Study of the Thermal Decomposition of Green Coconut Fiber in the Presence of a Nano Structured Catalyst

Felipe Z. R. Monteiro [a], Rogério N. C. Siqueira [a], Francisco J. Moura*[a], Alexandre V. Grillo[b]

a Department of Chemical and Material Engineering (DEQM). Pontifical Catholic University of Rio de Janeiro (PUC-Rio). Rua Marquês de São Vicente, 225 – Gávea, Rio de Janeiro – RJ, 22430-060, Brazil.
b Federal Institute of Education, Science and Technology (IFRJ), www.ifrj.edu.br, Rua LúcioTavares, 1045 – Centro, Nilópolis – RJ, 26530-060, Brazil.
moura@puc-rio.br

With increasing political and environmental concerns, it becomes imperative to develop efficient processes in economic and energy terms for the sustainable production of fuels and chemical products. Hydrothermal liquefaction (HTL) is a process for the transformation of organic materials such as bio-waste or biomass into crude oil at temperatures usually below 400°C under moderate to high pressures (5–25 MPa) in the presence of water and, depending on the process, of a catalyst. In this context, it is important to understand the behavior under thermal degradation of the material of interest under inert atmosphere, in order to investigate the possibility of breaking the initial polymer chains into smaller molecules during heating. In under high pressures, this small molecules can be converted into new products of higher molecular weight. In the present work the thermogravimetric (TG) behavior under inert atmosphere of pure green coconut fiber and mixtures thereof with a spinel phase (Fe_2CoO_4) as catalyst (50% w/w) has been studied. The spinel phase has been produced at 1000°C and different calcination times (3h, 6h and 9h). The materials involved in the present research were characterized through different techniques, such as scanning electron microscopy, X-ray diffraction and Infrared Absorption Spectroscopy. According to the TG data, the catalyst produced for a calcination time of 9h showed a superior behavior regarding the full thermal degradation of the lignine present, which developed through a new mechanism, without the formation of fixed carbon. The results further suggest that the mixing process has a significant effect over the measured degradation kinetics. The kinetic modelling applied to the dynamic TG signal allowed a quantitative representation of the experimental data. The activation energy obtained was 85.291 kJ / mol and the order of the reaction was 0.1227.

1. Introduction

Energy needs and increasing environmental issues stimulate the search towards alternative energy resources, in substitution to non-renewable and polluting fossil fuels. Biomass, for example, is a good feedstock for biochar production through the pyrolysis process (Kumar, 2015).

The growth of the consumption of green coconut water and the natural tendency towards its industrialization have brought difficulties of final disposal of the associated fruit shells, the main residue generated (Rosa et al., 2001). The fiber obtained through mechanical shell processing can be used as raw material for industrial applications (Carrijo et al., 2002), as, for example, in the production of bio-oil through atmospheric or hydrothermal pyrolysis. In this context, hydrothermal processing routes, which are based on heating the biomass in the presence of water in a sealed autoclave under high pressure, and also, in some cases, the presence of a catalysts to accelerate the reaction and induce the desired selectivity, can indeed be seen as a promising alternatives towards liquid oil production in an industrial scale (Cortez et al., 2008).

The coconut fiber is basically composed of three main components consisting of about 30-50% cellulose, 15-35% hemicellulose and 10-20% lignin (Limayem and Ricke, 2012). Generally speaking, the thermal degradation of lignocellulosic materials is associated with the following trend: moisture, hemicellulose, cellulose and, finally, lignin degradation (Raveendran et al., 1996; Yang et al., 2007). The knowledge of these

phenomena is fundamental for better stablishing the operation conditions for processing biomass raw materials.

As all of them are associated with some sort of mass loss, thermogravimetric analysis (TG) can be applied for a quantitative evaluation of the kinetics of each one of these processes, with or without the presence of a specially designed oxidized catalyst (Tomczak et al., 2007).

The large volume of coconut shell generated and the few studies exploring the reuse of such residue stimulated the present work, which is based on the thermogravimetric (TG) study of the thermal degradation of green coconut fiber, and mixtures thereof with a cobalt ferrite (Fe_2CoO_4) of spinel structure. The knowledge constructed through the present research serve as a motivation for applying the produced catalyst during hydrothermal pyrolysis of the same coconut fiber, which demands the complete degradation of the initially present polymer chains.

2. Methods and Materials

2.1 Lignocellulosic residue

Coconut fruits (Cocos Nucifera) obtained from city trade were used. The coconut fruits, after having their endocarps (green and ripe) separated, were crushed and dried first in the open air and then in a stove, set at 60 °C, for 48 hours. The produced fiber particles were classified in a set of sieves up to 60 mesh, resulting in a final material of particle size around 0,2 mm. Finally, the coconut shell fiber was again subjected to the drying process and the material was stored in dry and closed containers.

