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Physical – Chemical Characterization of Biomass Samples for Application in Pyrolysis Process

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The use of lignocellulosic biomass as an energy source has considerably increased. Due to the diverse natures of biomass materials, their properties widely range and exhibit different behaviors in thermal processes. The most important properties that provide information about a fuel are heating values, ash composition, proximate (determination of moisture, ash, volatile and fixed carbon content), and ultimate analysis (C, H, N, S and O composition). Moreover, the kinetic study of the thermal behavior of a fuel can be useful for the understanding of the complex decomposition process of each material. This study focuses on the physical-chemical characterization of six lignocellulosic biomasses, namely coffee husk, tucumã seed, sugar cane bagasse, peanut shell, rice husk and pine sawdust, widely available in Brazil. A thermogravimetric analyzer was used to study their decomposition behavior in a pyrolytic environment. Non-isothermal thermogravimetric data were used and the application of a model-free isoconversional method enabled the evaluation of the activation energy (E_a) of the biofuels. The curves also show that the behavior during thermal decomposition varies from one biomass to another and these differences imply the importance of a comprehensive characterization study of fuels for the development and optimization of reactors. The knowledge on biomass properties enables the prediction of environmental impacts and technical aspects related to thermal processes. Therefore, thermal decomposition behavior is a consequence of the feedstock physical-chemical characteristic, which also provides valuable information regarding features of the complex reactions that occur throughout the pyrolysis of the biomass.

1. Introduction

Currently, most energetic systems in the world are dependent on fossil fuels (coal, oil and gas), which are the main source of carbon dioxide (CO_2) emissions and, among the major challenges today is the production of energy minimizing environmental impacts (Vergrat et al., 2011).

Biomass is an attractive energetic source, since it is renewable, available in most countries and can replace fossil fuels. For its efficient application to energy conversion processes, the knowledge on its physical-chemical properties is very important and determines the behavior of the fuels in processes such as combustion, gasification and pyrolisis (Kazagic and Smajevic, 2007). In addition, identify and classify potential biomass based on its potential value, will allow higher quality of its integration and optimized result (Lim et al., 2013).There are several routes of biomass conversion focusing the generation of electrical/heat energy, transport fuel and chemical feedstock. To select a specific conversion process, several factors should be taken into consideration and the chemical and physical characteristics of the fuel are an important aspect because they can influence the performance of a specific fuel in a process. For example, ash content and composition is an important parameter in thermal conversion, because it can impact the operational system leading to the formation of slag, reducing the efficiency of the process, and influencing the economic aspects as a whole (McKendry, 2002).

Pyrolysis is a complex phenomenon in which the thermal decomposition in the absence of oxygen enables the release of volatile compounds, leading to the formation of liquid (oil tar) and solid products (char) with more energetic density and high calorific value. Such a characteristic makes these products to be used as fuels (Garcia et al., 2012).

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Both chemical (endothermic and exothermic reactions) and physical (softening, resolidification) changes determine the decomposition reaction rates, which are dependent on kinetic parameters. The knowledge on the behavior of such parameters that accompanies the process can be useful to interpret the reaction kinetics mainly regarding the mechanism of the process.

Studies on the kinetic analysis of major biomass constituents (hemicelluloses, cellulose and lignin) have been conducted under inert atmospheres. For instance, Braga et. al (2013) reported activation energy of hemicelluloses + cellulose of two biomasses (rice husk and elephant grass) using thermogravimetry and two mathematic models. They found average activation energy values between 220 and 229 kJ mol^{-1} and concluded that both models are suitable for the proposed study.

Jereguirim and Trouvé, 2009 studied the biomass A. Donax and found 110 kJ mol^{-1} for activation energy of hemicelluloses and for cellulose, values between 90 -140 kJ mol^{-1}. Yao et al. (2008) studied ten different types of biomass and values ranged between 160 - 170 kJ mol^{-1}.

However, understanding the correlation between pyrolysis behavior and characteristics of biomass is still far from completion, as the biomass thermal degradation is a very complex process governed by several chemical reactions.

The chemical changes in different products depend on kinetic rates and suitable mathematical models are important to know the evolution of the process (Jeriguim and Trouvé, 2009).

This study focuses on the physical-chemical characterization of six lignocellulosic biomasses widely available in Brazil. The characteristics were evaluated by means of elemental analysis, calorimetry and thermogravimetry. Kinetic parameters of the thermal decomposition of those materials in inert atmosphere were obtained by thermogravimetry and a mathematical model (Model Free kinetics).

