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BIODIESEL PRODUCTION FROM MICROWAVE IRRADIATED REACTOR USING HOMOGENEOUS AND HETEROGENEOUS CATALYSIS

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Abstract. *Biodiesel was successful produced in a microwave irradiation reactor using homogeneous and heterogeneous catalysis. The reaction time was significantly reduced compared to the conventional process. In only one minute of reaction, the methyl ester (FAME) conversion obtained was 98.9% with the homogeneous catalyst and within 15 minutes, the heterogeneous catalysis accomplished 100%. In addition, a heterogeneous catalyst was developed based on wasted eggshells. The results indicated that the eggshells treated with KOH presented great potential to be used for microwave-assisted transesterification reactions of oils. The physico-chemical properties of the catalysts were characterized by XRD and TGA-DTG.*

Keywords: *biodiesel, homogeneous catalysis, heterogeneous catalysis, microwave reactor, wasted eggshells*

1. INTRODUCTION

The biodiesel is a renewable fuel, which is produced and used worldwide in large scale, mainly for being an excellent alternative to petroleum diesel (Chen *et. al*., 2015) . It is obtained by a transesterification process of vegetable oils or animal fats in the presence of alcohol using acidic or basic catalyst (Balat *et al*., 2010).

Currently, researches and investments are focused on looking for new biodiesel production technology employing other heating techniques such as microwave and ultrasound irradiation. Leadbeater and Stencel (2006) reported that by using microwaves irradiation, they achieved a methyl esters conversion rate of 98 % using a molar ratio of 1: 6 (oil/alcohol) and 5% of NaOH or KOH catalyst.

The process of microwave irradiation accelerates the reactions, mostly because the energy is dissipated directly to the reaction components, resulting instantaneously high temperature. The transferred heat is more effective than the conventional heat, and the reaction can be completed in a much shorter time (Motasami and Ani, 2012). In addition, an experimental and theoretical study of molecular simulation performed by Asakuma et al. (2011) concluded that microwave irradiation promotes flat triglyceride molecules causing a reduction of the dipole moment and activation energy, increasing the vibration intensity of the carboxylic grouping. Thus, with the flat molecule, the space for alcohol attack the triglyceride molecule is amplified favouring the transesterification reaction.

Besides the significant reduction in reaction times, the main advantages of using a microwave reaction synthesis are: reduction of the undesired products; higher heating rates (extremely fast heating); energy saving; greater selectivity and efficiency and reduction in operating costs (Octavio and Miranda, 2011).

Also, several studies highlight the development and production biodiesel using heterogeneous catalysts. The transesterification reaction for heterogeneous catalysts provides cleaner biofuels, which are more selective, that separate easily from the reaction mixture, reduce process steps and can be reused avoiding waste (Borges and Diaz, 2012). Literature studies show that the use of calcium oxide, magnesium oxide, strontium oxide, and mixed oxides are generally the most commonly studied (Borges and Diaz, 2012; Tariq et al., 2012). The calcium oxide is highlighted for being the most used oxide due to the CaO long life cycle, high catalytic activity, low solubility, especially with methanol, and requiring mild reaction conditions. Furthermore, the CaO can be easily found in various natural or industrial waste sources such as eggshells, and shellfish shells (Cho and Seo, 2010; Viriya-Empikul et al., 2010).

In recent years, some studies also reported biodiesel production using heterogeneous catalysis irradiation by microwave. Koberg et al., (2012) worked with strontium oxide (SrO) in the production of methyl esters with a power of

1100 W and they achieved 99.8% conversion in 10 seconds. Khemthong et al., (2012) investigated the production of biodiesel by microwave irradiation using calcium oxide from eggshells (CaO). The results showed that with a molar ratio ethanol/oil 18:1, power of 900 W, 15% of catalyst, and four minutes of reaction, a conversion rate of 96.7% was obtained.

In this study, the purpose is to evaluate the feasibility of an effective biodiesel production in microwave reactor employing the homogeneous and heterogeneous catalysis in order to optimize parameters such as reaction time, molar ratio alcohol/oil and catalyst percentage. Also it aimed to develop a heterogeneous catalysis based on wasted eggshells. According to Oliveira et al. (2009), eggshells wastes correspond to roughly 5.92 million tons per year of worldwide.

