Calcium rich food wastes based catalysts for biodiesel production

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Abstract

Today most of the energy is based on fossil fuels, which have a negative impact on the environment. In order to produce a sustainable first generation biodiesel, low grade raw materials were used. Biodiesel was produced using waste frying oil (WFO) and lime catalysts obtained from calcium rich alimentary wastes. The catalysts were prepared by high temperature calcination of mollusc, crab, shrimp, eggs shells and cuttlebone. The majority of the Ca rich wastes were crystalline with patterns similar to calcite and aragonite. After calcination at 800 ℃ for 3 h, the chalky white materials, presented XRD patterns ascribable to lime but with different crystallinities.

All the powdered calcined materials were able to catalyse the methanolysis of soybean oil. A FAME yield around 96 % was obtained after 2.5 h of reaction. In analogous conditions, the use of WFO decrease the catalytic performances with a considerable reduction on the FAME yield (65 %) with simultaneous production of soap. The use of WFO and soybean oil mixtures allowed to attenuate such loss of catalytic performances.

The post reaction catalysts showed formation of a calcium diglyceroxide phase which can be related with soap formation and catalyst deactivation when more acidic oils are used. Thermograms of the post reaction catalysts showed that considerable amounts of oil remain adsorbed on the catalysts.

The reuse of catalysts without intermediate reaction showed that catalysts are stable. When pure WFO was used the reused catalysts showed improved performance probably due to formation of calcium hydroxide and Calcium diglyceroxide.

**Keywords:** food wastes, biodiesel, lime catalyst, heterogeneous catalysis.

1. Introduction

Nowadays, most energy used is based on fossil fuels (Fig 1), but the negative impact on the environment and energy crises pushed the research to alternative renewable and eco-friendly energies.

Biodiesel is an alternative biofuel, viewed as a feasible renewable fuel for diesel engines, which can be produced from renewable sources. It presents several advantages in its use, like; it's safe, non-toxic and biodegradable [1]. In fact, the transportation sector is major contributor to greenhouse gases emissions (GEE) and it is imperative to find a low carbon fuel for this sector. Biodiesel leads also, to a substantial reduction of GEE's emissions, mainly CO_2.

Today, biodiesel can be produced by alcoholysis from vegetable oils, animal fats or even from recycled greases from food industry, restaurants, or domestic waste [1, 2]. In 2010, the amount of waste frying oils (WFO) manufactured in Portugal was 43,000 – 65,000 t [3]. The production of biodiesel in 2014 was 340,781 t, corresponding to 324,200 t from virgin oil and 16,581 t of WFO in Portugal [4]. These numbers show that just a small amount of biodiesel is manufactured from WFO, which calls for a substantial increase of this utilization.

In general, biodiesel is manufactured by transesterification of triglycerides with short-chain alcohols such methanol using a catalyst. Homogeneous or heterogeneous, acid or basic catalysts can be used.
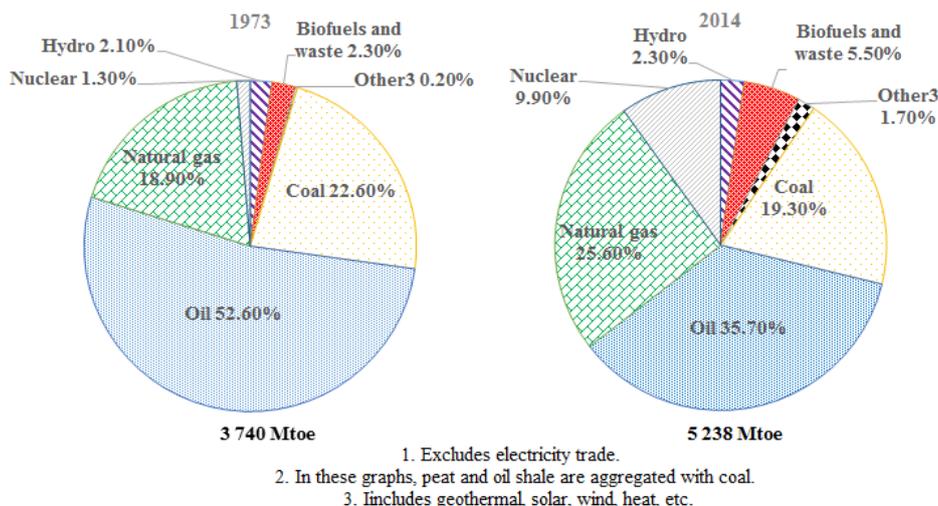
Figure 1 – World energy mix, excluding electricity, for 1973 and 2014 (adapted from 2015 Key World Energy Statistics, International Energy Agency).

