

## CASE REPORT

# Green coconut fiber thermal behaviour under the presence of a cobalt spinel catalyst

Felipe ZR Monteiro<sup>1</sup>, Rogério NC Siqueira<sup>1\*</sup>, Francisco J Moura<sup>1</sup>, Alexandre V Grillo<sup>2</sup>

<sup>1</sup> Department of Chemical and Material Engineering (DEQM), Pontifical Catholic University of Rio de Janeiro (PUC-Rio), Rua Marquês de São Vicente, Gávea, Rio de Janeiro-RJ 22430-060, Brazil. E-mail: rnavarro@puc-rio.br

<sup>2</sup> Department of Physical Chemistry, Federal Institute of Technology (IFRJ), República do Paraguay, Vila Sarapuí, Duque de Caxias-RJ 25050-100, Brazil.

## ABSTRACT

With increasing environmental concerns, much effort has been spent in research regarding development of sustainable processes for production of fuels and chemical products. In this context, hydrothermal liquefaction (HTL) has gained increasing attention, as a possible route for the chemical transformation of organic raw-materials, some sort of biomass, for example, into liquid oils at temperatures usually below 400 °C, under moderate to high pressures (5–25 MPa), usually in the presence of a suitable catalyst. In the present work the thermogravimetric (TG) behavior under inert atmosphere of pure green coconut fiber and mixtures thereof with a spinel phase (Fe<sub>2</sub>CoO<sub>4</sub>), acting as catalyst has been studied. Spinel samples have been produced at 1,000 °C and different calcination times (3 h, 6 h and 9 h). Both raw and synthesized materials were characterized through different techniques, such as scanning electron microscopy (SEM), X-ray diffraction (XRD) and Infrared Absorption Spectroscopy (FTIR). According to the TG data, the catalyst produced during a calcination time of 9 h showed a superior behavior regarding the lignin full thermal decomposition, which developed without fixed carbon formation. The results further suggest that the mixing process has a significant effect over the measured degradation kinetics, as it has a direct influence over the contact between catalyst and fibers. The kinetic modelling applied to the dynamic TG signal allowed a quantitative representation of the experimental data. The global process activation energy and order have proven to be respectively, 85.291 kJ/mol and 0.1227.

**Keywords:** Coconut Fiber; Fe<sub>2</sub>CoO<sub>4</sub>; Pyrolysis

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## 1. Introduction

Energy needs and increasing environmental issues stimulate the search towards alternative energy resources, in substitution to non-renewable and polluting fossil fuels. In this context, biomass, has proven to be a promising green raw material, both for producing liquid as well as solid fuels<sup>[1]</sup>. An important example thereof is the green coconut fiber, which can be used as raw material for many industrial applications. For example, in the production of bio-oil through hydrothermal pyrolysis<sup>[2]</sup>, there is a chemical process based on the biomass heating in the presence of water in a sealed autoclave under inert atmosphere, usually in the presence of a solid catalysts, in order to stimulate reaction kinetics and achieve desired selectivity<sup>[3]</sup>. During pyrolysis, organic polymer chains are converted in smaller hydrocarbon molecules. Under pressure, these new smaller structures can rearrange in form of longer chains, which are partially oxidized. Therefore, understanding the thermal behaviour of the biomass under inert

atmosphere is a vital point for optimizing processing conditions, which can be studied with high precision through thermogravimetric analysis (TG)<sup>[4]</sup>. Additionally, as required for the oil production, some oxidized catalyst could be inserted into the autoclave so as to stimulate the polymer chain decomposition. Both issues build the basis for the present study.

The coconut fiber is a lignocellulosic raw material and is basically composed of 30–50% cellulose, 15–35% hemicellulose and 10–20% lignin<sup>[5]</sup>. Therefore during heating under inert atmosphere, some typical phenomena are expected. At lower temperatures, water molecules adsorbed over the fibers are eliminated, and is followed by degradation of hemicellulose, cellulose, and, finally, lignin decomposition<sup>[6,7]</sup>. The knowledge of the temperature intervals for these processes, and the associated kinetics, which is specific for each biomass material, is fundamental for better establishing the operation conditions for later chemical processing.

The large volume of coconut shell generated in Brazil, 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 decomposition of pure green coconut fiber samples, and mixtures thereof with a cobalt spinel (Fe<sub>2</sub>CoO<sub>4</sub>).

## 2. Materials and methods

### 2.1 Lignocellulosic raw material

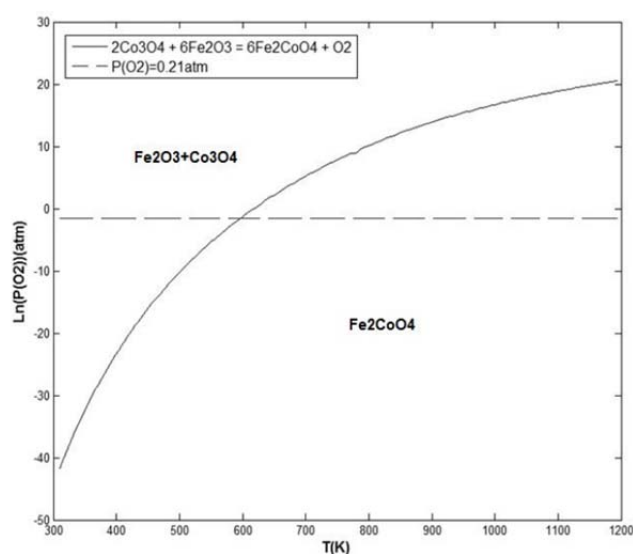
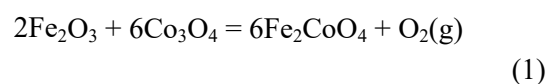
Coconut fruit shells obtained from city trade have been used as raw material for the present study. The material was crushed and dried at 60 °C for 48 hours in a stove. The produced fiber particles were classified in a set of sieves up to 60 mesh, resulting in a final material of particle size around 0.2 mm. Finally, the drying process has been again applied to the classified coconut shell fibers, and the resulting material stored for TG tests and further characterization.

