

# CASE STUDY: THE LIGNOCELLULOSIC COMPONENTS INTERFERENCES IN THE THERMAL BEHAVIOR OF BRAZILIAN SAVANA BIOMASS

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## ABSTRACT

The residual biomass has become increasingly important in the energy scenario due to its energetic potential and easy acquisition in isolated communities. The heterogeneous nature of biomass makes the analysis of its composition a relevant factor in the development of thermochemical processes. Several researchers show that understanding this heterogeneity of biomass can be a strategy for optimization and search efficiency of thermochemical processes, since it is possible to predict the results and in addition, the reactor design based on the characteristics of biomass. In this context, the purpose of this work was to study the behavior of three biomass of the Brazilian savana - *Dipteryx alata* (baru), *Hymenaea stigonocarpa* (jatobá-do-cerrado) and *Caryocar brasiliense* (pequi), comparing the lignocellulosic results with the thermal behavior obtained by thermogravimetric analysis. The analysis were compared with results of several researchers, confirming that those analysis are parameters that influence the yield of the desired product. The results of this work elucidate that the moisture and extractives content of pequi is greater than the other biomass and that the temperature peak of cellulose and lignin from all biomass in this study are quite close. However, the hemicellulose's temperature peak of pequi is lower than baru and jatobá's temperature peak. Moreover, the results showed that the composition of the lignocellulosic biomass is an extremely important factor in selecting the greater reactivity material.

**Keywords:** biomass composition, bioenergy, baru, jatobá, pequi

## NOMENCLATURE

ASTM American Society for Testing and Materials  
dm/dt derivative of the weight loss versus time,  
min<sup>-1</sup>  
DPP/UnB Decanato de Pesquisa e Pós-Graduação /  
Universidade de Brasília  
FAPDF Fundação de Apoio à Pesquisa do Distrito  
Federal  
HHV Higher Heat Value, MJ/Kg  
HPLC High Performance Liquid Chromatography  
NBR Brazilian Standard Reference  
N<sub>2</sub> Nitrogen  
O<sub>2</sub> Oxygen  
SFB Serviço Florestal Brasileiro  
T Temperature, °C

TAPPI Technical Association of the Pulp and Paper  
Industry

## Greek symbols

$\alpha$  heating rate, °C/min  
 $\rho$  energy density, Kcal/m<sup>3</sup>

## INTRODUCTION

The biomass is currently considered as a potential source of energy. Biomass utilization has becoming important due to the availability and versatility of existing biomass and also for being a sustainable source (Tilman et al., 2006). The biomass

from industrial residues is one of the most studied biomasses, given that the industries have shown concern with the disposal of their residues and also because the sustainability issue is now matter of survival for the future's guarantee. In this context, three industrial residues were chosen to be studied in this paper - baru, jatobá e pequi, which are wastes/residues of extractive activity in the Brazilian savana.

The baru (*Dipterix alata* Vog.) is an arboreous vegetal specie, belonging to the Leguminosae-Papilionoideae family. The baru tree has a lifespan around 60 years and has its early fruiting at about 6 years. For practical purposes, with respect to the commercial use, the baru tree presents a productive crop every two years (Carraza et al., 2010).

The jatobá-do-cerrado (*Hymenaea stigonocarpa* Mart.) is a tree that can normally reach up to 15 meters high, with records of up to 40 meters. The tree begins to bear fruits with 8-10 years. A tree does not usually bear fruits every year. Whereas some trees produce a small amount of fruits, others can produce up to 2,000 fruits. Nonetheless, the average is 800 fruits per tree. The jatobá's bark has approximately 40% water in its composition (<[www.cpac.embrapa.br](http://www.cpac.embrapa.br)> Acesso em 04/06/2015).