2.2. Catalyst synthesis

The production of the desired catalyst was based on the sol-gel strategy, with polyvinyl alcohol (PVA) acting as jellification agent, admitted into the system as an aqueous solution - 16.6 grams of PVA for 150 mL of water. The mixture is heated up to 60°C under continuous stirring for approximately two hours until a viscous transparent solution is formed.

An aqueous solution of iron and cobalt nitrates has been prepared, the quantities of each nitrate so controlled, in order to preserve the 2:1 ratio between the molar amounts of iron and cobalt, as required by the spinel stoichiometry (Fe_2CoO_4). The nitrate solution was added to the PVA solution and the system heated up to 90°C during 24 hours. The obtained solid powder was next transferred to a mullite crucible and heated, during 2 hours, in a muffle furnace under atmospheric air, prior settled at 350°C, stimulating the nitrates thermal decomposition and concomitant formation of the spinel oxide precursors - Fe_2O_3 and Co_3O_4. Finally, during a second calcination step performed at 1000°C and different times (3, 6 and 9h) with the same furnace employed before, the desired spinel structure is produced according to the following reaction:

$$Fe_2O_3(s) + Co_3O_4(s) = Fe_2CoO_4(s) + O_2(g) \tag{1}$$

2.3. Thermogravimetric Analysis

The thermogravimetric analysis was performed on samples consisting in pure fiber, oxide and mixtures thereof, in a Netzsch STA, model 449 F3 Jupter, in the temperature range of 20°C to 1000°C, and ultra-pure nitrogen (UP) atmosphere, under a flow of 70 mL.min-1, a heating rate of 20°C.min-1 and alumina crucible. Before each analysis, the same thermal program has been applied for the empty crucible, and the blank signal then subtracted from the data obtained for during the sample run. In all TG runs, sample masses varied in the range between XX and YY mg.

2.3.1. Kinetic study with thermogravimetric data

Based on the measured mass loss during a dynamic analysis, the global activation energy and reaction order can be concomitantly obtained from a single TG data if one supposes that only thermal decomposition processes are present (Speyer et al., 1993). According to the mentioned methodology, TG data should be treated according to Eq. (2), where, Φ denotes the heating rate, T_r is the reference temperature, R is the universal gas constant, n is the reaction order, E_A is the activation energy, t the elapsed time, and f the conversion achieved at a given instant, which is defined by the ration between the instantaneous mass loss and the maximum mass loss observed at the chosen TG step. The implementation of Eq. (2) requires the evaluation of the first and second time derivatives of f, which has been performed through an algorithm based on finite differences.

$$(\boldsymbol{\Phi} \cdot t + T_r)^2 \cdot \left(\frac{d^2 f}{dt^2}\bigg/\frac{df}{dt}\right) = -n \cdot \left(\frac{(\boldsymbol{\Phi} \cdot t + T_r)^2 \cdot df/dt}{1-f}\right) + \frac{E_A \cdot \boldsymbol{\Phi}}{R} \tag{2}$$

2.4. Materials Characterization

In the present research different characterization techniques have been employed. Scanning electron microscopy (SEM) with a TM300 Hitashi microscope, has been used for the study of the morphology and elemental composition through Energy Dispersive X-Ray Spectroscopy (EDS) analysis, X-ray diffraction (XRD) with a Bruker Discover 8 diffractometer, for the quantification of the phases present in the catalyst samples through fundamental parameters Rietveld analysis and Fourier-transform Infrared absorption spectrometry (FTIR), in order to identify the main chemical bonds present in the fibers.

