

## COMPARING THERMOGRAVIMETRIC RESULTS WITH A ROTARY KILN EXPERIMENTAL DATA OF SUGARCANE BAGASSE PYROLYSIS

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***Abstract.** The present work examines the experimental results obtained from sugar cane bagasse pyrolysed in an electrical rotary kiln and those from bagasse thermogravimetric curves, considering different heating rates (5, 10, 15 °C/min). To obtain curves considering the biomass thermal decompositions in the kiln, similar to the TG's curves, it is necessary to intercalate constant heating rates with constant temperature intervals. These curves show geometric similarity between them, including the slope values of the thermal degradation lines that correspond to the holocellulose and lignin regions. The final yield at 500 °C, however, does not match, (The TG values were situated between 6.5 and 17 %, while the kiln values were in the range 24.5 to 26.5 %). All these facts offer strong evidence that if there is considerable mass scale change from the thermogravimetric sample and that of the kiln reactor, information from thermal analysis may be somewhat misleading.*

***Keywords.** Pyrolysis, Thermal Analyses, Thermogravimetric Curves, Heating rate .*

### **1. Introduction**

The present energy world crisis resulting from the shortage of fossil fuels and from environmental problems caused by an abusive use of natural resources, has been motivating the scientific community to look for new technologies which would allow for the economical use of renewable sources of energy. In Brazil the main sources of exploration, considering the current levels of technology, are the hydraulic, the natural gas and the biomass, even knowing that the hydraulic is, nowadays, less attractive than it was in the past, due to environmental and economical restrictions, imposed by protection laws, and/or by the physical, or geographical limitations of the sites where hydraulic sources are still available. Moreover, the hydraulic source is dependent on the climatic changes, and therefore, it should count on Government policies and investments, to implement, for example, the thermoelectric sector to avoid the lack of water, generated by long droughts, as the one in 2001, Júnior (2001-2003). Thus, another Brazilian option is the thermoelectric plants, fuelled by natural gas, which has a high calorific capacity and is the cleanest of the fuels. But, as is known, this energy may be four times more expensive than the hydraulic. In addition, natural gas is not distributed everywhere in the country, Júnior (2001-2003). In such a context, biomass, through rational and sustainable programs, appears to be a very attractive source of energy, being also a renewable source and largely found in Brazil.

Biomass is any material belonging to the vegetable kingdom, such as plants, agricultural cultures and their residues, as sugarcane bagasse, rice husk or coffee shell, branches of trees, extractive vegetable oils, or from species planted as soy, palm oil and castor oil plant, besides the urban garbage and animals manure.

The use of bioenergy can also stimulate the job market in the countryside, promoting best conditions for the people, and the reduction of oil importation, Rocha (2003). Studies show that biomass may allow the perfect equilibrium of CO<sub>2</sub> emissions into the atmosphere, and may contribute to the reduction of 97% of such emissions. In consequence, there will be a decrease in the greenhouse effect.

Brazil is well known for the use of sugarcane biomass through one of the most important programs of renewable energy generation in the world. It has employed modern technologies to convert biomass into electricity, through cogeneration systems, in many paper, cellulose, sugar and alcohol industries. Sugarcane bagasse, for example, is used in several Brazilian distilleries, and sugar industries to supply all there energy needs (electric and thermal), Bezzon (1998).

However, the economical exploitation of biomass imposes full knowledge of the processes involved in the conversion of this energy source. Several researches have been conducted to improve the conversion efficiency of cellulose into solid, liquid, or gaseous products, and to reduce the environmental contamination of such conversions. One of the most practical ways of obtaining an efficient fuel from biomass is through pyrolysis - thermal decomposition through high temperatures ( $> 400\text{ }^{\circ}\text{C}$ ) in the absence of oxygen. The results are a combustible gas, liquid products (tar and pyroligneous acid) and a solid substance (charcoal) which can be converted into activated carbon, Cortex et. al. (1997).

Some parameters involved in thermal degradation processes in industrial furnaces, or in laboratorial kilns, may be understood considering thermal analyses (TA). There are different types of thermal analyses, among them, Thermogravimetry, (TG), which is defined as a technique that registers the percentage of variation in the mass of a sample in terms of temperature and/or time, for a chosen heating ratio, Willard et. al. (1996). To process a TG analysis, a minimum amount of mass, in mg, is utilized, while the industrial furnaces, or laboratorial kilns are charged with an amount at least a thousand times larger. This scale difference is the main reason of the disagreement between results obtained in furnaces and the ones originated in TG analysis.