It is believed that the production of a renewable fuel with a cheap and effective production process that utilizes industrial waste is a huge step to remedy many problems of the contemporary society.

2. METHODOLOGY

2.1 Biodiesel production from microwave-assisted

The production of biodiesel was performed by the transesterification reaction of the ABC soybean oil brand purchased at local shops in the city of Belo Horizonte (Brazil). The alcohol used in all reactions was grade methanol (100%, Synth, Brazil). Two types of catalysts were used: a homogeneous and heterogeneous. Sodium methylate (30% solution in methanol - NaOCH3, ISOFAR, Brazil) was used for the homogeneous catalyst and the heterogeneous catalyst was developed using wasted eggshells, which were acquired from local food markets.

All the reactions were carried out at microwave reactor (Start Synth - Milestone, Italy) in order to evaluate the prospects. The power and temperature were kept constant in every reaction being 800W and 200º Celsius, respectively.

Each transesterification reaction forms fatty acid methyl esters (FAME) and glycerol. The product (FAME´s) and sub product (glycerol) separation was performed by decantation process using a separating funnel. The decantation time for each sample was 24 hours. Figures 1 and 2 show a decanted sample from a homogeneous and a heterogeneous catalysis reaction, respectively.

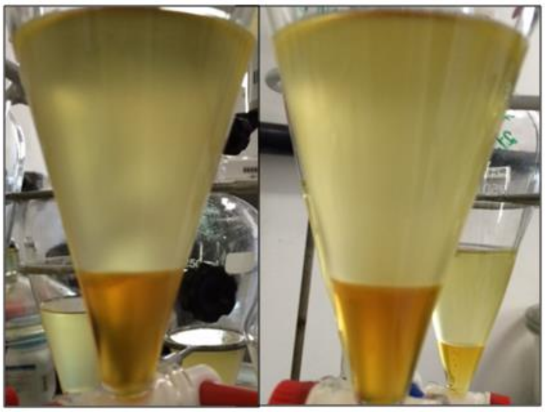

Figure 1. Biodiesel and glycerol produced in homogenous catalysis

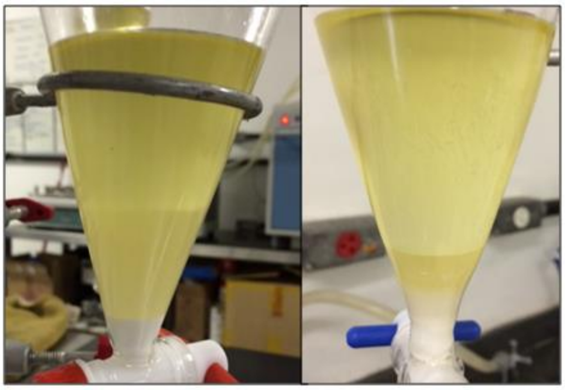

Figure 2. Biodiesel, glycerol and catalyst produced in heterogeneous catalysis

After the biodiesel separation, a purification stage was necessary to remove eventual residue of glycerol and catalyst. A dry washing system was applied adding the Amberlite BD10DRY as adsorbent. The quantity of adsorbent added to the solution corresponded to 10 % of the biodiesel (FAME) weight. The solution of biodiesel and adsorbent was shacked to orbital shaker at 200 rpm for two hours. Subsequently, for eliminate the excess of alcohol, the biodiesel was submitted to a rotary-evaporation heated at approximately 120º Celsius.

The purified FAME were analyzed by gas chromatography, performed in accordance with EU norm EN 14103, using a GC–FID HP7820A apparatus (Agilent Technologies, USA) equipped with an auto-sampler (Agilent 7386B series) and data acquisition software EZChrom Elite Compact (Agilent Technologies, USA). Separations were accomplished at a constant hydrogen flow rate of 3 mL min^{-1} in a 15-m long HP-INNOWAX capillary column (0.25 mm I.D. and 0.25 µm film thicknesses). Samples (1 µL) were injected in a split ratio of 1:50. Injector temperature was 250ºC and the temperature program of the oven started with an initial temperature of 120ºC, followed by an increase in temperature up to 220ºC at a rate of 7ºC/min for 12 minutes.