### 2.2 Catalyst production

The production of the desired catalyst was based on the sol-gel route, with polyvinyl alcohol (PVA) acting as stabilizer and 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 desired spinel stoichiometry (Fe<sub>2</sub>CoO<sub>4</sub>). The nitrate solution was added to the PVA containing solution, and the system heated up to 90 °C during 24 hours under continuous mixing. 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<sub>2</sub>O<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub>). Finally, a second calcination step, performed at 1,000 °C and different times (3, 6 and 9 h) in the same furnace employed before, stimulates the formation of the desired spinel structure, through a reduction process, whereas oxygen is eliminated (equation 1). Next, the material is allowed to cool to ambient temperature and is stored for TG tests and further characterization.



**Figure 1.** Predominance diagram for Fe<sub>2</sub>CoO<sub>4</sub> spinel formation from Fe<sub>2</sub>O<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub> mixtures.

Indeed, through using Gibbs energy models from SGTE data-base<sup>[8]</sup>, the predominance diagram

characteristic of the chemical process just mentioned indicate that under atmospheric air the spinel structure should be the limiting equilibrium state of a mixture containing  $\text{Fe}_2\text{O}_3$  and  $\text{Co}_3\text{O}_4$  for temperatures higher than 582 K, which is much lower than the one employed in the present work, proving that under the imposed conditions there is enough thermal energy for thermodynamic stimulating the desired synthesis.

### 2.3 Thermogravimetric analysis

The thermogravimetric analysis was performed in a Netzsch simultaneous analyzer, model STA 449 F3 Jupiter, in the temperature range of 20 °C to 1,000 °C, under UP nitrogen atmosphere (70 mL·min<sup>-1</sup>), at heating rate of 20 °C·min<sup>-1</sup> 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.

Besides tests performed with pure fibers and catalyst samples, four independent mixtures (50% w/w) have been prepared, three of them containing the catalyst produced with 3, 6 and 9 h of heat treatment at 1,000 °C and the last containing the catalyst produced with 9 h but instead of usual mixing employing a spatula, fibers and catalyst were mixed in a agate mortar crucible, in order to enhance the contact between fibers and catalyst particles.

#### 2.3.1 Kinetic study with thermogravimetric data

Based on the measured mass loss, the global activation energy and reaction order can be concomitantly obtained from a single TG run if one supposes that only thermal decomposition processes are present<sup>[9]</sup>. According to this approach, the TG data for the desired step, whereas the decomposition process of interest occurs, should be modelled according to equation (2), where,  $\Phi$  denotes the constant heating rate,  $T_r$  is the reference temperature,  $R$  is the universal gas constant,  $n$  is the global reaction order,  $E_A$  is the global activation energy, and  $t$  the elapsed time.

$$\begin{aligned} & (\Phi \cdot t + T_r)^2 \cdot \left( \frac{d^2 f / dt^2}{df / dt} \right) \\ = & -n \cdot \left( \frac{(\Phi \cdot t + T_r)^2 \cdot df / dt}{1 - f} \right) + \frac{E_A \cdot \Phi}{R} \end{aligned} \quad (2)$$

In equation (2),  $f$  denotes the conversion at a specific time instant, and has been calculated as the ratio between the maximum mass loss determined from the signal and the mass loss inside the step for a specific time instant.

#### 2.3.2 Materials characterization

In the present research different characterization techniques have been employed. Scanning electron microscopy with a TM300 Hitashi microscope, has been used for the study of the morphology and elemental composition through EDS analysis, X-ray diffraction with a Bruker Discover 8 diffractometer, for the quantification of the phases present in the oxide samples through fundamental parameters Rietveld analysis (TOPAS 4.2), and Infrared absorption spectrometry (FTIR, Perkin Elmer, Frontier), in order to identify the main chemical bonds present in the fibers.

## 3. Results and discussion

### 3.1 Characterization of biomass and cobalt ferrite

The fibers have been first characterized through SEM for morphology evaluation and FTIR for identification of the main functional groups.

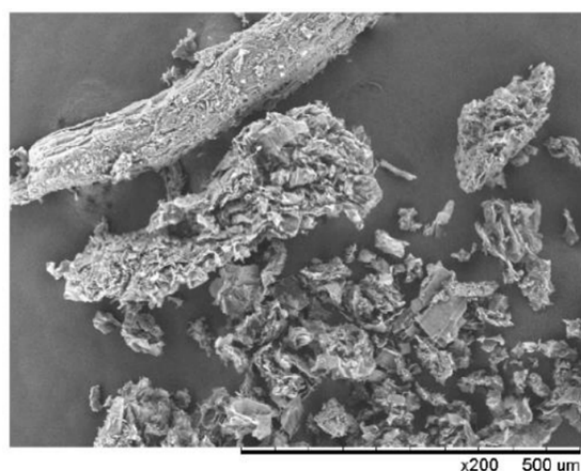


Figure 2. SEM image of green coconut fibers.

In Figure 2, a typical SEM image of some fibers is shown. The contrast is very similar than the

one for the carbon tab used for fixing the particles in the sample holder, which is also of organic polymeric nature. Also, it is seen that the fibers

surface is rough, which is positive for enhancing the contact with the catalyst.