The present work compares and discusses Thermogravimetric data obtained from sugarcane bagasse samples processed in a SHIMADZU, TGA-50, thermobalance, with results drawn from the sugarcane bagasse pyrolysis, obtained in a rotary kiln.

## 2. Experimental

### 2.1 The Raw Material

The raw material used in this research was the sugarcane bagasse, from Agroindústria Japungu S.A., a sugarcane distillery located in Santa Rita-PB-Brazil. The bagasse is a residue from the sugarcane, after the cane juice extraction. Essentially, it is a lignocellulose material, with chemical components, such as holocellulose, (cellulose and hemicellulose), lignin and organic and inorganic elements.

### 2.2 Equipment

#### 2.2.1 The Electrical Rotary Kiln

All the experiments related to pyrolysis were carried out in a Japanese electrical rotary kiln, made by CHINO, whose make and model are RICH TAKABAYASHI and RS-S, respectively. The kiln has a tubular fixed bed reactor (93 mm of internal diameter and length 900 mm). See Fig. (1). The heating system is formed by three sets of electrical resistances, in series, and disposed in two opposite semi-cylindrical cradles. The longitudinal length of the resistances is 700 mm. The kiln may be programmed to settle heating rates, and temperatures limits.



Figure 1. The Electrical Rotary Kiln.

#### 2.2.2 The Thermogravimetric Balance

The TG curves describing the thermal decomposition of the sugarcane bagasse were obtained from a thermobalance SHIMADZU, model TGA-50. The whole apparatus was in a room at  $25\text{ }^{\circ}\text{C}$ . The TG experiments took into account three different heating ratios, (5, 10 and  $15\text{ }^{\circ}\text{C}/\text{min}$ ), and temperatures ranging from ambient to  $510\text{ }^{\circ}\text{C}$ . The sample masses varied between 3.5 to 4.5 mg.

### 2.2.3 The Thermocouples

For each set of electrical resistances in the rotary kiln there were a K type thermocouple, and a temperature dial. Temperatures could also be registered by a plotter. All these devices were disposed in a frontal control panel. Another K type thermocouple was used to determine the temperatures at the geometrical center of the biomass samples.

### 2.2.4 The Sample Capsules

To store the samples during the pyrolysis, iron cylindrical capsules, with a lid at the top, having internal diameter of 48 mm, length of 140 mm, and weighting between 250 and 270 g, were built. See Fig. (2).



Figure 2. The Sample Capsules

### 2.2.5 The Samples

#### 2.2.5.1 Samples for TG Analysis

All the samples taken to the thermogravimetric balance, were formed by the raw material from bags brought from a distillery, and sieved - mesh 0.7 (ABNT) – to guarantee a certain uniformity in the grains. Just 3.5 to 4.5 mg of the sieved material filled up the cylindrical alumina cell (6 mm diameter and 2.5 mm long) of the TG balance.

#### 2.2.5.2 Samples for the Rotary Kiln

Two kinds of samples were considered to be used in the kiln reactor: 1. An amount of 30 g of raw material, not sieved. 2. 30 g of raw material: a) With 8 % of reduction in its original mass. b) With 10% of reduction in its initial mass.

The reason for using samples with fixed moisture reduction was determined by the thermogravimetric data, which showed curves initializing with 8 or 10 % of moisture content losses.

### 2.2.6 The Sample Temperature

To plot and evaluate TG curves, it is necessary to know, the heating rate, the temperature behavior of the sample, some physical characteristics of the sample, as well as the thermogravimetric balance principles, (Cortex et. al., 1997; Wendlandt, 1986 and Keattch et. al. 1975). To obtain the thermal decomposition data from pyrolysis in a furnace, or in a kiln, similar parameters are required, but they are much more difficult to pin point. The heating rate is an example. Some furnaces, or kilns, as the one used in this research, may control the heat flux of the electrical resistances, however, this controlling cannot guarantee, as is obvious, that the sample will undergo the pyrolysis under the established heating rate. To increase the control of the thermal decomposition of the samples inside the capsules, a thermocouple, K type, was placed in the axis of the capsule, at the center of the cylinder. The temperature measured at this point represented the instant temperature of the whole sample, during the heating process, which started at ambient temperature, and finished at 500 °C, when the kiln was turned off, opened and cooled by a fan placed in the room. These temperatures were registered using a Micrologger 21X.

