A THERMOGRAVIMETRIC STUDY ON DEVOLATILIZATION BEHAVIOR OF RICE HUSK DURING PYROLYSIS

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Abstract.

A renewable source most abundant is biomass and is possible to reduce the greenhouse gasses emission using alternatively for power generation. The energy recovery from biomass can be performed by thermochemical processes (combustion, gasification e pyrolysis), however, pyrolysis has been receiving special attention than other processes. Pyrolysis of biomass is a process of thermochemical decomposition in an inert medium of lignocellulosic material. This process has great potential for producing biofuels using non-food sources such as agricultural, urban, industrial and animal wastes. The rice is the cereal most used in the world and 20% of weight is husk, thus provides a large amount of waste. The low density of the rice husk is an important factor in the unfeasibility of its power generation use due to the high cost of transport. In this way; rice producers often perform uncontrolled burning leading to the emission of pollutants. The Brazilian Institute of Agricultural Economics (IEA) indicates the Paraiba Valley as the largest producer of this cereal in the São Paulo state, which accounts for about 50% of production. In this study, the slow pyrolysis of rice husk using thermogravimetric analysis (TGA) is studied. Preliminary results demonstrate that the rice husk has 62.24% of volatile matter and 29.34% is biochar (15,88% fixed carbon and 13,46% ash). The PCS of rice husk was 15768±23,66 Joule/g, showing perfect conditions to submit this biomass under pyrolysis process. For better understanding the pyrolysis performance was studied based on work Lin et al., (2014).

***Keywords**: Devolatization, biomass, pyrolysis, rice husk, biomass.*

1. INTRODUCTION

The use of fuels from fossil resource has increased due to demand for energy. This has intensified the emission of greenhouse gasses (GHGs) that poses a serious threat to the socio-economic and political balance of the human population and ecologic interference (IPCC, 2014). According to the IPCC reports, these implications are given global warming and climate change (Heede and Oreskes, 2016).

Preventively to this eminent situation, the UN (United Nations) realized many international conferences to discuss proposals actions to reduce or even eliminate the GHGs emissions, especially greenhouse gases and the last international conference accomplished was based in Paris in 2015 receiving the name of COP21 that had the main objective to establish a legal and universal agreement to keep the temperature rise below 2 °C, for this one of bedazzled scenarios is the zero emission, which would promote the stability of GHGs (Hsu, 2015; Tokimatsu, 2015).

To support these proposals, studies have been conducted to develop mitigation technologies for GHG emissions, among these, the use of biomass as partial or complete alternative substitution of conventional fuels. Biomass is the most abundant renewable source of solar energy. However is necessary to improve processes to maximize the efficiency of the systems for better use of its energy potential (Thornley et al., 2015).

According to Demiral (2006), energy recovery from biomass has focused on thermochemical processes (combustion, gasification, pyrolysis, carbonization and direct liquefaction). However, pyrolysis has received special attention, for to present real potential conditions to produce biofuels with a high energy density from non-food sources (agricultural, urban, industrial and animal waste). Pyrolysis is one of the promising ways to convert biomass to various solid, liquid and gas products. Therefore, it is important to understand the fundamental pyrolysis characteristics under different reactions conditions.

Pyrolysis of biomass is defined as the process of thermochemical decomposition under inert medium of lignocellulosic material from 300 °C to about 700 °C (Park et al., 2014), wherein temperature and time determine which type of fuel will be prioritized since this process provides fuel in different phases: solid (charcoal or biochar), liquid (bio-oil) and gas (pyrolytic gas). The versatility of the pyrolysis process is evidenced by the diversification of its products and shows economically advantageous for obtaining mainly bio oil atmospheric pressure, and can be used as a chemical platform of high energy density. The efficiency of the pyrolysis process is increased due the use of part of fuel yielded for driving operation, so is, a sustainable process (Shemfe et al., 2015).

The rice is the cereal most commonly used in the world and second Chungangusit et al. (2004), the shell of the cereal, which represents 20% of the total weight generates a large amount of waste. The low density of rice coat is an important factor in the unfeasibility of its energy use for generating high cost of transport (Almeida, 2010). In this sense, rice producers often perform uncontrolled burning leading to emissions and loss of energy use or without other rice husk destinations is discarded in rural areas, remained unchanged for years because its biodegradation is slow due to the high content of phenolic (Almeida, 2010).