Several solids can be used to catalyse the transesterification/esterification of vegetable oils [5]. Lime catalysts have been extensively studied for the methanolysis of vegetable oils. [6] In a recent review on catalysts for biodiesel, Avhad and Marchetti (2016) stated that among basic catalysts, lime was found to be gaining consistent scientific as well industrial attention because of its high basicity, low solubility in methanol, and it is easy derivatization from natural resources [7]. Natural calcium sources from wastes such as eggshells, molluscs and crustacean shells, are calcium rich materials available from food industries that can be used as cheap raw materials to produce CaO by calcination process. [8, 9, 10, 11]. Many researches used eggshells to prepare CaO catalysts for biodiesel production. Also mollusk shells are reported as raw materials for lime catalysis [12, 13, 14].

Only in 2015, in Portugal, 749 t of crustacean and 19,172 t molluscs were captured. Egg production, for consumption only, in last year was 106,784 t, whereas 10 % weight of eggs is shell, corresponding to approximately 10,678 t [15].

In the present study, the solid and liquid wastes from food industry in Portugal were selected for biodiesel production. In this way, wastes are reused, minimizing the solid wastes costs and biodiesel production costs.

In order to improve the knowledge on the CaO/biodiesel catalytic system, several catalysts were prepared from food wastes with high content of Ca: eggs shells, mollusc shells and shrimp shells. Particular emphasis is given to the post reaction catalysts characterization in order to characterize the deactivation processes usually mentioned for such catalysts when low-grade oils are used.

2.   Materials and Methods
2.1 Materials and catalysts preparation

The semi-refined **vegetable** oil (soybean) was obtained from commercial source and the WFO were collected from restaurant and ISEL canteens. The samples were filtrated and dried until 110 ºC to remove remaining water content. The acidity index of the several samples collected, were obtained through the European Standard NP EN 14204.

The food wastes were obtained from source separated domestics wastes and same crustaceous (mussels, rose shells mollusc, clams, conch and limpet) were collected from the beach. The eggshells, cuttlefish bone were not boiled, while the shrimps, scallops, crabs were cooked. All wastes were washed, dried and reduced to powder using ceramic mortar. The catalysts were prepared by calcination in an oven at 800 ºC during 3 h, with a heating rate of 5 ºC/min. The calcination temperature was chosen from the thermal degradation profile of each raw material obtained under air flow (30 ºC/min).

2.2 Oils and catalysts

The oils (soybean and WFO) were characterized by the determination of acidity, according to European Standard NP EN 14204. Procedure details are given elsewhere [16].

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The catalysts, before reaction, were extensively characterized by physical-chemical methods including FTIR (reflectance mode), X-ray diffraction (XRD) and SEM-EDS. The surface basicity was assessed by Hammett indicators as described elsewhere [17]. The raw Ca wastes were characterized by XRD in order to identify the Ca crystalline phases. The diffractograms were recorded with a Rigaku Geigerflex diffractometer with Cu Kα radiation at 40 kV and 40 mA (2 o/min). Additionally fresh and post reaction catalysts were characterized by infrared spectroscopy using a reflectance mode to evaluate the surface adsorbed species [18]. A FT-MIR equipment from BOMEN (FTLA2000-100, ABB) with a DTGS detector was used. A horizontal total attenuated reflection accessory (HATR), from PIKE Technologies, with a ZnSe crystal was used. Sixty-four scans were accumulated for each spectrum to obtain an acceptable signal-to-noise ratio.