## 2.2.7 The Kiln Thermal Decomposition Curves

Eight capsules properly loaded with bagasse were employed to help to plot the curves of thermo-decomposition, related to the kiln. To get the first point of the curve, the kiln was turned off when the temperature of the biomass reached 140 °C. Then the kiln, and consequently the biomass was cooled to 100 °C, and then weighed. After reaching ambient temperature, a second capsule was put in the kiln, which was then turned on, being turned off again when the temperature of the biomass arrived at 190 °C. At this stage the kiln was put out. And when the temperature decreased to 100 °C the sample was weighed, giving the second point of the curve. In this way, and by considering the temperatures at 240, 290, 340, 390, 440 and 500 °C up to end of the pyrolysis process, the thermo-decomposed curve was built. The steps below were also sequentially followed:

- The kiln was heated with a 10 °C/min heating rate, for a period of 30 minutes;
- After the above period, the temperature was kept constant for 10 minutes;
- A heating rate of 7.1 °C/min was then applied for 8 minutes;
- And after that the heating rate was settled to 8.4 °C/min, for 7 minutes;
- Finally, the heating rate was turned to 10.4 °C/min, for 10 minutes.

This procedure guaranteed a heating rate, for the whole period, close to 7.2 °C/min. It has been noticed that the kiln programmed to be heated at a heating rate of 10 °C/min, from ambient temperature to 500 °C, produces very high levels of heating rates at the center of the sample.

## 3. Results and Discussions

### 3.1 Thermogravimetric Curves

Figure (3) shows the thermogravimetric and the derivative of the thermogravimetric curves, for the sugarcane bagasse, considering a heating rate of 5 °C/min. (It was observed that for 10 and 15 °C/min, all TG and the corresponding derivative curves have almost the same profiles of the ones shown in Fig. (3)). Figure (3) shows three different configurations for mass losses. The first one corresponds to the bagasse dehydration reaction, occurred between the room temperature and 100 °C. The second, represents the holocellulose thermal degradation, which may be subdivided in two regions: the first one, presenting slower changes, corresponding to the hemicellulose degradation, happened in the range between 220 °C and 340 °C. The other one, showing faster changes in the profile, is relative to the cellulose degradation, and occurs between 350 °C and 400 °C. The third region of thermal decomposition, is due to the lignin presence. It was done in the interval between 400 °C and 650 °C. From the derivative curve, it is much easier to distinguish all these different regimes, or regimes.

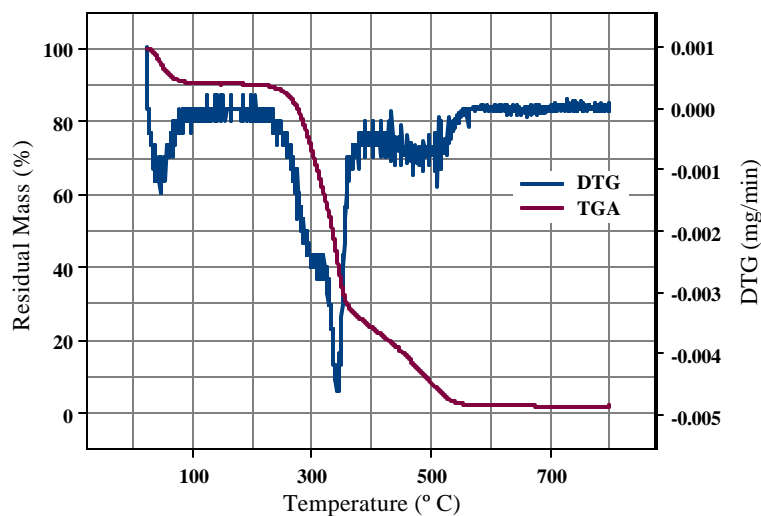


Figure 3. The thermogravimetric and the derivative of the thermogravimetric curve plotted considering the heating rate equal to 5°C/min.