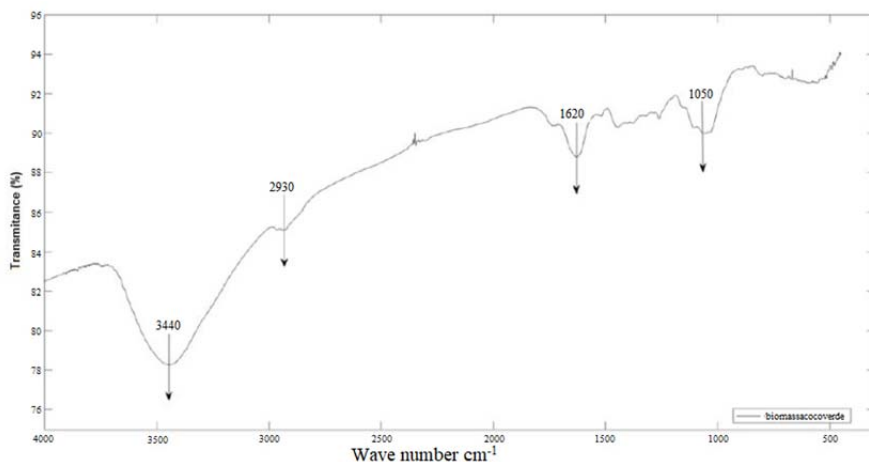


Figure 3. FTIR pattern of green coconut fibers.

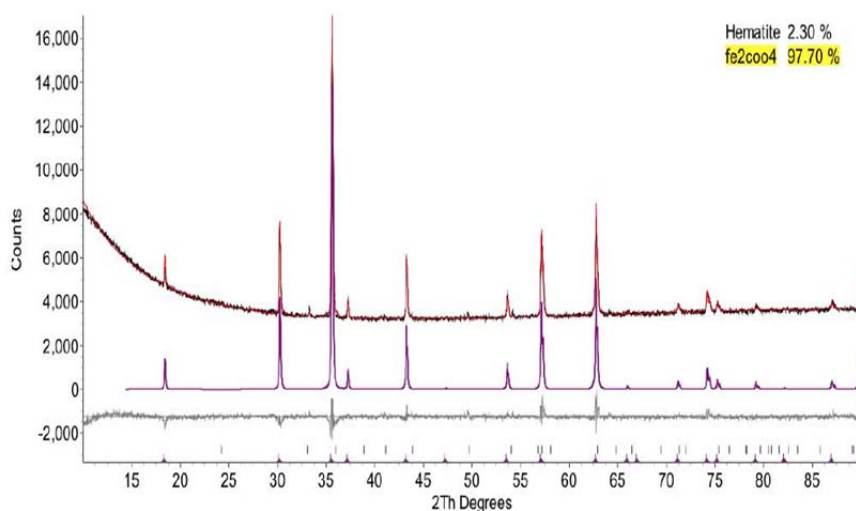


Figure 4. XRD pattern of catalyst sample produced at 9 h and 1,000 °C.

The FTIR signal (Figure 3) presents typical peaks of lignocelulosic materials, which are associated with the excitation of functional groups from cellulose and lignin structure units, such as C = O, C-C (aromatic) and O-H.

The produced catalyst sample calcinated during 9 h at 1,000 °C has been characterized through XRD and after Rietveld analysis it has been revealed that the sample consisted of almost 98% of the desired spinel phase and a minor amount of Fe<sub>2</sub>O<sub>3</sub>, which can be explained by a little deviation from the initial nitrate solution concentration from the one desired for producing a fully stoichiometric sample (Figure 4). On what touches the spinel phase crystal structure used during the Rietveld assessment, it should be noted that a stoichiometric

distribution of Co<sup>2+</sup> and Fe<sup>3+</sup> cations has been considered. This is an interesting fact considering the characteristic that spinel materials can be associated with considerable cationic disorder, depending on the synthesis conditions and chemical nature of the spinel phase<sup>[11]</sup>. Although an XRD analysis has not been performed for all catalyst samples, based on the thermodynamic viability of the process at 1,000 °C and the fact that the same conditions have been applied, the authors agree that in all cases the same chemical nature should be present. However, the samples can indeed be different regarding particle size and cationic disorder, a fact that should be addressed in a second publication.

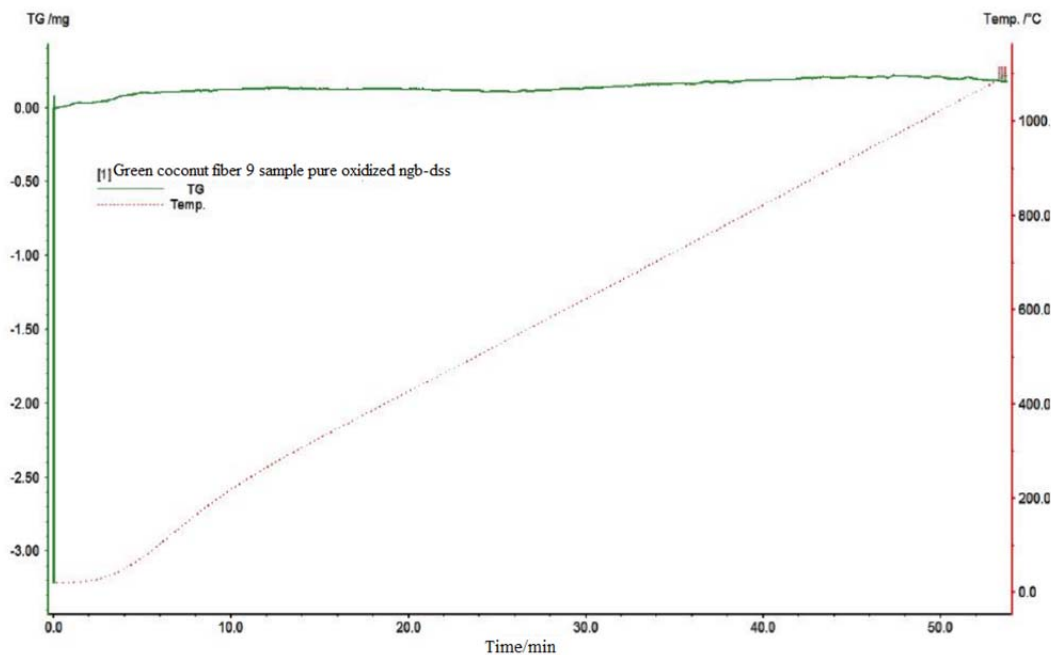


Figure 5. TG signal from pure catalyst sample calcined for 9 h at 1,000 °C.