The post reaction catalysts were also characterized by thermogravimetry, under air flow, in order to evaluate the reaction species which remain adsorbed [19] and thus to infer about their stability.

2.3 Reaction Procedure

The transesterification reaction was carried out in a 500 mL round bottom reactor equipped with a condenser and a magnetic stirrer. The reaction temperature was kept at methanol reflux temperature by using a nest shape heating jacket with temperature control. A mixture of catalyst 5 % wcat/woil and methanol was added to 100 g of oils (soybean, WFO and WFO/soybean mixtures) both were pre-heated to methanol reflux temperature. The methanol/vegetable oil molar ratio adopted was 12:1 and the time of reaction implemented was 2.5 h. At the end of the reaction time, the catalysts were removed by filtration and the biodiesel products were transferred into a decantation funnel, in order to separate the phases formed. More details on the experimental procedure are given elsewhere [19].

2.4 Determination of biodiesel yield

The biodiesel oily phase, containing the FAME and the unreacted oil, was characterized by thermogravimetry in order to evaluates the reaction extend [20]. Liquid Samples (100-200 mg) were heated from room temperature to 1000 ºC under an air flow 20 ºC/min. The collected thermal degradation profiles (TG) were differentiated (DTG) to underline the different degradation processes. The mass composition was computed using the equipment software.

The thermal decomposition of raw oil, WFO and WFO/soybean mixtures were used as standard as well as a purified FAME sample obtained by classic methanolysis using sodium methylate. The glycerine quality was evaluated for each reaction batch and the catalysts stability was studied by re-using the same sample in consecutive reaction batches.

3. Results and discussion
3.1 Material Characterization

Acidity of soybean oil was 0,567 mg KOH/g and the acidity index of WFO was 2,180 mg KOH/g.

In Figure 2, it is possible to visualize the DTG profiles of the raw Ca wastes, used as frsh catalysts. Mainly, the peaks correspondents to signifficative weight losses, 500 ºC and, in the range of [800 – 900[ºC, are addressed, respectively, to $Ca(OH)_2$ thermochemical decomposition in calcium oxide and, CaCO3 thermochemical decomposition in calcium oxide, also.

The raw Ca wastes were, also characterized by XRD (see Figure 3) in order to identify the Ca crystalline phases. Calcite and aragonite were the main calcium carbonate phases of the Ca containing raw materials, as well, Portlandite as calcium hydroxide crystalline phase. Only the shrimp shells sample presented low crystallinity which difficult the identification of Ca phases. As expected, taking into account the thermogravimetry data, the samples obtained at 600 ºC are mainly calcium carbonate with different degrees of crystallinity depending on the nature of the raw materials. Some of those samples presented grey shades, which is ascribable to carbon residues resulting from incomplete combustion of the organic compounds present in the raw materials.