3. Results and discussion

3.1 Characterization of biomass and cobalt ferrite

Figure 1(a) shows a point EDS analysis over a single fiber, which is basically consisted of carbon and oxygen, followed by some minor amounts of Al, Si and K. The presence of oxygen is expected based on the well – known chemical structure of liginin and cellulose, which should both contain oxidized functional groups. In order to identify the possible binding sites in the biomass, the infrared spectrum of the pure material was obtained, and is depicted on Figure 1(b), indicating the presence of typical bands of chemical bonds with oxygen atoms.
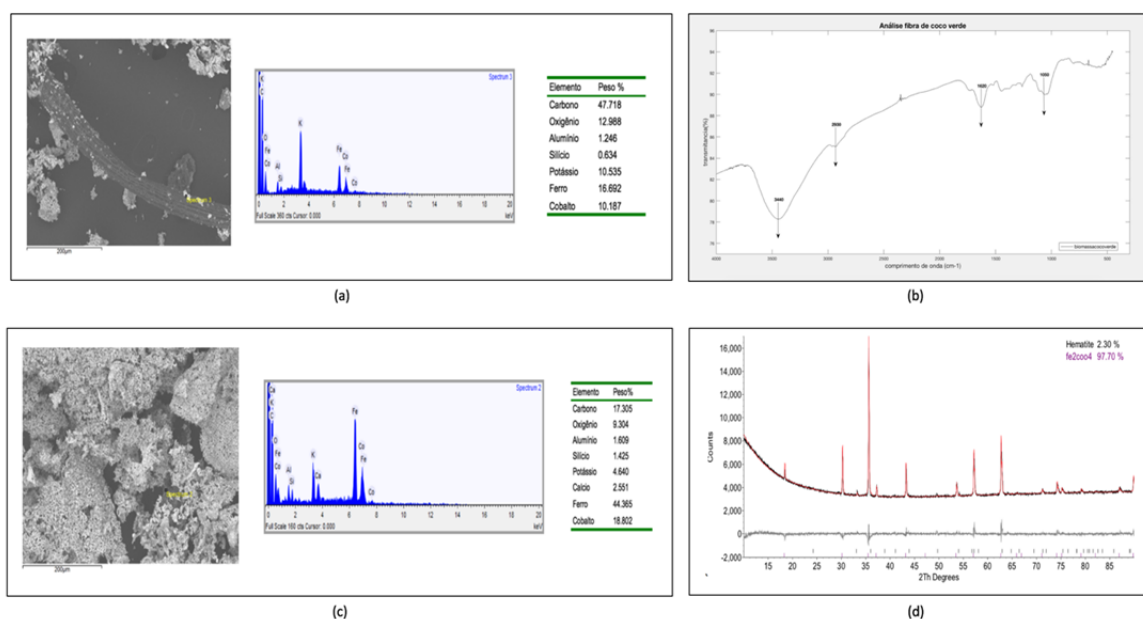

Figure 1: (a) SEM and EDS for the pure green coconut fiber. (b) Infrared spectrum of pure green coconut fiber. (c)SEM and EDS for pure cobalt ferrite sample. (d) XRD pattern for a catalyst sample.

The EDS analysis performed in region of the catalyst sample (Figure 1c) revealed the presence of iron, cobalt and oxygen as the major elements, as expected considering the presence of Fe_2CoO_4 crystals. Moreover, the image contrast suggests the presence of a single phase. This hypothesis has been corroborated through Rietveld analysis of the XRD data (Figure 1d), which indicates the presence of the desired spinel with a weight fraction of 97.7%. Since this spinel is the major compound, the catalytic activity detected (see topic 3.2) should be, according to the authors, associated with the presence of Fe_2CoO_4 crystals. It is worthwhile to mention that, according to literature, Fe_2CoO_4 can indeed exhibit catalytic activity for other reactions of technological importance, such as for use as hybrid material in nanotechnology of great interest in commercial applications due to the particularity of the properties obtained (Gonçalves, 2007; Camilo, 2006). Cartopassi et al. (2011) investigated the use of Fe_2CoO_4 nanoparticles for the physical extraction of oil droplets from water suspensions.

The thermal behavior associated with the pure fiber can be observed in Figure 2a. The TG signal depicts the typical thermal degradation behavior for lignocellulosic based samples (Rambo et al, 2015). In total, three well defined stages can be identified: release of moisture in the range of 50 to 100ºC, decomposition of hemicellulose and cellulose in the range of 200 to 400ºC, and above 400°C a slow and continuous degradation of lignin resulting finally in some amount of fixed carbon and ashes. This explains why no full conversion has been achieved for temperatures as high as 1400ºC, after which the signal curvature should be, according to the authors, dominated by instrumental effects (baseline shift) not eliminated during the blank subtraction.
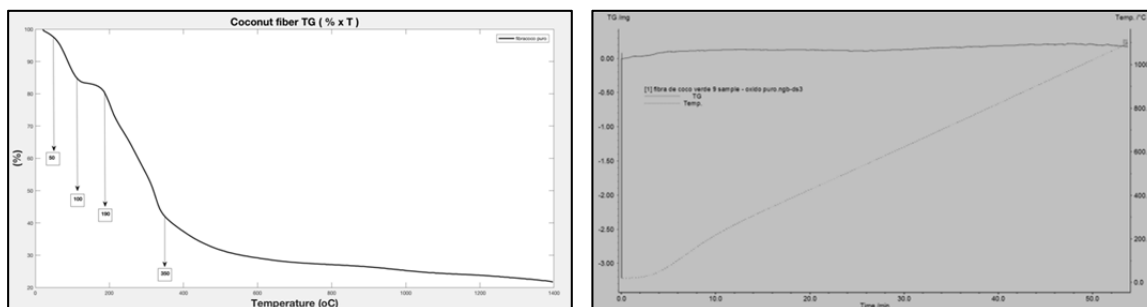

Figure 2: (a) TG signal for pure fiber under inert atmosphere (N_2). (b) TG signal of pure oxide sample under inert atmosphere (N_2).