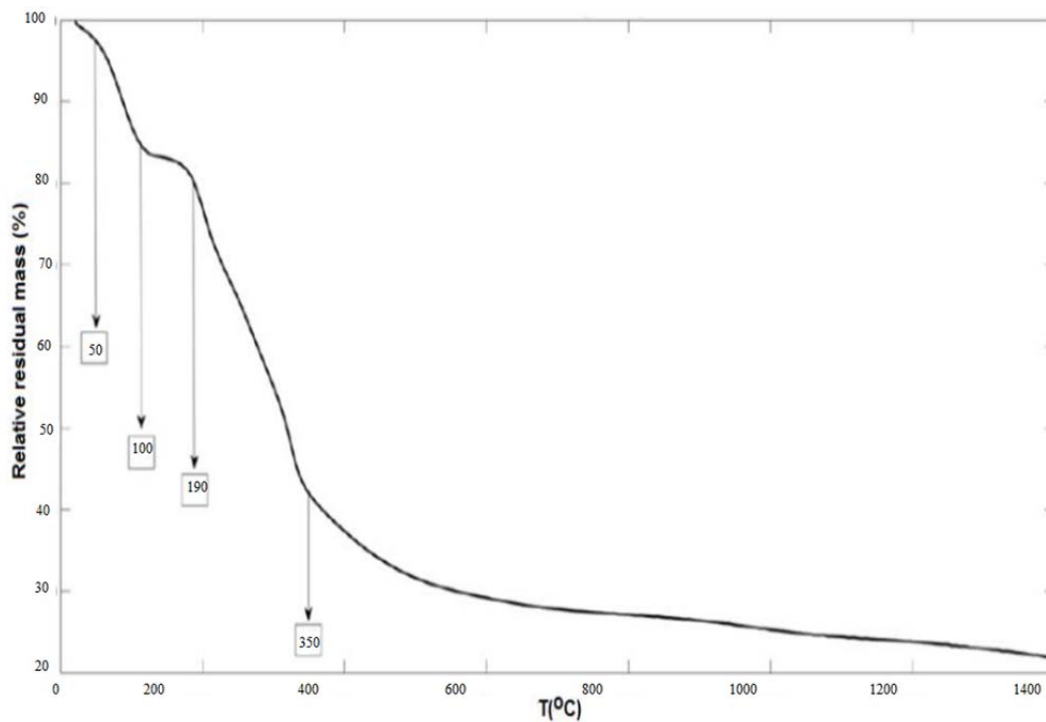


Figure 6. TG signal for pure fibers in inert N<sub>2</sub> atmosphere.

### 3.2. Pure fibers and catalyst TG behavior

After the initial characterization presented on topic (3.1), pure fibers and catalyst samples thermal behavior have been studied under inert atmosphere through TG analysis. For the catalyst analysis, the same sample as the one used for the XRD study has been employed. The data indeed suggest (Figure 5) that no mass loss is present, indicating that the catalyst does not react at all

during the thermal treatment. Regarding the pure fiber signal (Figure 6), three well defined stages can be identified, which can be explained by release of adsorbed water molecules in the range of 50 to 100 °C, decomposition of hemicellulose and cellulose in the range of 200 to 400 °C, and above 400 °C a slow and continuous degradation of lignin resulting finally in some amount of fixed carbon and ashes.

Formation of a high carbon containing material

(fixed carbon) after all polymer chains have been fully decomposed explains why no full conversion is achieved for temperatures as high as 1,400 °C (Figure 7), after which the signal inclination

should be, according to the authors, dominated by instrumental effects not eliminated after the blank subtraction.

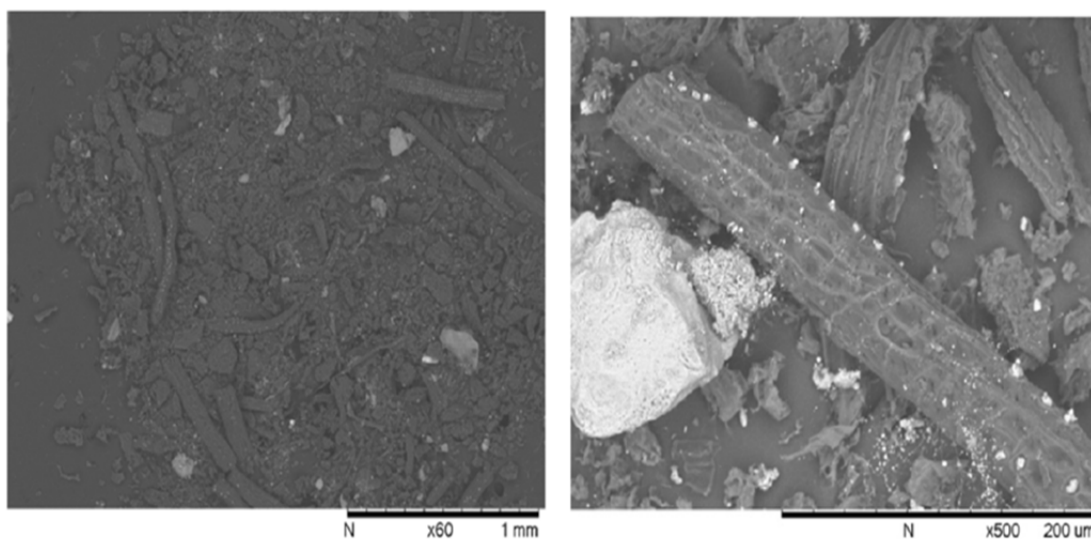


Figure 7. SEM images of high carbon product obtained after TG at 1,400 °C.