The chalky-white samples obtained at 800 ºC displayed XRD patterns belonging to lime (CaO) with crystallites sizes around 1,000 Å.
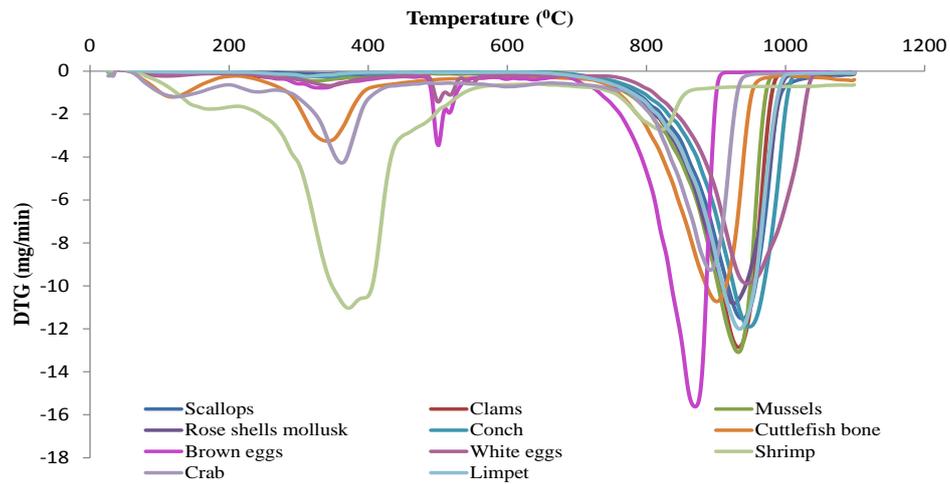
Figure 2 – Thermal degradation differential profiles (DTG) of the raw Ca wastes (under air; 30 ℃/min)
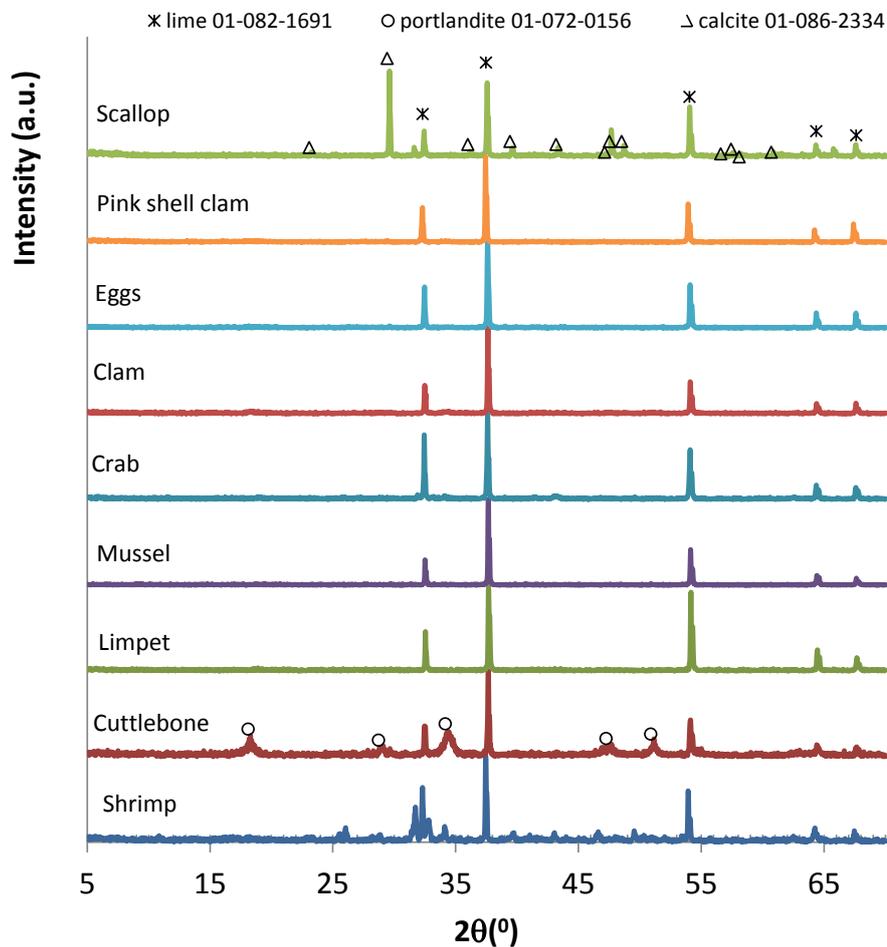
Figure 3 – XRD patterns of fresh catalysts prepared by calcination at 800℃ (overlaid lime, calcite and portlandite standards (JCPDS files).

