24th COBEM - 2017

24th ABCM International Congress of Mechanical Engineering
December 3-8, 2017, Curitiba, PR, Brazil

COBEM-2017-2258
A STUDY OF BIOCHAR YIELD FROM SLOW PYROLYSIS OF RICE HUSK

Fábio Roberto Vieira; Gretta Larissa Aurora Arce Ferrufino; Ivonete Ávila
UNESP - São Paulo State University, School of Engineering, Department of Energy, Laboratory of Combustion and Carbon Capture (LC_3), Guaratinguetá-SP, Brazil
fabiorobertovieira@bol.com.br; *grettagaf@yahoo.es*; *iavila@feg.unesp.br*

Carlos Manuel Romero Luna
UNESP - São Paulo State University, School of Engineering, Department of Production, Campus of Itapeva-SP, Brazil
c_romeroluna@itapeva.unesp.br

Abstract. Rice is the most consumed cereal in the world, with rice husk equivalent to 20% of total weight, thus generating a significant amount of residue. The rice production emits a significant amount of CH_4, becoming a source of emission of greenhouse gas (GHG). In order to reduce this impact, biomass pyrolysis was proposed to produce biochar and to use in crop fertilization. The application of biochar in crop fertilization was demonstrated by many works. However, in literature there is scarce information regarding its production through the slow pyrolysis. The preliminary results have demonstrated the potential use of rice husk to produce biochar by slow pyrolysis process. Around 36% of biochar was produced from rice husk.

Keywords: *slow pyrolysis, rice husk, biochar.*

1. INTRODUCTION

Rice is the most consumed cereal in the world, with rice husk equivalent to 20% of total weight, thus generating a significant amount of residue(CHUNGSANGUNSIT et al., 2004). The low specific mass of the rice husk is the factor that makes its use unviable for energy generation due to the high cost of transportation (ALEGRE; ALMEIDA, 2010). In this sense, the farmers promote uncontrolled burning, consequently polluting air and wasting the available energy in this waste. Another practice is that, without another destination, the rice husk is discarded in rural areas and, due to its composition rich in phenolic material and slow biodegradation . it emits a significant amount of CH_4 becoming a source of emission of greenhouse gas (GHG) (MOHAMMADI et al., 2016; SINGH; COWIE; SMERNIK, 2012). One way to reduce the impact of rice production is by harnessing rice husk. Among the various options, biomass pyrolysis is the most appropriate thermochemical process, since it can produce a solid product (biochar), a liquid (bio-oil) and a gas (pyrolytic gas) (PARK et al., 2014a). Biochar has many applications, among that crop fertilization in agriculture. Bio-oil and pyrolytic gas can be used as a source of heat in the process itself making it energy-efficient (SHEMFE; GU; RANGANATHAN, 2015)

In the last decade the introduction of biochar for crop fertilization has grown, being able to mitigate the environmental impact because it is one of the techniques developed for carbon sequestration, and the carbon concentration is obtained between 45% and 92% (SHEMFE; GU; RANGANATHAN, 2015) .According to Liu et al., 2014 and Zhao et al., 2014, the use of biochar reduces soil CH_4 emission and reduces nutrient loss. Among the different types of biochar used, the rice husk presented the highest efficiency in reducing the emission of this gas (DONG et al., 2013; LIU et al., 2012).

However, the agronomic benefits of biochar depend on rice husk characteristics, soil type, climatic conditions and type of crop. Moreover, the characteristics of the biochar depend on the pyrolysis conditions (temperature, residence time, and heating rate). Regarding the biochar derived from the rice husk, there is scarce information regarding its production through the slow pyrolysis. In this way, this article presents an experimental study on the productivity of rice husk by slow pyrolysis.

2. MATERIALS ANS METHODS

2.1 Materials

Rice husk was supplied by producers from the Vale do Rio Paraíba do Sul (SP). Figure 1a shows a sample of rice husk *in natura* used in the slow pyrolysis assays. For the thermogravimetric analyzes, a sample of rice hulls was milled and sieved in a particle size of 212 µm as showed by fig.1b

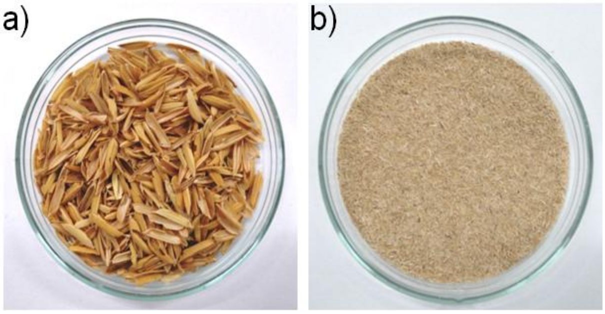

Figure 1 - (a) Rice husk *in natura*, (b) Rice husk milled (212 µm).