The pequi (*Caryocar brasiliense*) is part of one of the most important Cerrado's vegetal species family, belonging to the *Caryocaraceae* family and to the *Caryocar* gender. The pequi tree production, from seedlings produced from seeds, starts 4 to 5 years after planted. The yield of pulp oil is 30% to 40% by fruit weight. In 1 hectare there is, approximately, a productivity of 1,200 boxes of fruit per year. Each hectare of crop produces up to 3,200 liters of oil, and each plant provides, on average, 6,000 fruits per year (<[www.agencia.cnptia.embrapa.br/gestor/agroenergia/arvore/CONT000fbl23vmz02wx5eo0sawqe3egcicvo.html](http://www.agencia.cnptia.embrapa.br/gestor/agroenergia/arvore/CONT000fbl23vmz02wx5eo0sawqe3egcicvo.html)> Acesso em 04/06/2015).

The cellulose, hemicellulose and lignin percentages will depend on the biomass in study and the thermal degradation process is mainly influenced by the biomass composition. Thus, it is necessary to know the lignocellulosic components, given the importance to predict effectiveness of the biomass conversion process (Perez et al., 2002; Faravelli et al., 2010). These organic substances contained in the biomass can be converted into heat an energy without contributing to the emission of CO<sub>2</sub>. This fact allows the biomass to work as a carbon neutral power source. Therefore, it has become a very important energy source in recent decades (Pang et al., 2013). The lignin has an important role in the formation of coal, since the lignin acts in the second stage of thermal decomposition of biomass in an oxidizing atmosphere (Demirbas, 2001; Shen et al., 2009). The high ash content is associated with the lignin content. High ash contents jeopardize the equipment with inlaid in the pipelines and they can also absorb heat causing their fusion. As a result, the ash content can clog and wear

out the construction material of the reactor or furnace. Therefore, the smaller the ash content, the lower the residual material inside the burning equipment (Ollero et al., 2003; Gilbert et al., 2009; Kleinlein, 2010).

Even though biomass has been used as an energy source for many years, it is still important to understand the thermal behavior of biomass in order to ensure an efficient use (Pang et al., 2014). It is possible to predict the yield and composition of pyrolysis products of any biomass, if its composition is known (Stefanidis et al., 2014). Several authors have studied the biomass composition in the literature however, few of them have studied the effect of the major components of the thermochemical conversion process (Raveendra et al., 2014; Yang et al., 2006; Worasuwannarak et al., 2007; Wang et al., 2008). Due to the variations in the chemical composition, the difference in reactivity of biomass should be better understood in order to optimize the process to obtain fuels and chemicals with high selectivity and efficiency (Carrier et al., 2011).

There are few studies regarding the pyrolysis of these biomasses and also few studies predicting the type of product and its yield trough the composition of biomass are even more scarce (Silveira, 2012). According to that, this work aims to analyze the contributions of hemicellulose, cellulose and lignin for the thermal behavior of three Brazilian savana biomass - baru, jatobá and pequi, in order to understand the influence of those biomass on the thermochemical process.

## MATERIALS AND METHODS

• **Origin of the studied biomass:** the experiment was conducted with the core of pequi without pulp, peel of baru fruit and bark of the jatobá tree from a fruit extraction of a plantation located in the state of Goiás, Midwest region of Brazil, which belongs to COOPCERRADO (Rede de Comercialização Solidária de Agricultores Familiares e Extrativistas do Cerrado - Empório do Cerrado). (<[www.emporiocerrado.org.br/pt-br/documentos/artigo-rede-um-novo-protagonismo-social.pdf](http://www.emporiocerrado.org.br/pt-br/documentos/artigo-rede-um-novo-protagonismo-social.pdf)> Acesso em 17/06/2015).