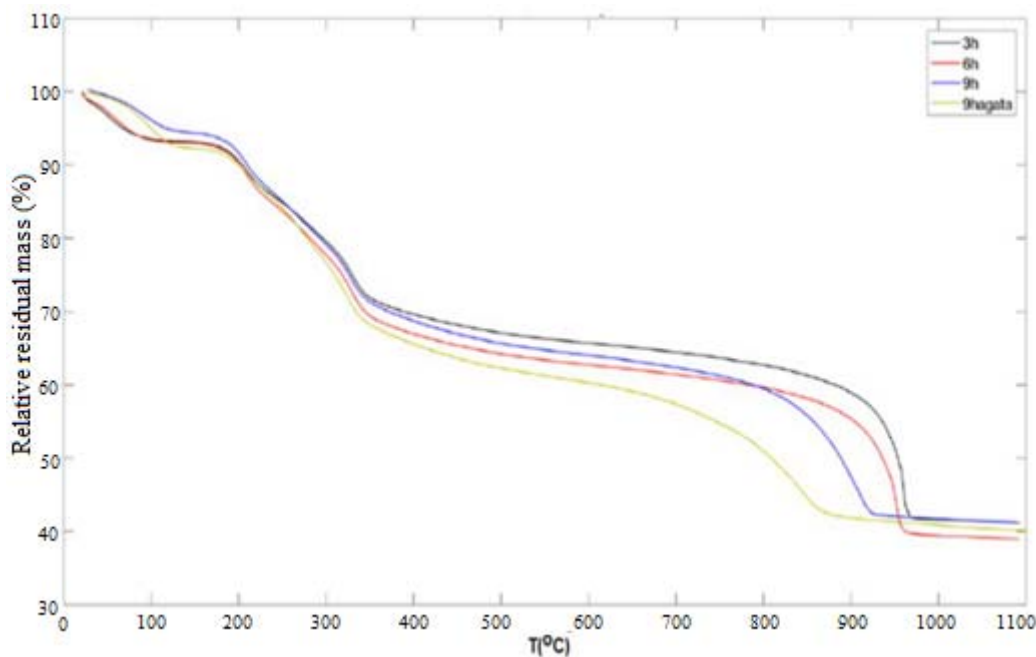


Figure 8. TG signals for fiber and catalyst mixtures.

### 3.2.1 SEM of pure fiber after TG

After TG analysis, the SEM images of the pure fiber sample indicate the presence of particles with a similar morphology observed for the fibers before TG analysis. It is also evident that a higher density of ash particles can be detected, supporting the idea that the decompositions mentioned above indeed result in a significant production of volatile

hydrocarbons, possibly besides, CO, CO<sub>2</sub>, H<sub>2</sub>O and H<sub>2</sub>. Regarding the contrast, it can be deduced that the produced solid material should bear a similar chemical constitution as the original fibers and SEM carbon tabs, which is consistent with the idea of the formation a high containing carbon product after full lignin decomposition.

### 3.3 Thermogravimetric analysis of the mixtures

The TG analysis performed on the mixtures is presented in **Figure 8** and **Figure 9**. In **Figure 9**, only the result for the sample produced with the catalyst calcined for 9 h and mixed with the fibers under agate mortar is shown for comparison with the pure fiber signal.

In all cases, the same first events detected in the case of the pure fiber thermal treatment are present, which, as said before, should be associated with moisture elimination and thermal degradation of cellulose and hemicellulose chains. On what touches the lignin decomposition, it is seen that in the samples containing the spinel catalyst, thermal

degradation of lignin appears to follow another mechanism, without formation of fixed carbon. This explains why in these cases, a full conversion has been achieved, which could be explained by the formation of volatile hydrocarbons, and not through fixed carbon production.

Data contained in **Table 1** presents the main global characteristics of each TG signal for comparison. At a first glance, the weight loss of the pure fiber sample seems to be higher than the one for the mixtures. However, if one takes the actual weight fraction of fibers in the mixtures, it can be deduced that all organic material initially present should have been transformed to volatile compounds.

**Table 1.** Initial mass, maximum weight loss, final residual weight and catalyst weight fraction for samples used in TG tests

Sample	Initial sample mass (mg)	Maximum weight loss (mg)	Final relative residual mass (%)	Catalyst weight fraction (%)
Pure fiber	49.9	-37.0	25.8	0
3 h	26.3	-15.9	39.5	45.27
6 h	26.3	-15.8	40,0	45.40
9 h	42.2	-24.8	41,2	45.97
9 h + agata	42.1	-24.7	41,3	46.01

As said in the methodology section, the fiber/catalyst mixtures have been produced, considering a theoretical value for the fiber weight fraction of 50%. However, when one takes into account the initial sample total mass together with the maximum weight loss, in all experiments with the mixtures, a final negative mass result. This fact suggests that the real weight fraction of fibers and catalyst should deviate from 50%, and also, that in all cases a higher amount of fibers should be present in the mixtures, as the weight loss, as said before, should be entirely associated with the fibers and not with the catalyst (**Figure 5**). It must be said, that for the mixtures production, a normal digital balance have been employed, which shall have a precision of  $\pm 0.005$  g. The additional fiber mass in the case of the mixture samples, can then be used for the composition reevaluation, and as a result, a more reliable computation of the catalyst weight fraction. The data indicates that in all cases, although very similar, the catalyst concentration is appreciably lower than the theoretical value (50%).