Figure 4 shows the DTG profiles of 9 raw Ca wastes as fresh catalysts. The peaks corresponding to 500 ℃ and 800 ℃ are addressed to thermochemical process of calcium hydroxide and calcium carbonate, respectively; into calcium oxide.
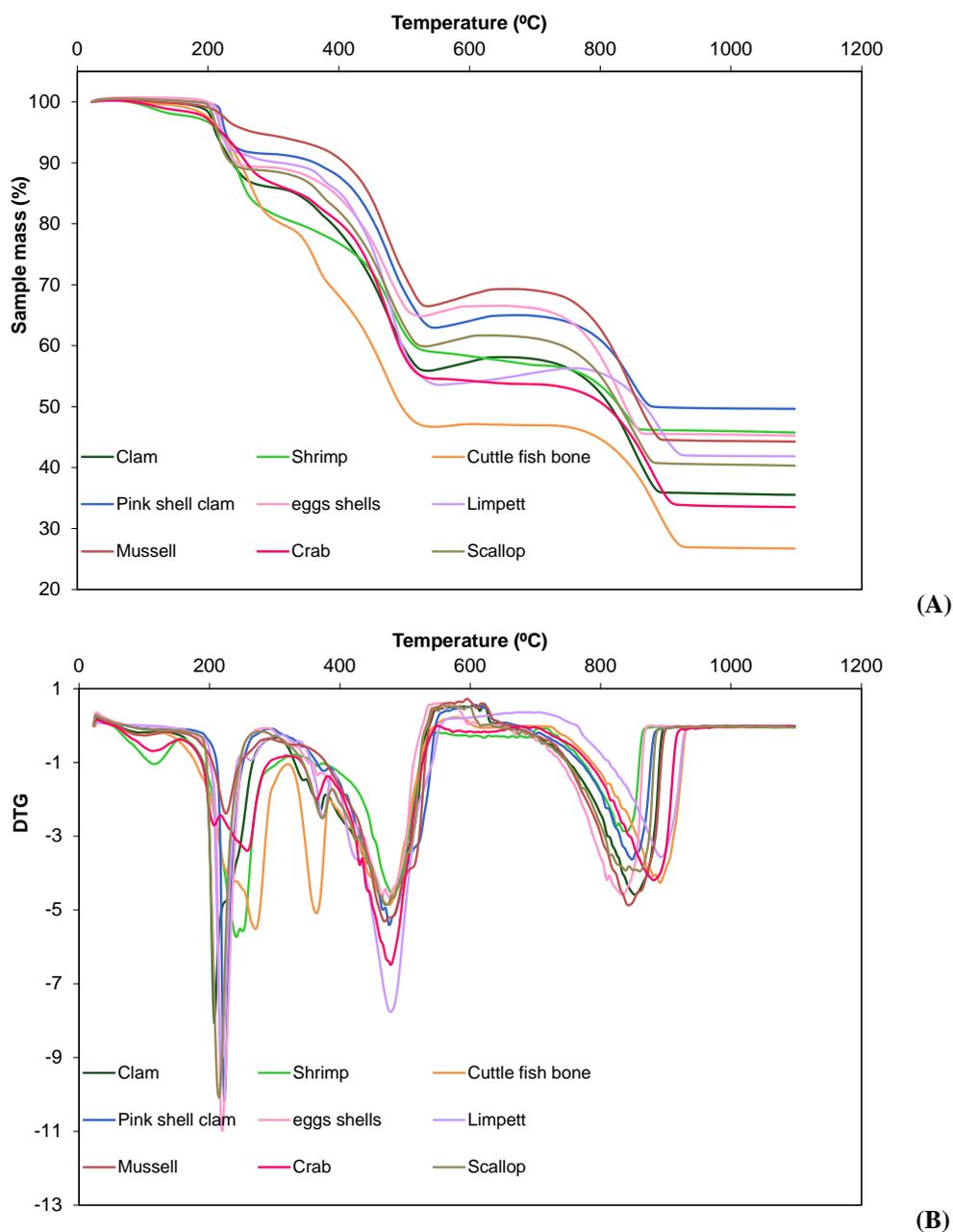
Fig 4 - Thermograms of the post reaction catalysts with refined soybean oil as raw material (under air; 30ºC/min): (A) – TG lines; (B) – DTG lines.