2.2 Heterougenous catalyst prepartion and characterization

The waste chicken white eggshells obtained to local market were washed with distilled water many times to remove impurities. Then, the eggshells were dried in a muffle for three hours at 80º Celsius, followed by twelve hours at 100º Celsius. In the biodiesel production reaction were tested pure calcined eggshells and KOH-doped eggshells. The KOH-doped catalysts were prepared using wet impregnation method at concentrations of 10, 30 and 50% weight of KOH by weight of eggshell.

Afterwards, the dried eggshells were calcined at 1000°C in air atmosphere at a heating rate of 5°C/min for 1 h. In all cases, the final product was a fine white powder. Figure 3 showed the doped eggshells with KOH (50%) before and after calcination respectively.

Figure 3. Heterogeneous doped catalyst with 50% of KOH before and after calcination, respectively

PHILIPS X-Ray (XRD) diffractometer for powder samples (PANALYPTICAL) with the X'Pert-APD system, PW3710/31 controller, 1830/40 PW generator, and PW 3020/00 goniometer was used to analyze heterogeneous catalysts. The thermogravimetric techniques also were employed to simulate the muffle effects with heating gradient was 5º Celsius per minute until achieving 1000º Celsius, and the insufflation of synthetic air with a flow rate of 100mL per minute.

3. RESULTS AND DISCUSSION

3.1 Homogeneous and heterogeneous catalysis

Given the results obtained with the gas chromatography, it was possible to quantify the grade of methyl esters formed and verify which parameters: molar ratio oil/alcohol, catalyst percentage and time, were great to the production of biodiesel in a microwave reactor using homogeneous and heterogeneous catalysis.

The results showed that the best conversion rate for homogenous catalysis was obtained with 3% of catalyst (sodium methylate) in 7 minutes of reaction, resulting in 99,1% methyl esters conversion (Fig. 4). Even in one minute of reaction the esters yield formed were 98,9%, showing that noticed that the transesterification reaction by microwave irradiation is highly promising comparing to the conventional heat for the same reaction conditions (Fig. 5).

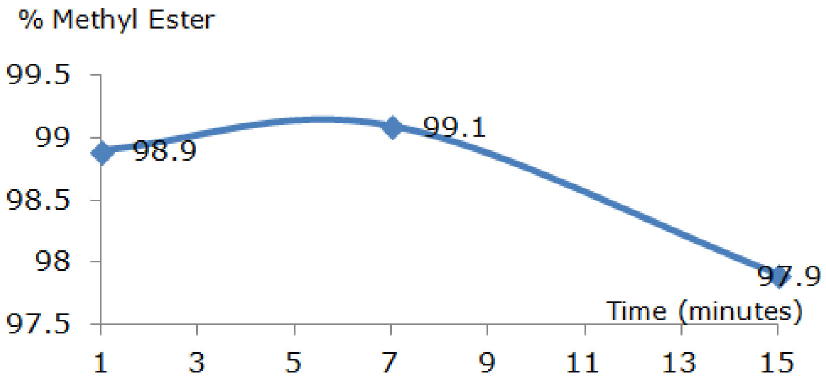

Figure 4. Time variation for homogeneous catalysis
Note: the reactions were performed with 3% of catalyst and molar ratio of 1:6 (oil/alcohol)

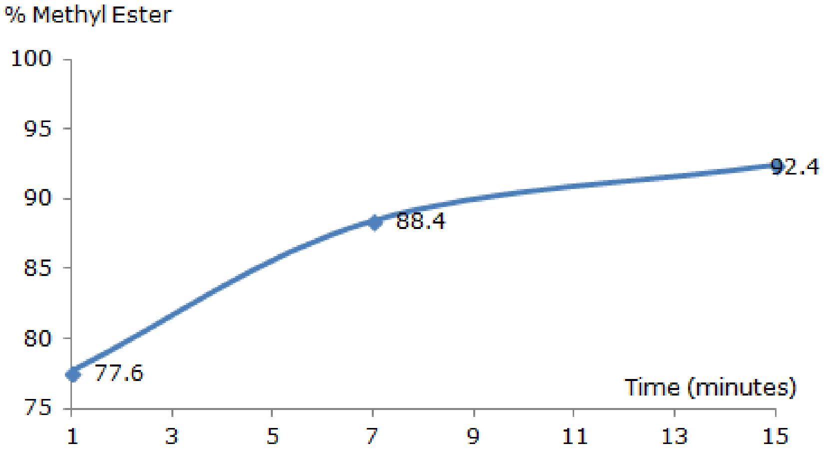

Figure 5. Time variation for conventional method
Note: the reactions were performed with 3% of catalyst and molar ratio of 1:6 (oil/alcohol) at 60° Celsius

For heterogeneous catalyst, the best results were acquired when the doped catalyst contained 50% of KOH. Figure 6 shows that for fifteen minutes, the 3% and 5% catalyst reaction achieved esters percentage of 97% and 100%, respectively.