As appointed by Kongkew et al, (2015) among differents biomass which could be used through the pyrolysis process have the agricultural waste from rice cultivation. Energy recovery of rice husk through the pyrolysis generates a bio-oil, studied and used as fuel for steam generator (Chiaramonti et al., 2007), and stationary engines, turbines, and diesel engines though there barriers due to the characteristics inherent bio-oil, such as low volatility, high viscosity, coking and corrosiveness (Czernick; Bridgwater et al, 2004). The products yielded changes in physical properties and chemical composition, consequently, have distinct technical and economic challenges.

A proposal for a better understanding of the pyrolysis process was presented by Lin et al (2014), where they are analyzed and correlated different parameters by TGA, generating an efficiency indicator named devolatilization index (D), that represent a parameter that determines feasibility to liberate volatile matter from raw. However, in the literature, there are scarce studies applying the devolatilization index (D) in order to evaluate the performance of biomass pyrolysis.

In this study was investigated the devolatilization behavior of rice husk using thermogravimetric analysis (TG). The effect of particle size and heat rate on devolatilization behavior was studied, through the devolatilization index.

2. MATERIALS AND METHODS

2.1 Rice husk

Rice husk provided by rice farmer from Paraiba Vale region/SP. Figure 1(a) shows the raw material, which was milled and separated in two different particle sizes, 63 µm and 212 µm respectively. A mass approximately of 10mg was used for all tests.

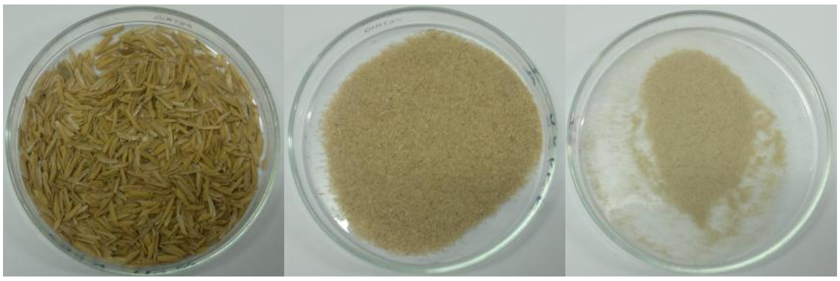

Figure 1. Rice husk samples: (a) *in natura*, (b) particles of 212µm and (c) particles of 63µm.

2.2 Thermogravimetric analyzer

Thermogravimetric analyzer SDT-Q600 (Fig.2) was used to study the thermal decomposition behavior of rice husk under pyrolysis condition. Three different heating rates were used being 10 °C/min, 20 °C/min and 40 °C/min, all samples were heated up from room temperature until 1000 ºC. Nitrogen was used as carrier gas for pyrolysis conditions with flow rate 100.0 ml/min. The tests were performed in duplicate.

Figure 2. Thermogravimetric analyzer SDT-Q600 (TA instruments).

2.3 Devolatilization index (D)

According to Biagini and Tognotti (2014), the devolatilization is a basic mechanism and the first step in all the thermochemical processes (combustion, oxy-combustion, gasification, pyrolysis) and influences the overall reactions of the fuel inside the reactor. A detailed characterization of biomass devolatilization is required to provide fundamental parameters for the feasibility, design, modeling, optimization and scaling of biomass conversion systems.

Devolatization index is a mathematic method developed to define the efficient of the pyrolysis process, determining empirically the relationship among events occurred during the process, analyzing fraction of volatile matter yielded and the event time was taken and the lead time between each event, indicating a preview of the viability of the process. It is, therefore, important to evaluate the devolatilization behavior in order to assess and optimize the production of valuable products such as char, tar, and gas (Hattingh 2013). Eq. (1) exhibit the devolatilization index proposed by Lin et al. (2014).

$$D = \frac{(-R_p) \times (-R_v)}{T_i \times \mathrm{T_p} \text{ x } \Delta \mathrm{T}_{1/2}} \tag{1}$$

Where, D is the comprehensive devolatilization index, $-R_p$ is the maximum weight loss rate each phase, $-R_v$ is the average pyrolysis rate, T_i is the initial decomposition temperature, T_p is the terminal decomposition temperature and $\Delta T_{1/2}$ is the temperature width at half of $-R_p$.