3.2 Biodiesel production

Biodiesel purity was measured through the fatty acid methyl esters content (% FAME), according with described in section 2.4. The TG and DTG profiles are showed in figure 4 for several Ca rich alimentary wastes, all of them with soybean oil as raw material employed in the transesterification reaction. It's possible to see that, the weight losses and DTG profiles observed in that figure, at 200 ºC, 500 ºC and 800 ºC corresponds, all of them, to thermochemical transformations of catalysts bulk structures. At 200 ºC, it occurs the thermochemical process of calcium diglyceroxide conversion into calcium carbonate, at 500 ºC, the thermochemical conversion of calcium hydroxide into calcium oxide and, at 800 ºC, the conversion of calcium carbonate into calcium oxide, as related elsewhere [5, 17, 18]. This means that, all post-reaction samples contains, in bulk and/or surface catalyst, calcium diglyceroxide, calcium hydroxide, calcium carbonate and, probably, some calcium oxide. More characterisation techniques will be needed to confirm these sentences, like XRD, FTIR and SEM.

Nine samples of raw Ca wastes catalysts, calcinated at 800ºC and, after one transesterification step with refined soybean oil was characterized also, by XRD, according with section 2.2. The post reaction samples were

characterized by XRD in order to evaluate eventual modifications leading to deactivation, according with Figure 5.
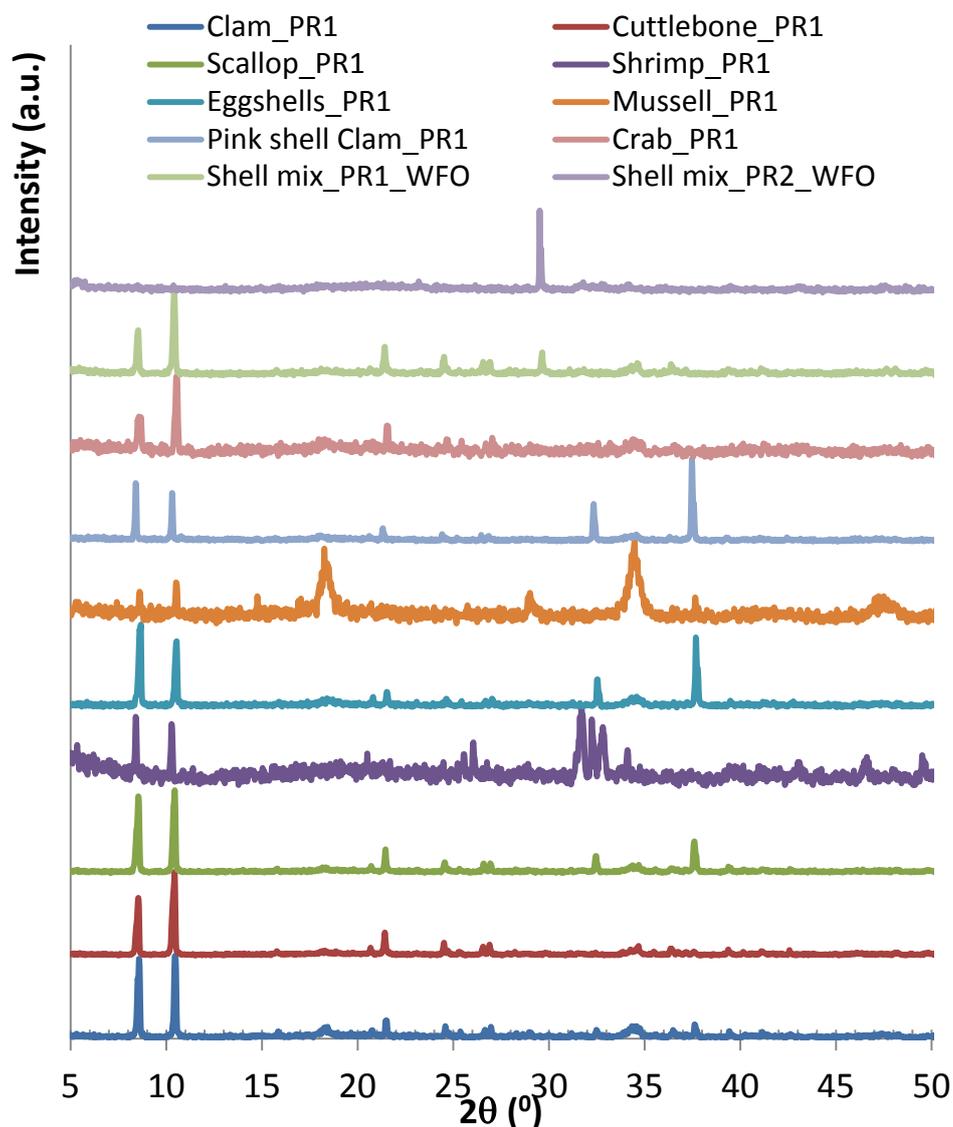
Figure 5 – XRD diffractograms of raw Ca wastes natural catalysts, calcinated at 800ºC, after one transesterification step, with refined soybean oil.