• **Extractives content:** The methodology used for the oil extraction was the policies standart TAPPI 204 om-88 Technical association of the pulp and paper industry, with adaptations (TAPPI – T204);

• **Ash content:** The methodology used to determine the ash content without extractable, used the policies standart TAPPI T211 om-93 “Ash in wood, pulp, paper and paperboard combustion at 525°C” (TAPPI T 211);

• **Lignin content:** Laboratory procedures were adopted, LAP #003 and LAP#004, in accordance with Templeton & Ehrman's article, 1995 (Templeton and Ehrman, 1995);

• **Holocellulose content:** It was calculated by difference. The percentage contents of total lignin and

“free ash” were subtracted from 100%;

• **Moisture content:** Immediate analysis according to the standard NBR 8112/86 with adaptations (NBR 8112/86);

• **Thermal analysis (TG/DTG):** The TG/DTG curves were obtained in a simultaneously analyser Model SDT 2960 from TA Instruments, with a heating rate ( $\alpha$ ) of 10°C min<sup>-1</sup> from room temperature ( $\cong$  25°C) up to 1000°C under a 100mL/min flow of synthetic air ( $80 \pm 0.5$  of N<sub>2</sub> and  $20 \pm 0.5$  of O<sub>2</sub>);

• **Energy density:** It was calculated from the product between the higher heating value – HHV, and the basic density – Bd (ASTM NBR 7190/1997).

## RESULTS AND DISCUSSION

The physicochemical results of each biomass are elucidate in Table 1. It is possible to see that the results from moisture and extractives from pequi were far greater than the other biomass. A high moisture content interferes in the reaction since biomass spends more energy to initiate the process of decomposition of the components and the high content of extractive and ash inhibits the formation of certain compounds during the thermal decomposition (Gómez, 2002; Barakat et al., 2015). Some authors studied the effects of moisture and biochemical properties for the specific energy requirement. The lignin content according to the authors, was determined by Klason method and HPLC analysis was used to quantify monosaccharides (glucose, xylose, arabinose and uronic acids). They concluded that the higher the cellulose and lignin content, the lower is the energy required in the conversion processes (Barakat et al., 2015). On the other hand, they also concluded that the greater the amount of hemicellulose, the higher is the energy requirement. Another aspect to be noticed is related to the density of the material. It is noteworthy that one of the main objectives in the pyrolysis is to obtain products with an energy density higher than the original biomass. Therefore, the density is also a relevant factor to select the biomass (Bridgwater et al., 2008). It may be observed that there is a correlation between the energy density and the ash content. This fact was also verified by some authors that analyzed the ash content for the bagasse (Vieira et al., 2010).

Table 1. Physicochemical characterization.

	Baru	Jatobá	Pequi
Moisture	12.02 %	11.56 %	28.56 %
Energy Density ( $\rho$ )	1,707.91 kcal / m <sup>3</sup>	1,020.28 kcal / m <sup>3</sup>	1,284.19 kcal / m <sup>3</sup>
Holocellulose	65.82 %	60.69 %	60.65 %
Lignin	31.82 %	38.07 %	36.99 %

Extractive	21.65 %	13.25 %	40.73 %
Ash	2.6 %	1.08 %	1.22 %

Other authors have studied the effects of cellulose, hemicellulose and lignin to obtain gaseous products in the thermochemical conversion using pyrolysis or gasification of certain biomass. They noticed in their results that the biomass composition significantly affects the gas release profile. They concluded that high cellulose and hemicellulose content may result in higher concentrations of CO and CO<sub>2</sub> and high lignin content results in a higher concentration of CH<sub>4</sub> (Pasangulapati et al., 2012). Other researchers obtained their results that a biomass with high lignin content presents a high yield of coal. However, the complete combustion of lignin is achieved at higher temperatures, at 750°C, and hence the maximum efficiency is achieved at higher temperatures, since the authors carried out pyrolysis on a microcalorimeter at a rate of 1 °C/s (Dorez et al., 2014). With this assumption, it can be verified that there is a direct influence on the composition of biomass for the yield of products, for example, biomass with higher content of lignin should be used to obtain coal. Either way, it is important to emphasize that the composition and other parameters have influence, as previously mentioned.