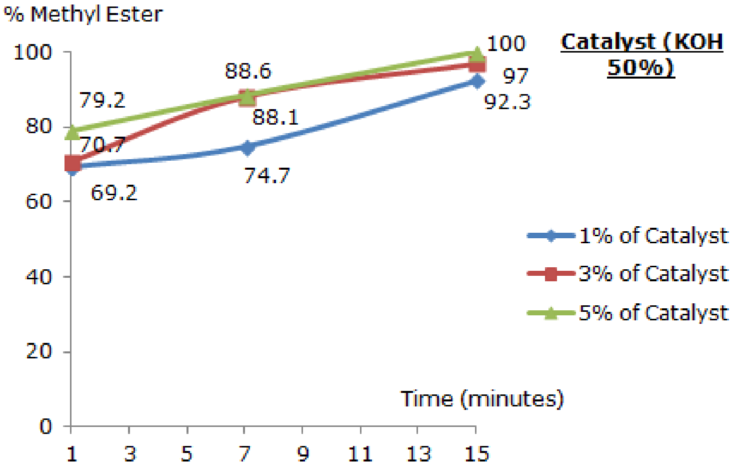

Figure 6. Transesterification reaction results with heterogeneous catalyst (50% KOH)
Note: all the heterogeneous reactions were performed with a molar ratio of 1:6 (oil/alcohol)

Figure 7 and 8 showed the results obtained with 10% and 30 % of KOH doped catalyst varying time and catalyst percentage.

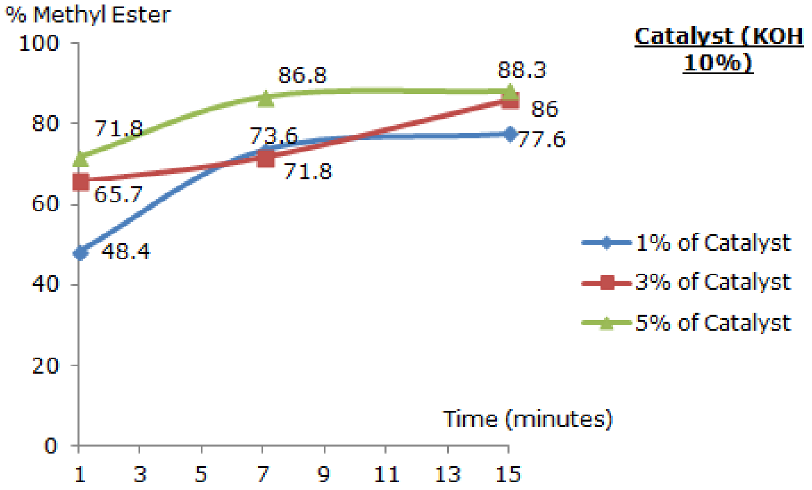

Figure 7. Transesterification reaction results with heterogeneous catalyst (10% KOH)

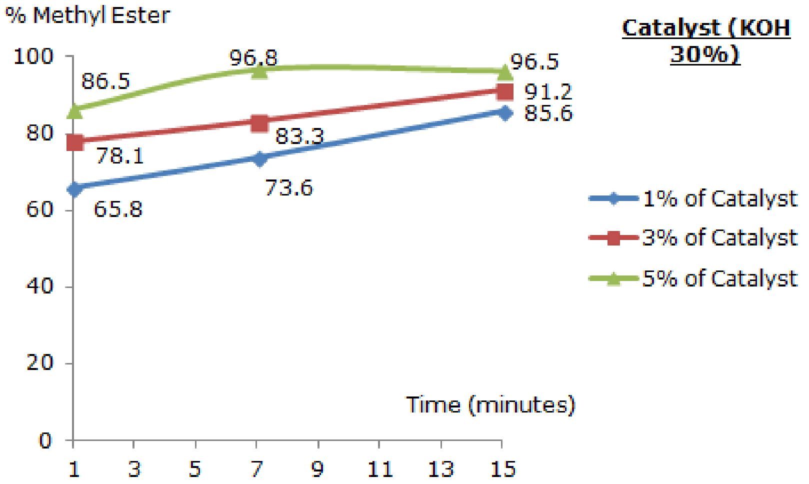

Figure 8. Transesterification reaction results with heterogeneous catalyst (30% KOH)