Figure (4) presents three TG for 5, 10 and 15 °C/min heating rates, in terms of the biomass temperature. As expected, see Fig. (4), generally speaking, the higher the heating rate, the more the curves dislocate to the right. It is visible, however, that the curve concerned with the rate of 10 °C/min has a quicker evolution to the left than the one of 15 °C/min, inside the lignin region. The fact that the higher the heating rate, the faster the lignin region is reached, Rocha (2003), explains the superposition of curves of rates 10 °C/min and 15 °C/min, in Fig. (4).

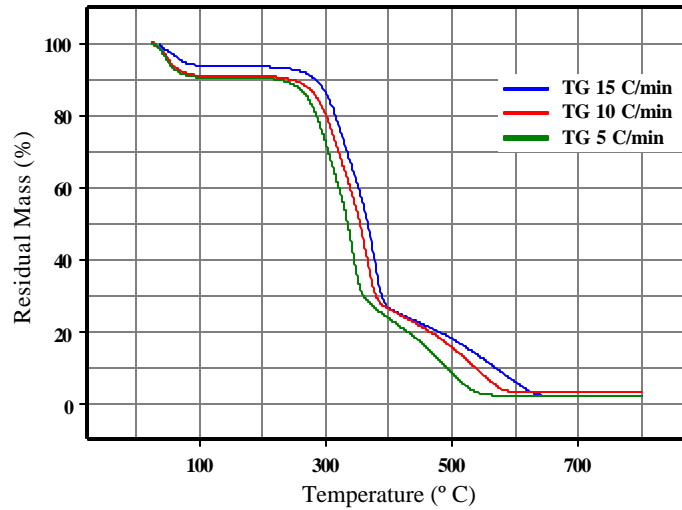


Figure 4. TG curves in terms of the sample temperature for heating rates, such as 5, 10 and 15 °C/min.

### 3.2 Temporal Temperature Distribution

Figure (5) presents three temperature distributions. The first one shows a line which represents the temperature distribution of the kiln electrical resistances. The other two curves were plotted from data obtained considering the procedures described in section 2.2.6, and taking into account two samples: the first one consisting just of raw material picked from a bagasse bag brought from the distillery, the second formed by bagasse taken from the oven, having a 8 % moisture content reduction.

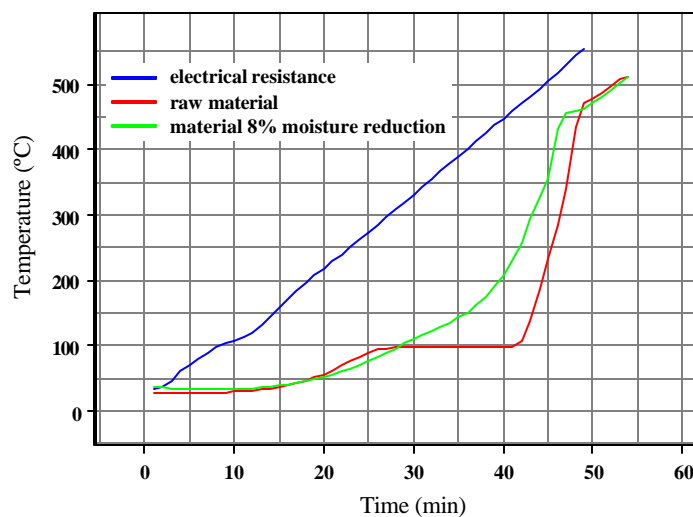


Figure 5. Temperature distributions of the electrical resistance, raw material and material with 8 % of moisture content reduction, using a heating rate of 10 °C/min in the kiln.