The different behavior in the presence of the

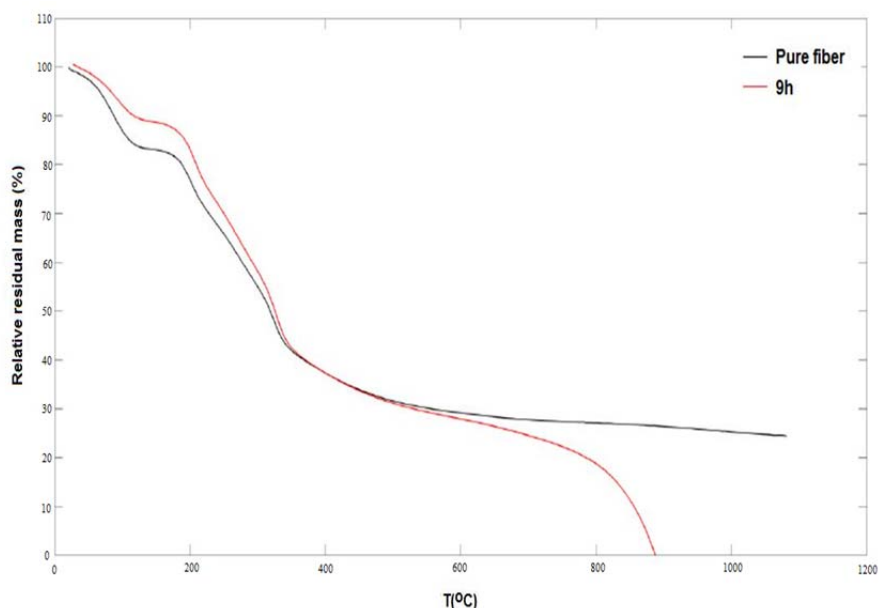
oxide particles can be better appreciated on **Figure 9**.

It is also interesting to note that the calcination time and mixing process both have a strong effect regarding the kinetics of the final decomposition of lignin. According to the data, mixtures containing the catalyst produced with a calcination time of 9 h are associated with a much higher kinetics (lower temperatures) regarding the decomposition of lignin, a fact that should bear a relation with the cationic distribution of  $\text{Co}^{2+}$  and  $\text{Fe}^{3+}$  inside the spinel crystal lattice<sup>[10]</sup>, or some specific morphology characteristic, for example, the particle size distribution, which naturally affects the surface area, and in the end the observed catalytic effect. Such investigation is important, and shall be considered in a future publication.

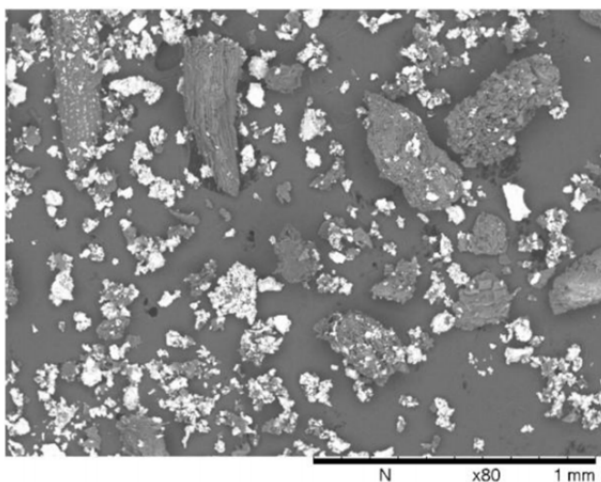
On what touches the mixing process, the use of an agate mortar crucible enhances the contact between catalyst and sample. As a result, a much efficient catalytic action is achieved, resulting in lower initial temperature for lignin decomposition. For example, the SEM image obtained for the mixture with the catalyst calcined

for 3 h before the TG test (**Figure 10**), which has not been produced with the agate mortar crucible, clearly shows that many catalyst particles appear to agglomerate, and not to have any contact with the

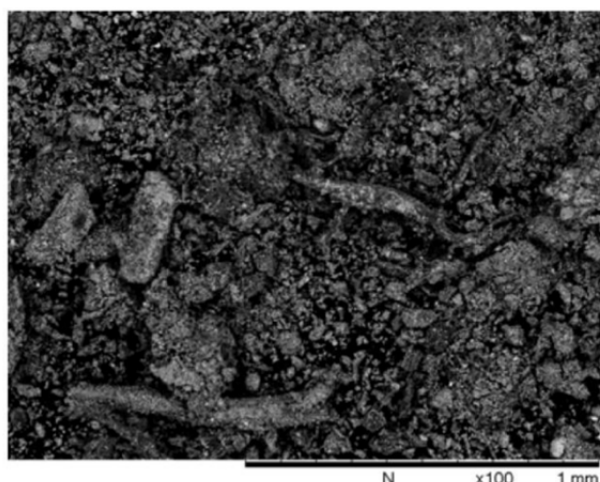
fibers at all. Considering the mixture produced with the agate mortar crucible, a much higher coverage of the fibers surface is achieved, as observed on **Figure 11**.



**Figure 9.** TG signals for pure fiber and mixture with agate mortar—catalyst produced at 1,000 °C for 9 h.



**Figure 10.** SEM image of mixture containing catalyst particles produced for 3 h at 1,000 °C.



**Figure 11.** SEM image of mixture containing catalyst particles produced for 9 h at 1,000 °C and mixing using agate mortar crucible.