Another important result is related to the carbon conversion efficiency. Some researches show that cellulose had a higher conversion efficiency of 99%, followed by hemicellulose with 92% and finally lignin with 52%. Carbon conversion efficiency is defined as the ratio of available carbon in gaseous and liquid products with respect to the total amount of available carbon in the biomass (Pasangulapati et al., 2012; Lv et al., 2004). Figures 1 and 2 show the results of weight loss of biomasses. It is possible to observe that the jatobá -*Hymenaea stigonocarpa* has a faster weight loss at the beginning of the reaction. Nonetheless, the pequi - *Caryocar brasiliense* after the decomposition of hemicellulose is replaced by a faster weight loss than other biomasses.

Figure 2 shows the results of the derivative of the thermogravimetric analysis at 20°C/min. It is possible to notice that the three biomasses picks are noticeable and that the decomposition of baru and jatobá are quite similar, however baru has a pick at 221,980°C that might be active cellulose or anhydrocellulose. Some authors studied the decomposition process and noticed that during the small weight loss before 250°C, different reactions occur and may lead to the formation of an intermediate, sometimes called as active cellulose or anhydrocellulose. The active cellulose refers generally to an intermediate resulted of a partial depolymerization of cellulose, while the anhydrocellulose consists in an intermediate formed after the dehydration reactions (Van de Venden et al.,

2010; Scheirs et al., 2001; Banyasz et al., 2001).

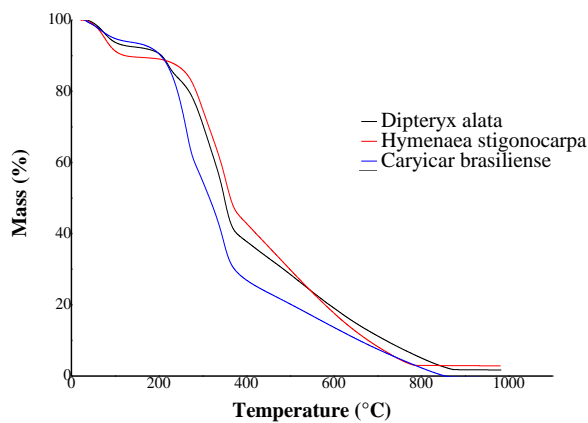


Figure 1. Weight loss at 20°C/min.

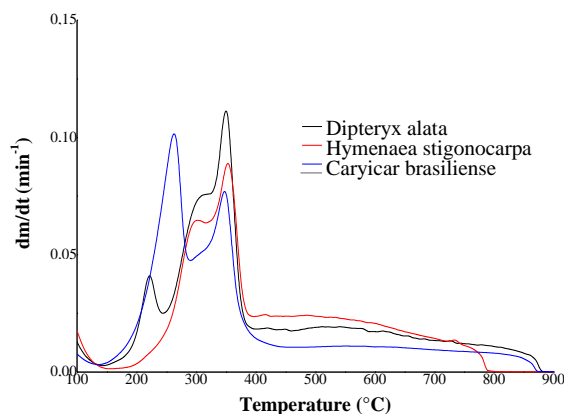


Figure 2. Derivative weight loss at 20°C/min.

It is important to emphasize that the difference between the curves of the two biomasses with pequi can be justified by the high oil content and high moisture of this biomass causing more complex and different reactions if compared with the others (Silveira, 2012). Furthermore, it is possible to notice that for the three biomasses, the beginning of decomposition occurs with approximately  $\pm 90\%$  by weight at a temperature of  $\pm 200^\circ\text{C}$ , which is related to moisture loss and early devolatilization. This same fact was observed by other authors that studied the lignocellulosic components in their decomposition (Pasangulapati et al., 2012). Another justification for the appearance of a differentiated peak from baru would be the largest amount of holocellulose and lower amount of bauru's lignin if compared to other biomasses. Researchers evaluated the effect of age with respect of the chemical composition of eucalyptus wood and found that the older the tree, the smaller is the holocellulose content and the higher is the lignin content (Silva et al., 2005). The results of these authors show that baru tree is younger than jatobá because of the results of holocellulose and lignin shown in Table 1. Furthermore, an excess of cellulose results in unprotect and exposed cellulose fibers,