On Figure 2 (b) the TG signal for the pure catalyst can be appreciated. As expected, no thermal degradation has been observed till 1200ºC, an experimental evidence that during heat treatment of the mixtures (fiber plus oxide), the mass loss can be associated exclusively to the thermal degradation of the polymer chains contained in the coconut fiber.

3.2 Thermogravimetric analysis of the mixtures

On Figure 3 (a) the TG signals of mixtures (50% w/w) of the fiber and the produced catalyst, calcinated at different times at 1000ºC (3, 6 and 9h) are presented. According to the data, the sample containing the oxide calcined for 9 h, the final degradation of liginin starts at much lower temperature (from 750ºC), suggesting a superior catalytic activity in comparison with the other samples (Figure 3a). It is worthwhile to mention that the final degradation is absent in the signal from the pure fiber sample, but all other reactions have not been affected by the oxide presence (Figure 3b). Therefore, the catalytic activity should be associated only to the process, whereas lignin is fully converted to volatile molecules. In this sense it can be said that the presence of Fe_2CoO_4 crystals activates another mechanism for the lignin degradation, where no fixed carbon results. The hypothesis of no fixed carbon formation is clearly supported by the final residual relative masses measured for samples produced with the catalyst calcined at 6 and 9 h. In both cases, values close to 40% are obtained, which are even lower than the theoretical expectation of 50%, the theoretical catalyst weight fraction.
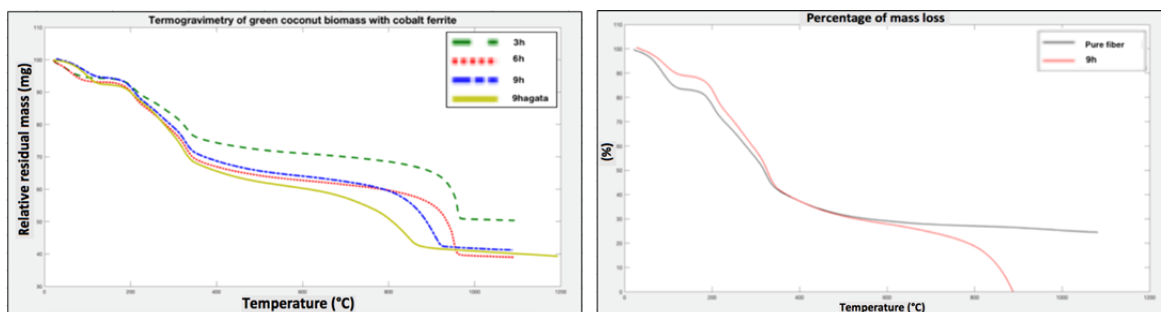

Figure 3 – (a) TG signals for mixtures of fiber and catalysts calcined at 1000ºC for different times (3, 6 and 9h). (b) Comparison between TG signal of pure fiber and mixture with catalyst produced at 1000ºC and 9h.

The lower residual masses can be explained by errors during weighing before mixing, which has been performed on a usual digital balance with a precision of 0,005 mg, with a much lower precision than the one

expected for the TG balance, and, in the end, resulting in a higher fiber mass. In case of sample produced with the 3h catalyst, a higher residual mass is found, lying between 50 and 55%. The higher deviation can be explained by the fact that some fibers did not have contact with the catalyst particles, a problem that can be avoided through mixing with the agate mortar crucible.

It is noticeable from the data of Figure (3a), that through enhancing the calcination time from 3 to 9h, there was a gain regarding the observed catalytic activity. This, on the other hand, may be linked to the cationic disorder (non-stoichiometric structure), since by increasing the process time, the spinel approaches a perfectly stoichiometric atomic distribution (Siqueira, 2014). Data of Figure (3a) also shows that the mixing process employed can have an appreciable effect over the measured activity. Mixing with an agate mortar crucible, promotes contact between catalyst particles and biomass fibers, stimulating, in the end, the desired catalytic effect.