Observing the curve related to raw material, one may see that there is no change in the temperatures during the first 15 minutes. Basically, it shows values of the room temperature. This sluggishness is caused by the thermal inertia, due to the low conductivity of the air between the capsule and the reactor walls, combined with the poor conductivity of the bagasse. After this period, and during the next 10 minutes, a heat wave front starts heating the raw material sample, keeping a heating rate constant and close to 6 °C/min, which increases the sample temperature to 100 °C. As it may be seen Fig. (5), this temperature is kept constant for about 14 minutes, seeming to indicate the existence of a phase change (the water evaporation). The sequence shows a fast increase in the sample temperature, when it quickly goes, from 100 to 475 °C, presenting a quite constant heating rate close to 62.5 °C/min. During this last period the holocellulose and the lignin kinetic reactions also took place. In spite of this abrupt change in the sample temperature, the heating rate of the kiln was maintained at 10 °C/min. Subsequently, the raw sample curve exhibits a slope very similar to the line which represents the temperature behavior of the kiln electrical resistances (See the “straight” line in Fig. (5)), which displays a heating rate nearly equal to 10 °C/min. This was expected, considering that all kinetic reactions have ceased, and the remaining pyrolysed biomass was just acting as a substrate to drive the heat coming from the electrical resistances.

The following procedures, using a bagasse sample with 8 % of moisture reduction, were used to examine if the first part of the curve considered above, really corresponded to the evaporation phenomenon: By filling the eight capsules with bagasse at 8 % of moisture loss, a new experiment, very similar to the one just described, was made, resulting in the third curve in Fig. (5) (green color) . Examining this curve, one can see that it perfectly coincides with the second one, during the first 30 minutes, see the red curve. Afterwards, however, between 30 and 45 minutes, the curve is not so flat as the other one, making it evident that there was no evaporation there, considering that the sample was already dehydrated. The rest of the third curve shows the action of the two kinetic reactions, related to the decompositions of the holocellulose and the lignin. Finally, at 450 °C, the slope of the curve becomes identical to that of the temperature of the resistances, overlapping the second curve.

### 3.3 Comparisons Between Thermogravimetric Plots and Curves of Thermal Decomposition

Figure (6) displays three TG plots (related with the three heating rates: 5, 10 and 15 °C/min) and two curves representing two cases of thermal decomposition of sugarcane bagasse previously dried: the first having 8 %, and the second 10 % of moisture content loss, based upon the initial mass. Concerning the TG curves, Fig. (6) shows just portions ranging between 140 °C and 510 °C, that is, the domain of temperature variations considered in the electrical kiln.

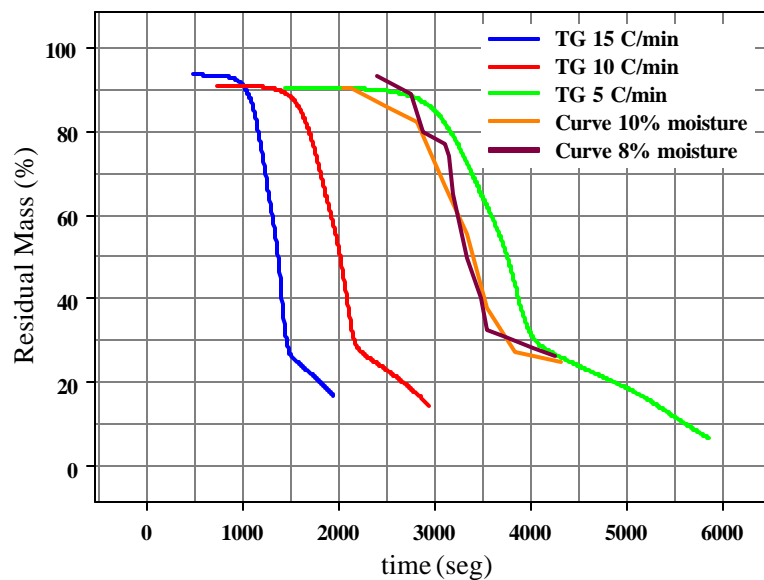


Figure 6. Curves of thermal decomposition in the kiln with 8 and 10 % of moisture content reduction and TG with 5, 10 and 15 °C/min, as function of the time.