Despite no result was under the National Agency of Petroleum, Natural Gas and Biofuels (ANP – Brazilian Institution) that determines the ester percentage minimum as 96.5%, the results obtained can considered reasonable. The majority of studies on heterogeneous catalysis present reaction time and molar ratio higher than the ones chosen in this work. It appears that the longer the reaction and the higher the catalyst percentage, higher the reaction conversion is.

In Figure 8 can be noticed that when used 5% of 30% KOH doped catalyst, the biodiesels produced in the reactions tested with 7 and 15 minutes already attend the specification of the Brazilian Standard, with formed methyl ester percentages of 96.8% and 96.5% respectively. This occurs, mainly, given the doped upgrade that increases the basic character of the catalyst, favouring the transesterification reaction.

The purity catalyst from eggshells (calcium oxide), which means, without KOH doping, reached only 31,2% of methyl ester in one minute of reaction, using 5% of catalyst and 1:6 molar ratio. Even Cho *et al.* (2010) and Viriya-Empikul *et al.* (2010) have reported successful biodiesel production with calcium oxide derived from eggshells or shellfish shells, the application of non-doping alkaline catalyst did not achieve satisfying outcome when submitted to microwave irradiation.

Khemthong *et al.* (2012) reported to use pure calcium oxide in the transesterification reaction employing microwaves, but the applied conditions were extremely high, raising the process costs with a catalyst percentage 15% and the molar ratio oil/alcohol 1:18.

The 50% KOH doped catalyst was recovered and reused in other reactions. Within 7 and 15 minutes reaction, with 5% of the recovered catalyst and 1:6 molar ratio resulted in a methyl ester conversion rate of 74,1 % and 87,2%, respectively. The catalytic performance of methyl ester formation decayed in 14.5% and 12.8% compared to the first reaction. It can inferred that this result is not ideal, but it is relatively satisfying.

3.2 Characterization of heterogeneous catalyst

The x-ray diffraction analysis provided the identification of the elements phases from the heterogeneous catalyst made by the eggshells. Figure 9 shows that after calcination the catalyst made by pure eggshells were predominantly calcium oxide CaO and a small part of hydrated calcium oxide ($CaO.H_2O$), because of the absorption of humidity.

In the doped catalyst was observed calcium oxide formation (CaO) and potassium ozonide (KO_3) in moderate quantities. It was also detected hydrated calcium oxide ($CaO.H_2O$), calcium carbonate ($CaCO_3$) and mixed calcium and potassium carbonate $K_2Ca(CO_3)_2$. The presence of carbonates indicates that the samples were not totally calcined, even in small proportions (Fig. 10).

