, which can determine the chemical elements superficially existent in the catalysts. This is important as to confirm the formation of several of the minerals identified by XRD and FTIR and show no lixiviation to biodiesel.

Table 1 – SEM-EDS data for FAES catalysts.

	FAES N°6	FAES N° 7	FAES N° 7 (PR)
Ca	24.47	35.32	31.85
Mg	3.58	1.68	2.81
Al	2.81	1.28	2.32
Fe	3.63	1.78	4.03
Cl	1.43	0.91	2.12

Source: Author.

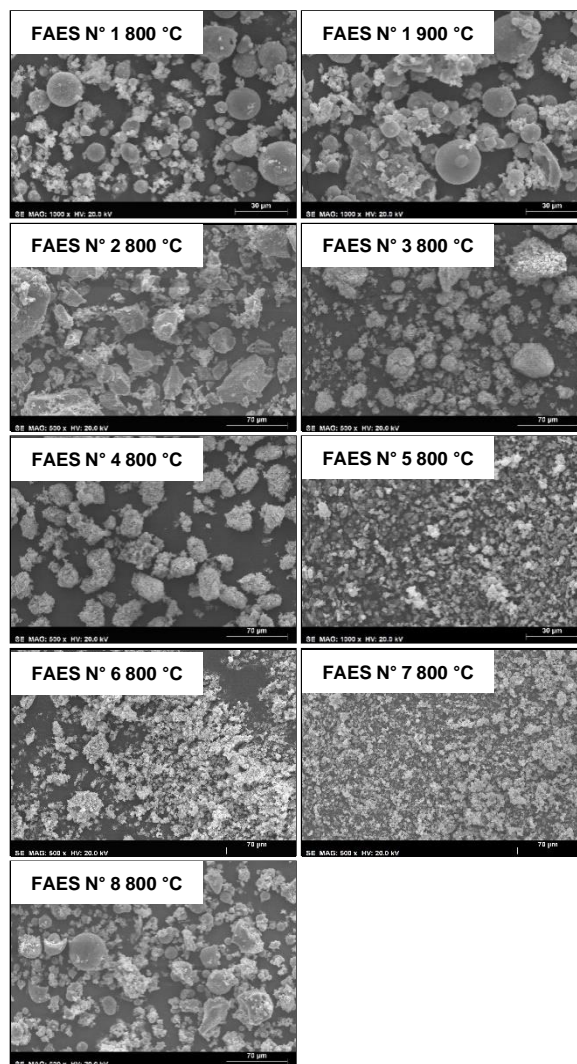


Figure 7 – SEM images for all the calcined FAES catalysts. Source: Author.

6.3 Biodiesel

All the catalysts developed in this work were evaluated with soybean-sunflower oil and WFO (for selected catalysts). Evaluating the experimental data in the Table 2, it is perceivable that NaOH conversion for soybean-sunflower and WFO oils are always around the 80 % level. Hence, it can be considered as a reference level in terms of quality and conversion to be reached by any catalyst evaluated under the same FAME conversion methodology used in this work. It is

possible to perceive two major regions in both figures, one in the upper part, between 70 % and 90 %, and another in the bottom part, between 30 % and 0 %. The former contains almost all the heterogeneous catalysts, all of them not containing FA in the synthesis methodology, only the acid leachate. In relation to the latter, FA is part of the synthesis methodology for FAES N° 1 900 °C and N° 8 800 °C. For FAES N° 2 800 °C, even though it does not contain FA, the methodology fixed a pH of 5, what probably not favored a good precipitation of chemical elements and a further formation of minerals.

Table 2 – FAME conversion data (%).

	Soybean-Sunflower	WFO
Raw FA	0.00	0.00
NaOH	77.60	79.01
CaO 800 °C	80.60	83.03
FAES N° 5 800 °C	81.87	-
FAES N° 6 800 °C	80.59	-
FAES N° 7 800 °C	81.30	77.04

Source: Author.

This is corroborated by data for FAES N° 6 800 °C and N°7 800 °C, which has an equal synthesis methodology, only differing in terms of pH (10 in these two cases). It is evidenced that the heterogeneous FAES catalysts synthesized have a very good performance for biodiesel conversion, too similar and superior to NaOH (77.60 %) and traditional and alternative materials CaO (80.60 %). FAES N° 5, N° 6 and N° 7 have an average FAME conversion of, respectively, 81.87 %, 80.59 % and 81.30 %. This can support the main driving force of this entire work. In fact, the literature is rich in examples of valorization of FA for heterogeneous

catalyst development, such as (Muriithi et al., 2017; Kuwahara & Yamashita, 2015).

7. FINAL CONSIDERATIONS

The data collected via XRD, FTIR and SEM-EDS indicate the most prominent catalysts developed were FAES N° 6 and FAES N° 7, both following an equal methodology, and holding very equivalent crystalline structures. Beyond that, these catalysts achieved equivalent conversion levels for FAME when compared to traditional catalysts, homogeneous (*i.e.* NaOH) or heterogeneous (*i.e.* CaO).

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