The diffractograms in this figure showed that lime XRD features were almost vanished leading to XRD patterns belonging to calcium diglyceroxide and calcium methoxide [21]. Only the mussel derived post reaction catalyst presented lines ascribable to nanocrystalized portlandite (wide lines). The shellmix catalyst after reaction batch with pure WFO showed a similar XRD pattern with lines belonging to calcium diglyceroxide and methoxide. After the second reaction batch, the shellmix catalyst showed a XRD pattern which cannot be identified with none of the Ca phases previously reported.

Table 1 and 2 and, also, Figure 6, shows the fatty acid methyl esters content (FAME yield) in several Ca wastes catalysts, used in the transesterification process, in the production of biodiesel.

Only the catalysts prepared from shrimp shells and cuttlebone presented FAME yield lower than 95 % probably due to the lower crystallinity and purity (other Ca phases in addition to lime) of the fresh catalysts. A mixture of catalysts was prepared with equivalent amounts of lime produced with the different raw materials but the cuttlebone was excluded. The resulting catalyst was named Shellmix and, the correspondent FAME yiels are showed in table 2.

Table 1 – FAME yield using WFO and WFO/Soybean mixtures assessed by thermogravimetry (under air, 30ºC/min), using the lime catalysts from Ca rich alimentary wastes (5% w_{cat}/w_{oil}; methanol/oil = 12; 2.5 h).