2. Materials and methods

2.1 Biomass preparation

Six lignocellulosic biomass samples namely coffee husk, tucumã seed, sugar cane bagasse, peanut shell, rice husk and pine sawdust were selected for this study.

All samples were chopped in a household blender and sieved as received i.e the samples were evaluated without pre-treatment and in a wet basis. Particles whose diameter was lower than 109 µm were selected.

2.2 Ultimate Analysis

The elementary composition (C, H, N, S) was determined by using approximately 2 mg of the sample in a CE Instruments analyzer, model EA 1110. The oxygen percentage was determined by difference and taking into consideration the wettability and ash contents obtained by the thermogravimetric curves under air environment.

2.3 Determination of heating values

2.4 Hight heating values (HHV), which are measured in terms of the energy content per unit mass (kJ/kg), were determined in triplicate using the calorimetric bomb IKA C 2000, according to ASTM E711-87 standard.Thermogravimetric analysis

Thermogravimetric experiments for both compositional analysis and kinetic studies were performed in a simultaneous TG/DTG and DTA TA Instruments (SDT 2960).

Compositional analysis comprises the determination of moisture (M), volatiles matter (VM) + fixed carbon (FC) and ash contents. The kinetic study is related to the activation energy determination for the thermal degradation process of the samples under inert atmosphere.

The experimental conditions for both studies are listed in Table 1.

Table 1. Condition analyses

Experimental conditions Studies	Heating rate (^{o}C min^{-1})	Sample mass (mg)	Atmosphere	Burn out temperature	Flow rate (mL min^{-1})
Kinetic study	1-10, 15, 20, 25, 30	2-10.0 ± 0.5	3- Nitrogen	1000	100
Compositional analysis	4-10	5- 5.0 ± 0.5	6- Air	700	100

2.5 Mathematical Model for the kinetic study

Model-free kinetics was used for the determination of the activation energy. This model is based on isoconversional techniques to calculate the activation energy as a function of conversion (α) of the chemical reaction. The theory is based on Eq.1.

$$\frac{d\alpha}{dt}=k(T)\,f(\alpha) \tag{1}$$

where t is the time, T is the temperature, f (α) is the model of the reaction and k (T) is the coefficient of Arrhenius reaction rate. After the necessary adjustments and considerations, as shown in several prior studies Vyazovkin (1999); the Model-free kinetics is represented by Eq.2.

$$\ln\frac{\beta}{T_{\alpha}^{2}}=\ln\left[\frac{RA}{E_{\alpha}g(\alpha)}\right]-\frac{E_{\alpha}}{R_{\alpha}}\frac{1}{T_{\alpha}} \tag{2}$$

where β is the heating rate, g (α) is an integrated model of reaction and subscript α represents the values of a given conversion.

The extent of conversion (α) is determined experimentally by means of mass loss. The conversion ranged from 0 to 1 and this interval is determined according to the different steps of thermal degradation, which is better observed through DTG curves.

For the kinetic study of a biomass, it is interesting to include hemicelluloses, cellulose and lignin degradation process and disregard moisture release in the model. Each sample is different and, therefore, the chosen interval of thermal degradation is also different. Figure 1 shows the TG and DTG curves for all biomass samples at heating rate of 20 °C min-1. Other heating rates (10, 15, 20, 25 and 30 °C min^{-1}) were applied for kinetic study and similar profiles were observed.

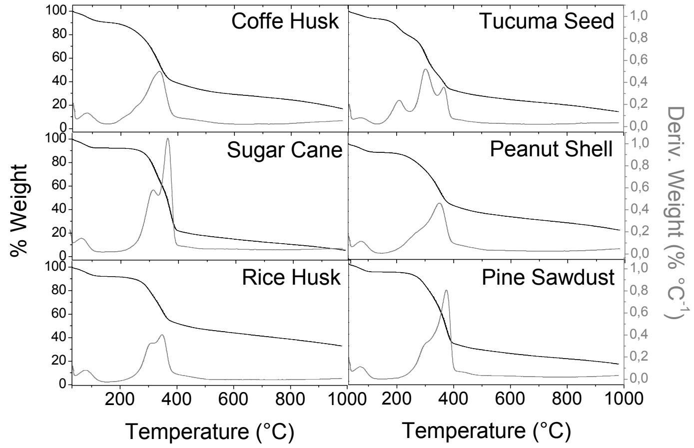

Figure 1: (a)TG (—) and (b) DTG (—) curves for six biomass samples. Conditions: Purge gas N_2. Flow rate of 100 mL min^{-1}. Heating rate: 20 °C min^{-1}

The DTG curves show different decomposition steps for all samples. These steps (from 130 up to 520 °C, depending on the biomass) correspond to approximately 80 % of the mass loss and are related to the release of volatile hydrocarbon from hemicelluloses, cellulose and lignin.