From Fig. (6), it is evident that the thermal decomposition based on steps presented above (section 2.2.7) produced profiles much closer to the 5 °C/min TG plot, than to the other TG curves. On the other hand, after the dehydration process in all TG curves, the thermal decomposition of the biomass started, for the heating rates of 5, 10 and 15 °C/min, respectively, at 2500, 1500 and 1000 seconds, right after the limit of 200 °C is reached, Figure (7). This fact is not

observed in the curves based on the thermal decomposition data using the kiln. In both cases for biomass previously dried (moisture content losses of 8 and 10 %) the thermal decomposition was initiated at 140 °C, showing a constant rate of mass reduction: 10.8 % (8% of moisture content losses) and 17,5% (10 % of moisture content losses), see Fig. (7). Following this decaying phenomenon, a quicker process of thermal decomposition takes place, for both cases (8 and 10%), which corresponds to the holocellulose degradation. Then, the new segment in each curve (thermal degradation of the holocellulose and lignin), shows a behavior similar to those presented by the TG curves, including the proximity of the slope magnitude. However, the final percentage of mass losses, evaluated at 500 °C, differs considerably from the experimental data collected from the thermogravimetric analysis. For example, from TG, under the heating rate of 5, 10, 15 °C/min, the final percentage values were respectively 6.5, 14 and 17 %, while the two curves concerning the previously dried material (8 and 10%) exhibited almost the same result, i.e., 25 % of its initial mass.

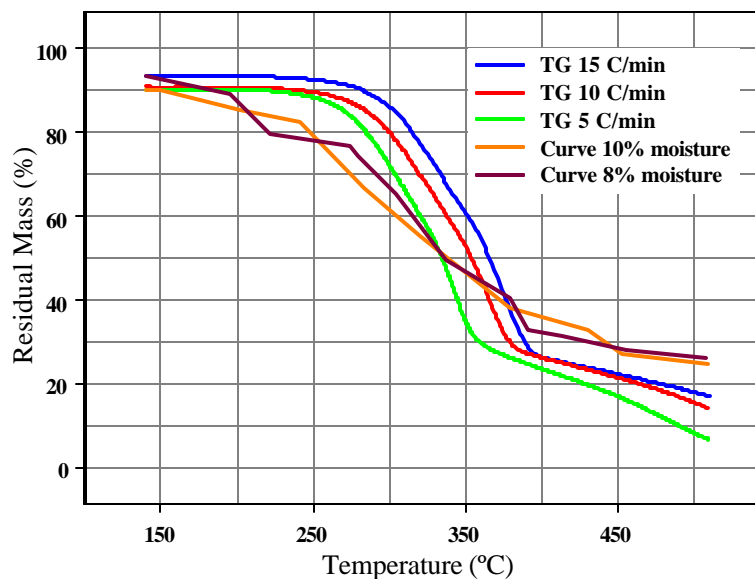


Figure 7. Curves of thermal decomposition in the kiln, with 8 and 10 % of moisture content reduction, and TG with 5, 10 and 15 °C/min, as function of the temperature.

#### 4. Conclusion

Several variables are involved in the final TG analysis result. These variables, among others, may be: the size and the uniformity of the particles, the compactness of the sample, heat convection currents in the kiln, or in the furnace reactor, the amount of the sample, the thermal conductivity of the sample material, etc., which, generally speaking, are not easy to control. Just these aspects may suffice to make it complex, and sometimes impossible, the comparison of measurements from thermo-balances, of different manufacturers.

Therefore, if the comparisons are made between results produced by thermogravimetric balances and those from industrial furnaces, or laboratorial kilns, the incongruences may be basically motivated by the incomparability of the amount of mass used in both situations. A TG analysis requires a sample having a mass which may vary from few milligrams to approximately 10 grams, depending on the raw material under consideration, or upon the equipment type, Jaroniec et. al.(1990). In this study, for example, the mass utilized in the TG analysis ranged between 3.5 to 4.5 mg. In contrast, the electrical kiln, where all the pyrolysis were conducted, which has a very small reactor compared to a semi-industrial furnace, required an amount of bagasse 7000 to 8500 times larger than the mass used in the thermogravimetric balance. As an immediate consequence, the heat of reaction in the kiln provided a significant temperature increase, inside the biomass in the reactor, while such an effect was not perceived during the TG analysis.

This study shows that to undergo a pyrolysis process having a fixed heating ratio in a furnace, or in a kiln, is not a simple task, as different from when a thermogravimetric balance is used.

Taking into account all the above remarks, one should be aware that for the indications and conclusions emerged from a thermal analysis to be transferred to furnace, kiln, or oven operation control, where the amount of mass employed, and/or the experimental conditions are completely different, they should at least be checked, corrected, or considered with caution.

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