3. RESULTS AND DISCUSSIONS

Pyrolysis process of biomass can be characterized by three events: drying (moisture evaporation), main devolatilization (active pyrolysis zone) and continuous solid residues decomposition (passive pyrolysis zone) (Idris et al. 2010). These events described is easily noticeable analyzing the TG curves, wherein each event is featured with drastic changes of its shape increasing or decreasing its trend. Fig. (3),

The TG curve the drying event is actually observed in the chart of the initial range between 30 °C and 100 °C where the evaporation of moisture present in the material is responsible for the weight loss in this phase. This feature the rice husk has a little moisture corresponding the close 7% of the mass of the sample, observe a brief stretch of relative stability in the mass of the sample to the process reaches a temperature of 200 °C where starts the most significant event the main devolatilization. In this event the loss of mass is forceful and this step is characterized by the release of most of the volatiles (gases) which compose the matter, this gases has a fraction condensable when it is condensed produce bio-oil and non-condensable part is the pyrolytic gas, this event is extended until the temperature of 400 ° C, close to 50% of the initial mass is lost at this phase, from this point the mass loss is smoothed starting the last stage, the passive pyrolysis which occurs release small fraction of volatile yet added to the solid matter. The matter remains released with increasing temperature until the final stretch of the graph where only remains the solid portion (bio-char). In DTG curve can observe the mass loss peaks with the first between 80 °C and 100 °C, the second between 320 ºC and 350 ºC and the latest and greatest in 375 ºC, that curve highlight the most significant milestones in the process.

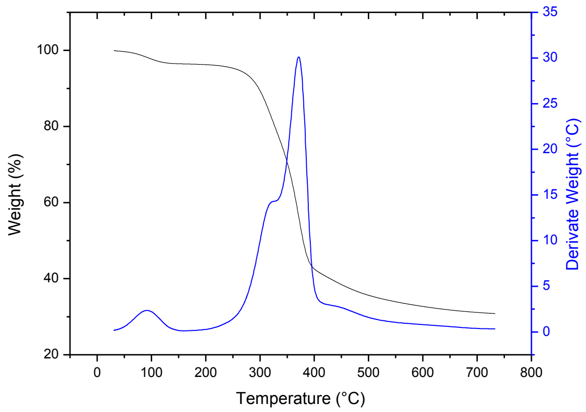

Figure 3. Pyrolysis TG/DTG Curves

Among the parameters of the pyrolysis process the heating rate is what determines the speed and intensity at which thermal decomposition occurs, and determine which products (bio-oil, biochar pyrolytic gas) will be prioritized. The thermal decomposition which corresponds to the decomposition of hemicellulose and cellulose and their conversion of rice husk to bio-char (fixed carbon with ash), is the most important phase for pyrolysis process and when to occur is just as important as then how intense occur, and heating rate is the protagonist in this step. Chen et al (2014) reported in your study an interesting phenomenon, named thermal hysteresis or thermal lag, and was decrypted as a shift of the in initial temperature of devolatilization, and through of the Fig. 4 is possible to notice this behavior roundly. Can be observed from the figure the higher the lower heating rate it is time to start the devolatilization of the greater event is the intensity. Exemplifying, the most evident peak of each curve, for the rate of 40 °C min^{-1} event. It occurred after 9 min releasing 32% of volatile material released per minute, while for the rate of 20 °C min^{-1} event occurred at 17 min with 15% volatile material per minute and 10 °C min $^{-1}$, 32 min with 7% material volatile released per minute (Thermal lag).

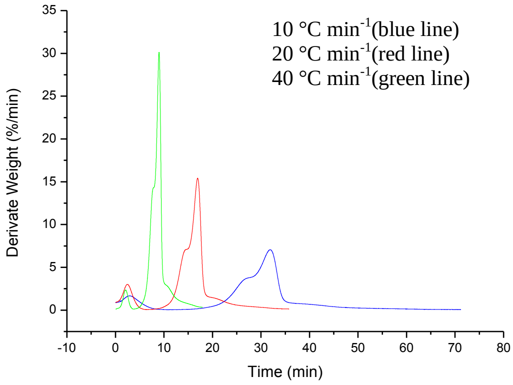

Figure 4. DTG Curves of 212µm particles size.