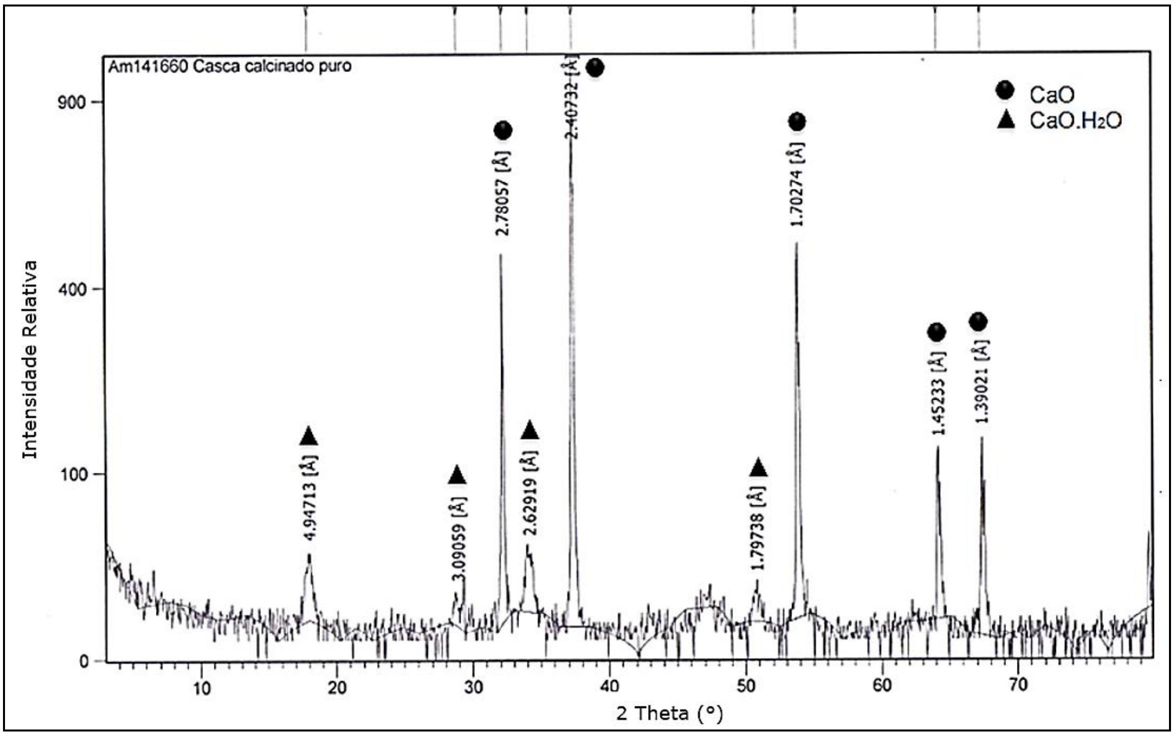

Figure 9. X-ray diffraction of the calcined pure eggshell.

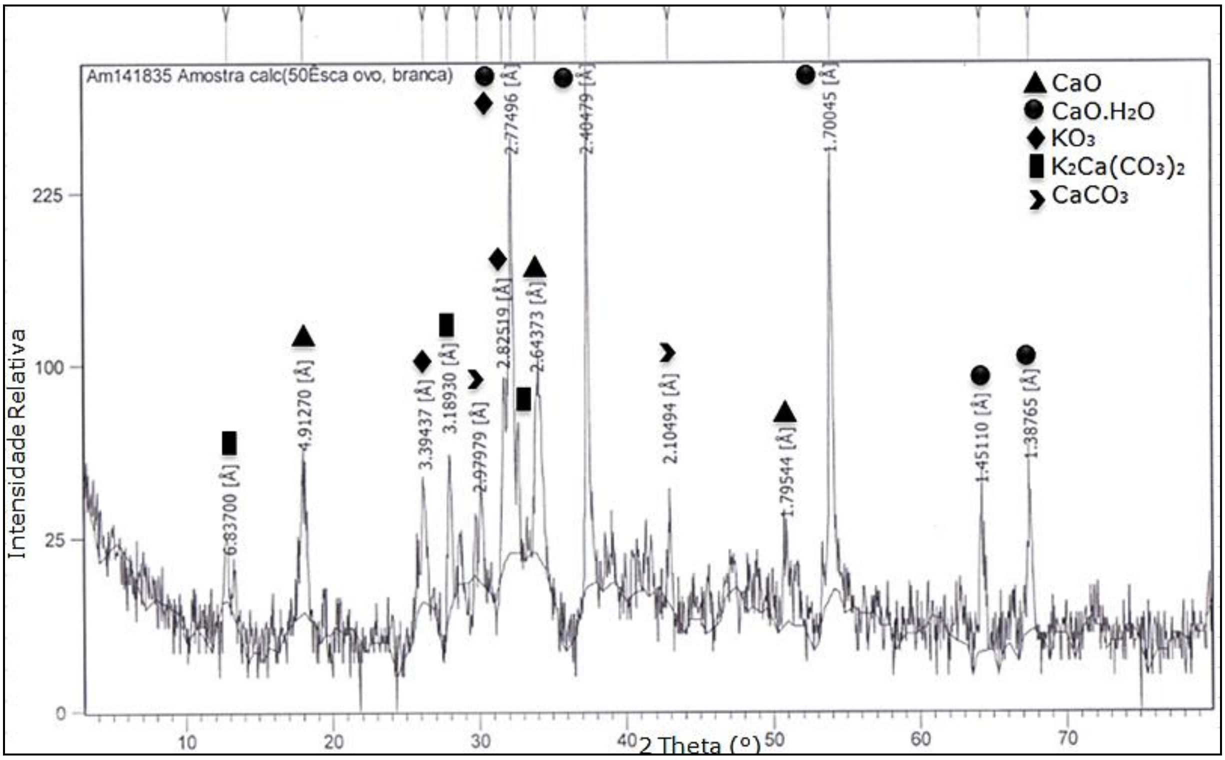

Figure 10. X-ray diffraction of the calcined 50% KOH doped eggshell.