3.3 Kinetic analysis

As pointed out before, the presence of the spinel catalyst stimulated another mechanism for liginin decomposition, whereas no fixed carbon formation is involved. The TG signal associated with this last reaction for the mixture with the oxide calcined for 9h, and mixed with the mortar crucible (Figure 4a) can be used, together with Eq. (2) in order to evaluate the process global activation energy (E_a) and reaction order (n). Before applying Eq. (2) to the experimental data, however, reference temperature (T_r) and heating rate (Φ) must be determined. This can be performed through adjusting a linear function to the experimental temperature profile, T_r and Φ being, in the present case, respectively equal to 19.89 K/min and 31.98°C.
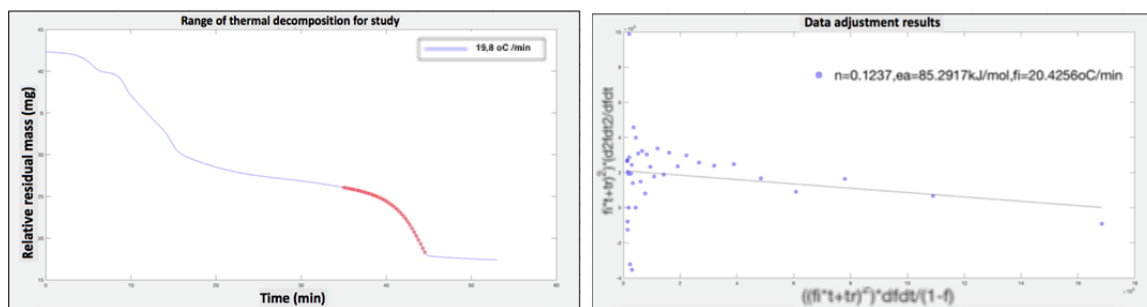

Figure 4 – (a) TG signal used for kinetic modeling. (b) Model quality using the estimated values of Ea and n.

Through use of a minimization MATLAB code, which implemented a simplex minimization algorithm applied to the quadratic difference sum of the calculated and experimental values of the left hand side term of Eq. (2), values of Ea and n can be simultaneously determined, being, respectively, equal to 85.291 kJ/mol and 0.1237. The experimental points used during the minimization process are represented on Figure (4a) and the quality of the optimization can be evaluated by data on Figure (4b). It is worthwhile to mention that computation of the first and second derivatives of the conversion (f), as required for evaluating the terms present in Eq. (2), were based on a simple finite difference algorithm. On what touches the second derivative, the authors believe, that this strategy is too simple, and explains the initial observed fluctuations. On the other hand, the present activation energy is in the range proposed by Raad et al. (2006) for organic biomasses, which studied the kinetics of carbonization of lignocellulosic biomasses - 46 kJ/mol to 98 kJ/mol. Finally, the fact that the global reaction order was close to zero was expected, as is typically found for the majority of thermal decomposition processes, when the rate of reaction if not a function of the solid reactant concentration.

4. Conclusions

The thermal behaviour of the pure green coconut fiber up to the temperature of 1400°C suggests that the thermal biomass degradation should end in the lignin decomposition, thereby forming some amount of fixed carbon. The thermogravimetric analysis of pure cobalt ferrite indicated that the material is stable throughout the whole temperature range studied, indicating that the mass loss can be exclusively associated with the polymer chains contained in the coconut fibers, which through heating are converted in components of lower molecular weight and higher volatility.

The calcination time in the preparation of the catalysts had measurable influence over the observed catalytic activity, which shall involve an alternative mechanism, whereas lignin is fully converted to volatile molecules, or, in other words, no fixed carbon is formed.

This fact is of extreme importance in order to increase the efficiency of bio-oil production in a hydrothermal pyrolysis process, because these smaller molecules, at high pressures, can reorganize, reducing the formation of coal and increasing the yield of the desired liquid product.

The homogenization conducted with an agate crucible confirmed that a greater contact between the biomass and the catalyst is of great importance for the process, stimulating the desired catalytic activity, and resulting in a lignin decomposition starting in a much lower temperature.

Finally, kinetic modelling according to Eq. (2) regarding the full lignin gasification enabled a quantitative representation of the experimental data obtained for a mixture with the catalyst calcined at 9h, and allowed the determination of both the global activation energy and reaction order of the reaction, which have shown to be respectively equal to 85.291 kJ/mol and 0.1227. The obtained activation energy value is in the range found by Raad et al. (2006) for typical organic biomasses of lignocellulosic nature. Moreover, the reaction order was very close to what was expected for a molecular simple thermal decomposition process of a solid material, whereas kinetics shall not depend on the initial solid material concentration.

Acknowledgements

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