### 3.3.1 SEM and XRD analysis after TG

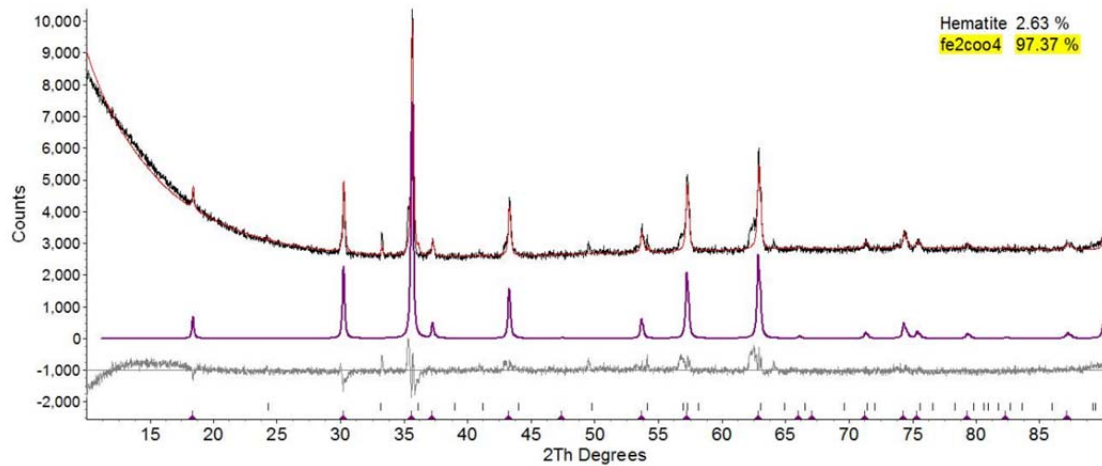
The observed effect of the spinel for decomposition of lignin should be interpreted as if the oxide particles are acting as a catalyst, which can be explained based on two facts.

First of all, the oxide material does not show any mass loss tendency (**Figure 5**), suggesting that the material does not react during the thermal process, which is expected for any catalyst.

Indeed, the XRD result from the material produced after TG analysis with the mixture

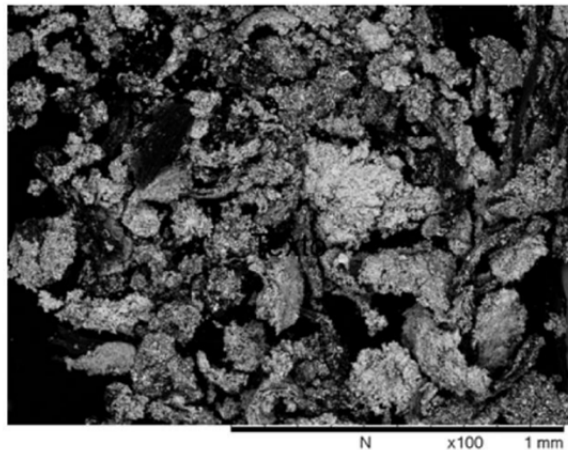
containing the catalyst calcined for 9 h and using the agate mortar crucible (**Figure 12**) evidences the presence of the same phases initially identified in the oxide pure sample— $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_2\text{CoO}_4$ , and in similar proportions. The remaining non identified peaks should be related to the presence of ash particles. It is also interesting to note that no trace of some crystalline phase containing carbon has been detected, corroborating the thesis that in this sample all lignin present has been converted to volatile organic smaller molecules.





**Figure 12.** XRD signal for mixture with catalyst calcined for 9 h and agate mortar crucible after TG.

Secondly, in the presence of the oxide particles, the decomposition of lignin should follow another path (**Figure 9**), which does not involve fixed carbon formation. This is also expected from the action of a catalyst, which, in the present case, activates another mechanism for accomplishing the thermal decomposition of the lignin molecules. Indeed, the SEM analysis of the same sample indicates the majority presence of the oxide, and visually no fiber particles (**Figure 13**).



**Figure 13.** for mixture with catalyst calcined for 9 h and agate mortar crucible after TG.

### 3.3.2 Kinetic analysis

As pointed out before, the presence of the spinel catalyst stimulates another mechanism for lignin decomposition, whereas no fixed carbon formation is involved.

The TG signal associated with this last reaction for the mixture with the oxide calcined for 9 h, and mixed with the mortar crucible (**Figure 14**), can be used, together with equation (2) in order to evaluate

the process global activation energy ( $E_a$ ) and reaction order ( $n$ ). Before applying equation (2) to the experimental data, however, reference temperature ( $T_r$ ) and heating rate ( $\Phi$ ) must be determined. This can be performed through adjusting a linear function to the experimental temperature profile,  $T_r$  and  $f_i$  being, in the present case, respectively equal to 19.89 K/min and 31.98 °C.

Through use of a minimization MATLAB code, which implemented a simplex minimization algorithm, values of  $E_a$  and  $n$  can be simultaneously determined, being, respectively, equal to 85.291 kJ/mol and 0.1237. The results from the optimization process can be seen on **Figure 15**, which shows that the model describes in a quantitative level the experimental data.

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 equation (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.

Finally, it should be mentioned that the present activation energy is in the range proposed by Raad *et al.*<sup>[11]</sup> for organic biomasses, which studied the kinetics of carbonization of lignocellulosic biomasses (46 kJ/mol to 98 kJ/mol). 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.