2.2 Experimental setup

Figure 2 shows the experimental setup used for the study of the slow pyrolysis of rice husk. An electric heater was used as coupled around of the fixed bed reactor, manufactured from metallic cylinder. In the study a heating rate (β) equal to 20°C/min was considered, since the slow pyrolysis is carried out in heating ratios lower than 100°C/min [11]. The temperatures of the pyrolysis process was 300ºC, 400°C and 500ºC, once theses temperatures were reached, it was maintained for the intervals among 1, 1,5 and 2h (isothermal process). Nitrogen at a flow rate of 100 ml/min was used as the gas carrier. Before the start of the tests, nitrogen was injected for the purpose of creating an inert environment. A shell and tube heat exchanger with a stream of water at 5°C was used for the condensation of the volatile material. These tests were carried in duplicate.

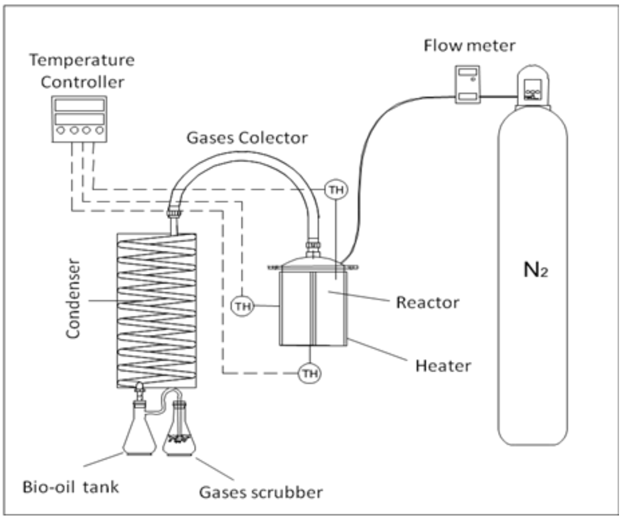

Figure 2 – Slow pyrolysis schematic diagram

2.3 Mass Balance

Park et al., 2014b, proposed in their work a procedure matching the raw mass with quantity of three products obtained in the process of slow pyrolysis. The quantities of each of these products, as well as their chemical compositions, depend on the experimental conditions and type of biomass used. Considering the products obtained, the mass balance of the process is defined by Equation (1), where m is the mass of the biomass and the products generated (biochar, bio-oil and pyrolytic gas).

$$m_{biomassa} = m_{biochar} + m_{bio-óleo} + m_{gás} \quad (1)$$

3. RESULTS AND DISCUSSION

3.1 Thermal behavior of rice husk under slow pyrolysis conditions

Figure 3 shows the thermal behavior of the rice husk under nitrogen atmosphere (N2). DTG curve indicates that the decomposition starts at 250°C, exhibits three events corresponding to the decomposition of hemicellulose (290°C), cellulose (345°C) and lignin (420°C). These events have different intensities which are related to the release of volatile material from the rice husk. The events that correspond to the decomposition of hemicellulose and cellulose are the most prominent of the pyrolysis process observed by the intense peaks in the DTG curve. However, the intensity and amplitude of the events-related DTG curve peaks will be a function of the heating rate (CHEN et al., 2015).

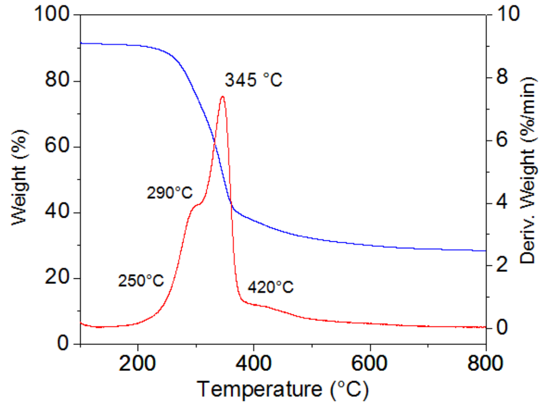

Figure 3 – TG/DTG curves of rice husk

3.2 Biochar production

3.2.1 Experimetal planning

Table 1 presents the factors and their respective levels, and the objective of the process is to obtain the highest biochar conversion from methodology proposed by Taguchi. These factors were defined by preliminary tests performed in the laboratory. Applying the Taguchi method, it was defined 3 levels for each factor, thus the matrix used for experimental test was a L9.