3. Results and Discussion

3.1 Ultimate Analysis and Heating Values (HHV and LHV)

Table 2 shows high heating values, elemental and compositional analyses of the biomass samples.

The correlations between hydrogen/oxygen (H/O) and carbon/oxygen (C/O) ratios were used to locate the six biomass materials in the Van Krevelen diagram (Figure 2), which provides information on the differences in the carbon, hydrogen and oxygen compositions. The lower the ratios the higher the energetic content. This correlation is related to the degree of aromaticity and carbonation (Nanda et al.,

2012) and can also be explained by Dulong's Equation defined as HHV (MJ kg^{-1}) = (33.5 x %C + 142.3 x %H - 15.4 x %O) / 100.

The materials with a relatively low O/C ratio have more energy density and higher HHV because there is more chemical energy in C-C bonds than in C-O bonds.

Table2. Physical-chemical characteristics of the biomass samples.

	Ultimate Analysis (wt% on wet basis)					Compositional Analysis			
Biomass	C	H	N	S	O	Moisture (%)	(VM+FC) (%)	Ash (%)	HHV (MJ kg^{-1})
Coffee husk	43.13	5.02	1.55	0.67	32.78	10 8.44	11 82.54	12 7.40	13 16.79 ± 0,07
14 Tucumã seed	48.83	6.12	0.88	-	32.20	20 6.08	21 88.18	22 5.97	23 20.77 ± 0,07
24 Sugar Cane	45.05	5.57	0.25	-	37.91	30 6.95	31 89.82	32 3.21	33 17.46 ± 0,10
34 Peanut Shell	41.52	7.43	2.12	0.60	27.96	40 7.98	41 79.10	42 12.80	43 16.52 ± 0,03
44 Rice Husk	31.47	6.67	1.04	0.50	23.03	50 8.19	51 61.68	52 29.53	53 15.39 ± 0,01
54 Pine Sawdust	45.95	7.47	0.32	0.57	34.32	60 6.90	61 88.37	62 4.71	63 17.03 ± 0,07

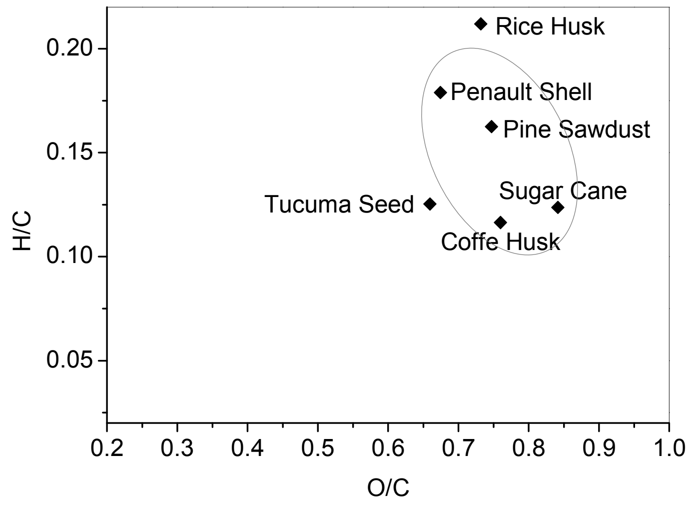

Figure 2: Van Krevelen diagram of atomic ratios for six biomass samples

Among the biomasses evaluated, tucumã seed has shown a higher carbon percentage (48 %), hence higher heating values (17.8 MJ kg^{-1}). Figure 2 shows this biomass is positioned on the left side of the Van Krevelen diagram. Rice rusk has a greater ash content than the other five materials, which is a strong condition for its lower HHV (12.44 MJ kg^{-1}) and to be positioned in the superior region of the diagram.

As penault shell, pine sawdust, sugar cane and coffee husk are positioned at the same region of the Van Krevelen diagram, it is supposed that they have similar reactivity. And it has been confirmed by experimental results of calorimetry, whose results have shown that these biomasses have similar calorific values (between 16.5 and 17.4 MJ kg^{-1})

The combination of elemental analysis, compositional analysis and calorific value is an important characteristic to qualify a fuel, however, in this study some complementary information is provided by means of a kinetic study as presented as follows.