The 50% KOH-doped catalyst was analyzed after use in the transesterification reactions and the X-ray Diffraction analysis revealed its composition to undergo chemical reaction, with a complete disappearance of the potassium ozonide species and an increase in the amount of mixed calcium and potassium carbonates.

It is important to highlight that diffraction spectrum noise observed were due to the lack of crystalline aspect of the samples analysed. According to NEVES (1998), the eggshell is considered a substantial amorphous material. When doping with KOH, the noises increased significantly.

Through the thermographic analysis, it was possible to keep up with the behaviour and mass changings of the sample in function of the temperature, in which could be visually observed where the sample transformations occurred.

Figure 11 shows that the 50% KOH doped catalyst had a small mass loss between 50º and 390° Celsius, which can be attributed for a water and an organic matter loss. Between 390º and 800° Celsius, a significant mass loss can be related to KOH doping, since in the purity catalyst this aspect was not observed. Probably, because of the doping, intermediate chemical composts were produced, causing the decomposing process to initiate in lower temperatures.

Another mass loss can still be noticed between 800º and 1000º Celsius, showing that a temperature increase would be necessary to provide a total decomposition of the sample (Fig. 11).

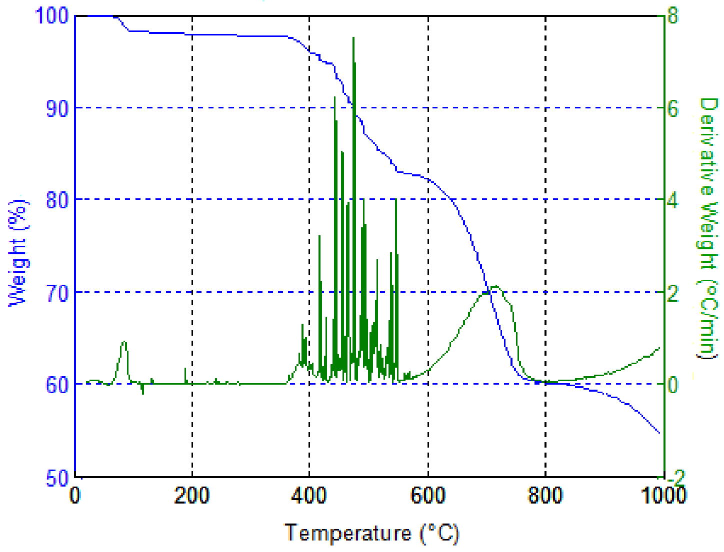

Figure 11. Thermal analysis of the KOH doped catalyst.

Comparing the thermal and diffraction analysis is possible to conclude that the remained carbonates in the calcined KOH doped catalyst are still there. For doped catalyst, the calcination temperature should be higher in order to achieve a total transformation of the carbonates into potassium and calcium oxides.

The total mass loss in the doped catalyst until 1000º Celsius was roughly 45%, which means, the sample was still vulnerable to change in higher temperatures.

4. CONCLUSIONS

The biodiesel production in a microwave irradiation reactor is extremely promising to the biofuel industry. It was possible to obtained excellent yields of methyl esters applying both catalysis, homogenous and heterogeneous. The reaction time was significantly reduced compared to the conventional process. In only one minute of reaction, the methyl ester conversion obtained was 98.9% with the homogeneous catalyst and within 15 minutes, the heterogeneous catalysis accomplished 100% using low molar ratios and moderate catalyst percentages.

In addition, the developed heterogeneous catalyst based on eggshells was compatible with the microwave reactor, especially when doped with potassium hydroxide. Despite the catalyst structure was not conserved intact after the transesterification reaction, the heterogeneous catalyst improved the biodiesel quality: make it easier to separate product and sub product produced, reduce purification steps, and have the possibility of being reused or regenerated that can be studying in future works.

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5. ACKNOWLEDGEMENTS

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