Table 1 – Pyrolysis process yield

Factor	Level		
	low (1)	middle(2)	high (3)
A – Heating rate - β (°C/min)	5	10	20
B - Reaction temperature - T (ºC)	300	400	500
C – Residence time - t (h)	1	1,5	2
D – Mass - M_b (g)	125	250	500

3.2.2 Pyrolysis products yields

Table 2 shows the interaction among factors and their levels based on Taguchi method and the yields of the slow pyrolysis of rice husk products obtained under the experimental tests.

It should be noted that in the mass balance the quantity of volatiles that were still contained in the solid material obtained in the tests. Thus, the amount of volatiles in thermal analysis was also determined. Note, except for test 3, the other tests show very close biochar yields. However, depending on the experimental condition adopted, different yields of bio-oil and pyrolytic gas are obtained. For example, in tests 1,2,3,4 and 6 it was not observed condensation.

It is also observed that test 5 presents the highest amount of biochar (38.08%). Condition 5 was performed in lower heating rate, higher temperature, shorter residence time and higher amount of mass. It is known that a higher temperature causes a greater release of volatile material and that an increase in residence time promotes the formation of pyrolytic gas. The experimental condition on test 3 has a surprisingly lower value in terms of biochar yield. In this case, duplicate tests must be performed to verify the repeatability of the test.

Experimental tests 7, 8 and 9, which used the highest heating rate, had very close biochar yields. The amount of bio-oil produced was in the range of 20 to 30%. It should be noted that the results presented in Table 2 are not conclusive, since they will depend on the subsequent biochar analyzes.

Table 2 – Pyrolysis process yield

Test	β (°C/min)	T (ºC)	t (h)	Mb (g)	Biochar (%)	Bio-oil (%)	Pyrolytic gas (%)
1	5	300	1	125	33,00	nd	11,63
2	5	400	1,5	250	32,06	nd	14,00
3	5	500	2	500	17,93	5,4	12,40
4	10	300	2	250	36,13	nd	51,84
5	10	400	1	500	38,08	nd	33,57
6	10	500	1,5	125	33,28	nd	49,56
7	20	300	1,5	500	30,86	28,50	38,30
8	20	400	2	125	33,98	18,22	44,03
9	20	500	1	250	31,88	30,10	32,70

3.3 Proximate analysis

Table 3 shows the results of the proximate analysis performed in TG analysis for the biochar samples obtained in each test. The results demonstrate some volatile material content in biochar yielded. The amount of volatile material is associated with the experimental pyrolysis conditions. When the pyrolysis is performed considering low temperature, heating rate and residence time. In some experimental conditions pyrolysis behaved similarly as torrefaction process.

The conditions with the highest heating rate (7, 8 and 9) had the biochar with the lowest content of volatile material and the highest fixed carbon content.

The heating rate and temperature are the most studied process conditions and state that a high heating rate promotes the production of more bio-oil, while a low heating ratio increase biochar production. The optimal temperature to maximize the production of bio-oil and biochar is in the range of 400-550 ° C.

This analysis was obtained using thermal analysis procedure and It is possible to verify the considerable increase in the fixed carbon content, in addition to a significant reduction of the volatile content. However, the ash content increased considerably.

Table 3 – Proximal analysis of rice husk and biochar

Test	Moisture (%)	Volatile (%)	Fixed carbon (%)	Ash (%)
Rice Husk	8,51	65,35	12,93	12,51
1	2,39	60,27	19,34	18,00
2	3,57	59,15	20,66	16,62
3	1,82	76,37	4,37	17,44
4	0,85	24,13	49,09	25,93
5	0,67	42,02	38,33	18,98
6	2,22	31,80	45,94	20,04
7	1,06	7,07	58,12	33,74
8	1,63	8,92	56,07	33,38
9	2,62	10,93	55,57	30,88

Figure 4a shows a sample of the rice husk after the pyrolysis process. For the thermogravimetric analysis of biochar a granulometry of 212µm was used (Fig. 4b).

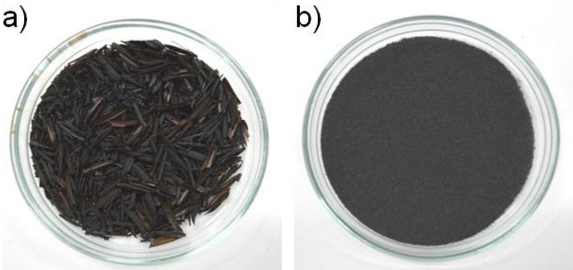

Figure 4 - (a) Biochar from rice husk, (b) Biochar milled (212 µm)

Thermogravimetric analysis of the biochar obtained in the experimental tests is showing by Fig. 5. The TG curve exhibits a gradual mass loss which is related to some volatile material content contained in the biochar. The DTG curve exhibits two low-intensity peaks, one of which is of a larger amplitude. These peaks are related to the decomposition of a fraction of cellulose (348°C) and lignin (462°C) respectively.