3.2 Model Free Kinetics

Activation energies for ninety conversions are shown in Figure 3 and the average values are reported in Table 3. An important information to evaluate the behavior of a fuel (Conconi and Crnkovic, 2012) is the profile of the Ea *versus* α curve. Notably the curve of tucumã seed doesn't remain constant, but varies during the thermal process. For other biomasses, the profiles of the curves are almost constant along the thermal degradation. Tucumã seed has also a lower average activation energy value in comparison to the other five biomasses.

Kinetic study resulted in a series of activation values with average values between 159 and 205 kJ mol^{-1}. However, it is interesting to observe that not only the values but also the profile of the activation energy *versus* conversion curves provides important information on the performance of the fuel.

For tucumã seed, the slope of the curve between 0.1 and 0.9 conversions is positive. Such a behavior can be explained based on the releasing of the low molecular weight compounds at the beginning of the thermal decomposition and as the reaction proceeds, the highest weight molecular compounds present in the tucuma seed are released.

The low activation energy value (70 kJ mol^{-1}) at the beginning of the process indicates that tucumã seed ignites more easily than the other biomasses.

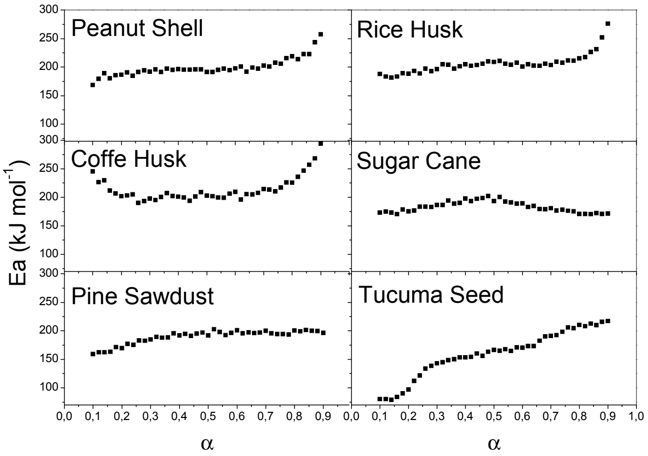

Figure 3::Activation Energy versus conversion for the biomasses in inert atmosphere

Table 3: Average values and standard deviation of the activation energies

Biomass	Temperature range (°C)	Activation Energy (kJ mol^{-1})
Coffee husk	1 167 – 423	2 214 ± 22
3 Tucumã seed	4 121 – 417	5 160 ± 41
6 Sugar Cane	7 210 – 416	8 183 ± 9
9 Penaut Shell	10 146 – 407	11 199 ± 16
12 Rice Husk	13 170 – 401	14 206 ± 17
15 Pine Sawdust	16 170 – 418	17 189 ± 12

4. Conclusions

Six lignocellulosic biomass samples (coffee husk, sugar cane bagasse, penut shell, rice husk and tucumã seed) with potential interest for energy production were evaluated under two aspects: physical-chemical characterization and kinetic study of pyrolysis.

Non-isothermal thermogravimetric experiments were carried out under inert conditions (N_2), whose data have been used to obtain activation energy versus conversion curves.

The curve of tucumã seed presented different behavior than the curves of other biomasses. Whereas for tucumã seed presents lower activation energy at the initial step of the thermal degradation and monotonously increases with the reaction, for the others, the profile have shown a more stable behavior.

Lower activation energy at the beginning of the process is indicative of the easy ignition of the fuel. In this case, all materials have oxygen in their composition, which explains ignition process even under absence of oxygen in the environment.

On average, activation values found in this study are within the range reported in the literature, but with additional information showing the variation of activation energy over the thermal decomposition.

The Van Krevelen diagram, suggests that peanut shell, pine sawdust, sugar cane and coffee husk have similar reactivity and H/C and O/C values, which is confirmed by the profile of the activation energy versus conversion curves.

Tucumã seed is characterized by the lowest H/C and O/C ratios, the lowest activation energy at the beginning of the thermal degradation and also the highest HHV value. All these characteristics indicate that tucumã seed is the most reactive material examined in the present study.

Calorific values, elemental and compositional analyses are important characteristics of a fuel. As complementary information of this statement, our finds have shown that the profile of the activation energy *versus* conversion curves also provides important indicative of the performance of the fuel in a thermal process.

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