which means that the fibers tend to form various inaccessible arrangements, once the cellulose has a tendency to agglomerate together. The cellulose fibers are contained inside the hemicellulose, which are intimately protected by lignin (Ding and Himmel, 2006; Ishizawa et al., 2009). These factors prove that the anatomical constitution influences the differences in the composition presented. The conversion of hemicellulose takes place between  $250^\circ\text{C}$  and  $350^\circ\text{C}$ , the cellulose occurs between  $330^\circ\text{C}$  and  $370^\circ\text{C}$  and the lignin decomposition rate is between  $300^\circ\text{C}$  and  $400^\circ\text{C}$  (Lv and Wu, 2012; Yang et al., 2007; Shen et al., 2010; Wang et al., 2009). The pequi has the temperature peak of hemicellulose at  $262,974^\circ\text{C}$ , and hence lower than the other biomasses. This is explained because the moisture content of pequi is higher than the other biomasses and, in addition, the pequi has higher oil content resulting in different reactions at the beginning, right after the loss of total moisture.

Some authors studied the lignocellulosic components and obtained by thermogravimetric analysis peak temperatures of  $291^\circ\text{C}$  for hemicellulose,  $320^\circ\text{C}$  for lignin and  $356^\circ\text{C}$  for cellulose. The authors concluded that the hemicellulose decomposes at a lower temperature followed by lignin and cellulose. Moreover, the authors also concluded that when the percentage of hemicellulose and cellulose is high, the temperature of its peak also increases, leading to a lower reactivity. Another important factor to be highlighted by the authors was that the peak of lignin is masked by overlapping of the other two components and that lignin decomposes over a wider temperature range and its peak varies in between hemicellulose and cellulose. Finally, they concluded that the lignocellulosic components do not act independent during the pyrolysis and hemicellulose is more reactive if compared to cellulose and lignin (Pang et al., 2014). The same conclusion was obtained on this work for the three biomasses, since the weight loss of lignin could not be noticed due to the overlap of the other components. In addition, the decompositions of each component followed the sequence hemicellulose, lignin and cellulose, as already mentioned by other authors. This is justified because the structural construction of the hemicellulose and lignin provides an inefficient packing, which decomposes at lower temperatures. On the other hand, the cellulose requires more energy to promote its combustion due to its crystal packing, so it decomposes at higher temperatures.

Besides all the above discussions, it is important to emphasize on the importance of higher calorific value of the final product. Many of the properties discussed above influence the potential energy, such as ashes. Some authors analyzed coal and high calorific value of the coal *Eucalyptus spp* resulted in  $31.06 \text{ MJ/kg}$ ;  $13.40 \text{ MJ/kg}$  for the peach pit coal;  $31.17 \text{ MJ/kg}$  for coal *Hymenaea stigonocarpa*;  $22.74$

MJ/kg for the coal castor bean meal, demonstrating that these results vary with the type of biomass and its properties (Barcellos, 2007; Vale et al., 2001; doumera et al., 2015). Thus, as a continuation of this work proposes perform pyrolysis and analyze the biomass with the greatest potential for energy generation, utilizing important information such as the characteristics described in this study.

## CONCLUSIONS

Each material exhibits a particular characteristic when it is pyrolysed due to the portion of components that constitute them. The reactions occurring during the pyrolysis can be explained by the composition of the biomass, which can interfere in the energy required, in the types of gases produced, in the yield of coal and finally, in the process efficiency as a whole. The biomasses studied in this work present energy profile and composition to be utilized by various thermochemical processes, which can be employed in isolated communities for decentralization of power generation of energy, because their composition is heterogeneous and these residues are usually obtained through extractive communities.

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