From the DTG curve it can be concluded that the volatile material content in the biochar is derived mainly from the rice husk lignin. This means that to obtain a biochar with higher fixed carbon ratio and less volatile the process temperature should be above 400°C.

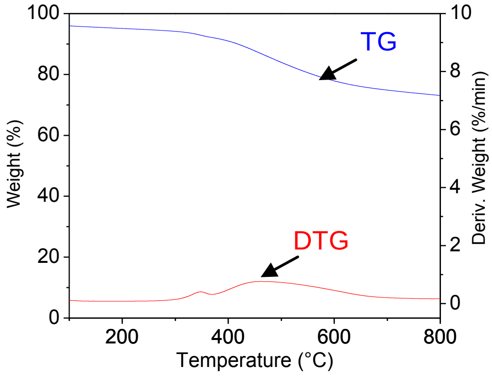

Figure 5 – TG/DTG curves of biochar

4. CONCLUSION

The results showed that different parameters adopted in each test, biochar quantities ranging from 17 to 38% in mass were obtained, Under these conditions the fixed carbon concentrations varied between 4 and 58%, highlighting characteristic as determinant for the indication of higher biochar productivity. In this sense, the experimental condition that presented the best productivity was 7 with 30.86% of biochar (58.12% fixed carbon and 33.74 ashes).

5. ACKNOWLEDGEMENTS

The authors are grateful to the Brazilian Council of Technological and Scientific Development (CNPq Processes 150894/2014-7, 134299/2017-5 and 150868/2017-0) and São Paulo Research Foundation (FAPESP - Process 2013/21244-5 and 2016/15749-5) for their financial support.

6. REFERENCES

Alegre, P.; Almeida "Pirólise rápida de casca de arroz : estudo de parâmetros e caracterização de produtos " *Universidade Federal do Rio Grande do Sul Programa de Pós-Graduação em Ciências*. 2010.

Chen, J. et al. "Pyrolysis of oil-plant wastes in a TGA and a fixed-bed reactor: Thermochemical behaviors, kinetics, and products characterization". *Bioresource Technology*, v. 192, p. 592–602, 2015.

Chungsangunsit, T. et al. "Environmental Profile of Power Generation from Rice Husk in Thailand". v. 24, n. December, p. 739–742, 2004.

Dong, D. et al. "Responses of methane emissions and rice yield to applications of biochar and straw in a paddy field." *Journal of Soils and Sediments*, v. 13, n. 8, p. 1450–1460, 2013.

Liu, J. et al. "Effects of biochar amendment on the net greenhouse gas emission and greenhouse gas intensity in a Chinese double rice cropping system." *European Journal of Soil Biology*, v. 65, p. 30–39, 2014.

Liu, X. YU et al." Can biochar amendment be an ecological engineering technology to depress N 2O emission in rice paddies?-A cross site field experiment from South China." *Ecological Engineering*, v. 42, p. 168–173, 2012.

Mohammadi, A. et al. "Biochar use for climate-change mitigation in rice cropping systems." *Journal of Cleaner Production*, v. 116, p. 61–70, mar. 2016.

Park, J. et al. "Slow pyrolysis of rice straw : Analysis of products properties , carbon and energy yields. *Bioresource Technology* v. 155, p. 63–70, 2014.

Shemfe, M. B.; Gu, S.; Ranganathan, P. "Techno-economic performance analysis of biofuel production and miniature electric power generation from biomass fast pyrolysis and bio-oil upgrading." *Fuel*, v. 143, p. 361–372, 2015.

Singh, B. P.; Cowie, A. L.; Smernik, R. J. "Biochar carbon stability in a clayey soil as a function of feedstock and pyrolysis temperature." *Environmental Science and Technology*, v. 46, n. 21, p. 11770–11778, 2012.

Zhao, X. et al. "Successive straw biochar application as a strategy to sequester carbon and improve fertility: A pot experiment with two rice/wheat rotations in paddy soil." *Plant and Soil,* n. Ipcc 2007, p. 1–16, 2014.

7. RESPONSIBILITY NOTICE

The authors are the only responsible for the printed material included in this paper.