Figure 5 exhibit the thermal behavior under conditions of pyrolysis of where the main event take place at 354,58 °C (63 µm, 20 ºC min) and 358,96 ºC (212 µm, 20 ºC min), also shows that no significant change in profile of elucidating the process the heating rate determines the speed and intensity of the event but does not change the process pattern profile. Chen et al (2015) explains the higher efficiency of heat transfer would be achieved with a lower rate of heating and from a mathematical perspective the effects of heating rate on the thermochemical conversion process can be explained by equation degradation rate. However, the increase in heating rate yields a larger temperature gradient due to low thermal conductivity rate of the rice husk is facilitated and thus the increase of the decomposition rate

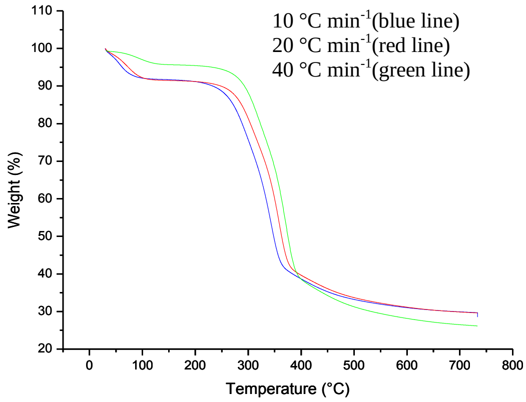

Figure 5. TG Curves of 212µm particles size.

The present study was attention concentrated on analyzing the samples of rice husk with 212µm, following indication of devolatilization index that presented improvement on Index under all heating rates proposed under this range of particulate size, and indicates as better set up the heating rate of 40 ºC/min.

Table 1. Pyrolysis characteristics of 63 µm and 212 µm at different heating rates

dp µm	β °C min^{-1}	T_i °C	T_p °C	$-R_p$ % min	$\Delta T_{1/2}$ °C	D/10^{-6} %°C min
63	10	284.9	342.28	6.846	171.14	0.41
	20	297.04	354.58	13.13	177.29	1.38
	40	304.87	364.48	22.75	182.24	3.96
212	10	289.59	343.71	7.06	171.855	0.40
	20	312.08	358.68	15.42	179.34	1.50
	40	326.73	371.52	30.11	185.76	4.79

Figure 6. shows devolatilization index shows a function of particle size and heating rate. In smaller particle size and heating rate, we can see that the devolatilization index remains unchanged. However, as the heating rate was an increase of 20 °C/min and 40 °C/min, devolatilization index had a considerable increase being most prominent with a particle size of 212 µm. Fig. 6 we can observe that the heating rate has a major effect on the devolatilization index, however, the index increases even more in larger particle sizes.

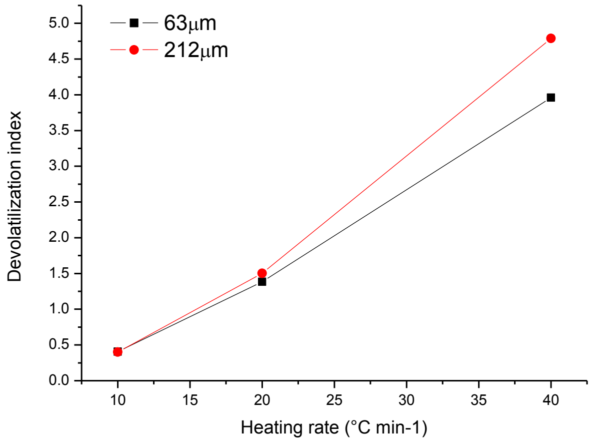

Figure 6. Devolatization index behavior of rice husk.

4. CONCLUSIONS

TG experiments indicated that pyrolysis characteristics were closely relation to sizes of biomass and heating rates, wherein heating rate is the parameter of more influence. The property mostly influenced is the maximum weight loss rate each phase (-Rp), following proportionally the changes of heating rate, confirming its direct relation. It is possible to conclude from this study that rice husk sample performed by thermogravimetry analysis (TG/DTG) confirmed the potential of good energetic resource showing a great occurrence of volatile matter (condensable gasses) ideal condition to submit this biomass for a pyrolysis process. Devolatization Index is an interesting parameter to identify the most appropriate condition to evaluate pyrolysis process efficiency and can be used as decision-making to pyrolysis process set up. For this study the most favorable parameters settings were 212 µm, 40ºC/min , rendering index D equal 4,79 %°C min/1 x 10^{-6} and the second indication was 63 µm, 40ºC/min, rendering index D equal 3,96 %°C min/1 x 10^{-6} presenting performance less, besides need milling and separation treatments.

5. ACKNOWLEDGEMENTS

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