Catalyst	Raw-material	FAME yield (%)
Egg Shell		97.2
Limpet		96.4
Pink Shell clam		97.1
Cuttlebone	Refined soybean oil	86.4
Shrimp Shell		94.2
Scallop batch#1		95.3
Scallop batch#2		76.3
Scallop	WFO + ref. soybean oil (1:1)	90.9
Shell mix	WFO + ref. soybean oil (3:1)	82.0
Shell mix	WFO	62.5
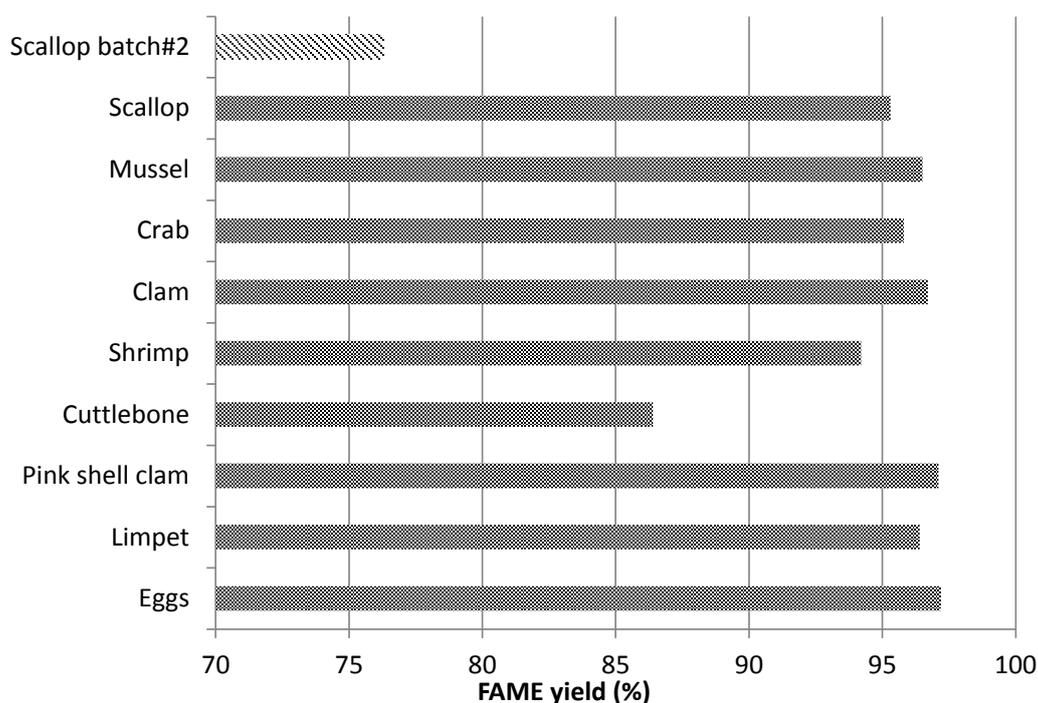
Figure 6 – FAME yield, assessed by thermogravimetry, obtained for soybean oil using the lime catalysts from Ca rich alimentary wastes (5% w_{cat}/w_{oil}; methanol/oil = 12; 2.5 h).

Table 2 – FAME yield using WFO and WFO/Soybean mixtures assessed by thermogravimetry (under air, 30ºC/min).

Catalyst	Raw-material	FAME yield (%)
Scallop	50%WFO_50%Soy	90.9
Shellmix		82.6
Shellmix	75%WFO_25%Soy	82.0
Shellmix batch#1	WFO	62.5
Shellmix batch#2		88.4

4. Conclusions

First generation biodiesel, a mixture of fatty acids methyl esters, was produced using low value raw materials in order to obtain a cheaper and sustainable fuel. Frying oils and calcium rich shells (eggs and mollusk among others) wastes from alimentary industry were used.

The raw Ca rich materials, mostly calcite ($CaCO_3$) and Portlandite ($Ca(OH)_2$), were calcinated at 800ºC to produce lime catalysts.

In standard conditions (methanol reflux temperature, 5% (wcat/woil) of catalyst and methanol/oil=12 molar ratio), high FAME yields were obtained for all the tested catalysts when alimentary refined soybean oil was used. For pure WFO a decline of the catalyst activity was observed with lower FAME yield and soap formation. These drawbacks are due to the WFO acidity, which was quite higher, about 2 mg KOH/g oil. Those drawbacks were overcome using WFO/soybean oil mixtures. Data pointed out that WFO can be processed mixed with neutral oil without significant loss of the catalytic performances thus avoiding the use of acid catalysts which require higher reaction temperature and pressure conditions, for the same reaction time.

The catalysts deactivations were investigated using the same catalyst sample in consecutive reaction batches without intermediate reaction and, only, with a simple washing step with methanol and, dried overnight at 105ºC. As expected, the WFO promotes faster catalyst deactivation than the neutral oil. The decline of the catalyst activity can be attributed to leaching of calcium diglyceroxide formed (homogeneous contribution) which, in presence of WFO, forms soap, which leads to more difficult biodiesel process purification and a decay of the biofuel mass yield.

Finally, it's possible to addressed that, these natural catalysts, rich in Ca compounds are very active and suitable for biodiesel production through the transesterification process, through a alkaline heterogeneous catalysis mechanism, even with WFO as raw-material, but with lower acidity or, mixed with refined vegetable oils.

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