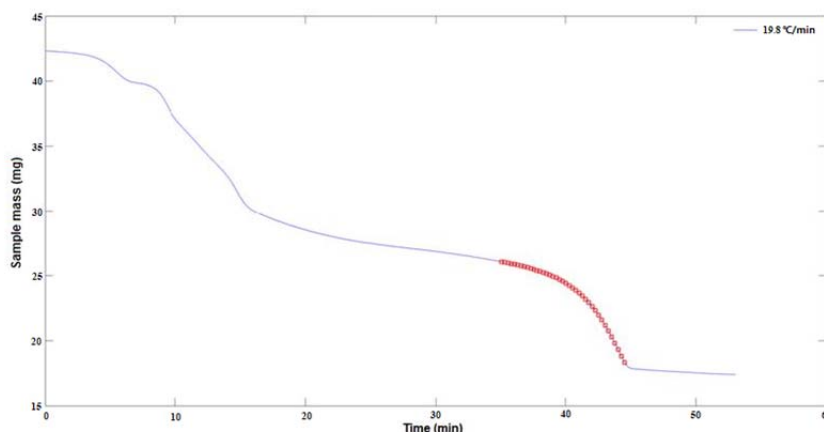


Figure 14. Selected TG data for kinetic analysis.

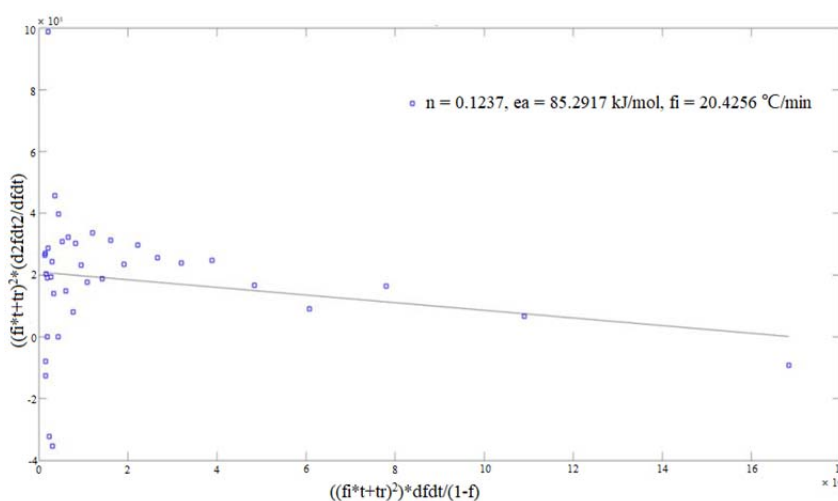


Figure 15. Result from kinetic analysis according to proposed dynamic model.

## 4. Conclusions

The thermal behavior of the pure green coconut fiber up to the temperature of 1400 °C suggests that the thermal biomass degradation should end with the lignin decomposition, thereby forming some amount of fixed carbon. The thermogravimetric analysis of pure oxide catalyst 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, which influence both particle size and cationic disorder, shown a measurable influence over the observed catalytic activity, which, according to the present results, shall involve an alternative mechanism,

whereas lignin is fully converted to volatile molecules, or, in other words, no fixed carbon is formed. Moreover, the mixing process with conducted with the agate crucible confirmed that a greater contact between the biomass and the catalyst enhances the catalytic activity, and, as a result, shifts the initial temperature for the lignin decomposition to much lower values. These facts are of extreme importance in order to increase the efficiency of bio-oil production during hydrothermal pyrolysis.

Finally, the proposed kinetic model for describing the full lignin gasification enabled a quantitative representation of the experimental data, 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.*<sup>[11]</sup>

for typical organic biomasses of lignocellulosic nature. Moreover, the reaction order was very close to zero, which is expected for a molecular simple thermal decomposition process of a solid material, whereas kinetic behaviour shall not depend on the initial solid material concentration.

## Conflict of interest

The authors declared that they have no conflict of interest.

## References

1. Kumar S, Selvarajoo A. Feed forward neural network modeling of biomass pyrolysis process for biochar production. *Computer Aided Chemical Engineering* 2015; 45: 1681–1686.
2. Carrijo OA, Liz RS, Makishima N. Fiber of green coconut as an agricultural substrate. *Horticultura Brasileira* 2002; 20(4): 533–535.
3. Cortez IAB, Iora ES, Gómez EO. *Biomass to energy*. São Paulo: Unicamp; 2008. p. 419–434.
4. Tomczak F, Sydenstricker THD, Satyanarayana KG. Studies on lignocellulosic fibers of Brazil. Part II: Morphology and properties of Brazilian coconut fibers. *Composites Part A: Applied Science and Manufacturing* 2007; 38(7): 1710–1721.
5. Limayem A, Ricke SC. Lignocellulosic biomass for bioethanol production current perspectives, potential issues and future prospects. *Progress in Energy & Combustion Science* 2012; 38(4): 449–467.
6. Raveendran K, Ganesh A, Khilar KC. Pyrolysis characteristics of biomass and biomass components. *Fuel* 1996; 75(8): 987–998.
7. Yang H, Yan R, Chen H, *et al.* Characteristics of hemicellulose, cellulose and lignin pyrolysis. *Fuel* 2007; 86(12-13): 1781–1788.
8. Spencer P, Ansara I. *SGTE casebook: Thermodynamics at work*. London: The Institute of Materials; 1996.
9. Speyer RF. *Thermal analysis of materials*. Boca Raton: CRC Press; 1993.
10. Siqueira RNC, Oliveira PF. Synthesis of  $\text{Al}_2\text{MnO}_4$  spinel via  $\text{H}_2$  reduction. *Tecnologia em Metalurgia, Materiais e Mineração* 2014; 11(2): 163–170.
11. Raad TJ, Pinheiro PCC, Yoshida MI. General equation of kinetic mechanisms of carbonization of eucalyptus spp. *Cerne* 2006.