THERMOCHEMICAL PROPERTIES OF INBRED AND HYBRID RICE BIOMASS FEEDSTOCK FOR BIOENERGY CONVERSION

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ABSTRACT.

The husks and straw produced from cultivating and processing of rice are the most commonly available biomass for conversion to bioenergy. Basic data on biomass properties are necessary for the analysis, design, and evaluation of any thermochemical conversion processes. The study provides information on heating value, proximate and ultimate compositions of these rice residues including rice husk char from popular Philippine inbred and hybrid cultivars, NSIC Rc222 and NSIC Rc132H, respectively. Results showed high volatile matter ranging from 57.7 to 65.5% and low ash content ranging from 17.4 to 25.1%, making these rice residues as ideal feedstock for gasification and pyrolysis. The ultimate analysis indicated carbon, oxygen and hydrogen as the major elemental constituents with weight fraction ranged from 21.64 to 40.83%, 2.0 to 36.3%, 0.43 to 4.99% respectively. The obtained low fraction of N and S which ranging from 0.23 to 0.68% and 0.02 to 0.1%, respectively, indicate that these rice residues are environment friendly fuel. The high and low heating values varied from 7.02 to 15.89MJ/kg.

Keywords.

Heating value, Proximate analysis, Rice, husks, Rice husk char, Rice straw, Ultimate analysis

INTRODUCTION

Husk and straw are biomass wastes produced from cultivating and processing of rice. Lim et al. (2012) reported that 0.41 to 3.96 kg of straw and 0.2 to 0.33 kg of husk will be produced for every kilogram of harvested paddy. Total paddy production in 2014 estimated by the Philippine Statistical Authority (PSA, 2015) at 18.97 million metric tons was an all-time high in Philippine rice farming history. The estimated production of rice hull is more than 2 million tons per annum which is equivalent to approximately 5 million BOE (barrels of oil equivalent) in terms of energy (Zafar, 2015). It is expected that the potential energy from straw is more than that of husk.

Thermochemical conversion is one of the convenient ways for converting biomass into energy (Wang et al, 2014). It includes direct combustion, gasification, and pyrolysis. In direct combustion, biomass is used as a fuel in a combustion boiler to produce steam in the presence of sufficient air in the combustion chamber (Lim et al., 2012). In a gasification process, biomass is directly converted to synthesis gas or syngas in a gasifier under a controlled amount of air. Pyrolysis, on the other hand, is a decomposition of organic matrix in the absence or very limited quantity of oxygen (Maiti et al., 2006; Lim et al., 2012).

Elauria et al. (1999) reported that one of the constraints of low adoption of these conversion technologies particularly in small-scale application is due to unreliable operation. The design and performance of these technologies are heavily dependent on the physical and thermochemical properties of biomass (Zhang et al., 2012; Jenkins et al., 1998). These include heating value, moisture, fixed carbon, ash, volatile matter and weight percentages of carbon, hydrogen, oxygen, nitrogen and sulfur. Proper understanding of these properties is therefore essential for efficient design of thermochemical conversion systems (Mansaray and Ghaly, 1997; Zhang et al., 2012).

Researchers in several countries have carried out extensive research to determine the properties

of their own available biomass. Some of them are Maiti et .al (2006) for rice husk char of India; Cuiping et al. (2004) for biomass of China; Garivait et al. (2006) for biomass of Thailand and Suarez et al., (2000) for biomass of Cuba. According to Shen et al. (2012) the different data published for rice husk are due to diversity of testing conditions and rice husk varieties. Mansaray and Ghaly (1997) recommended to use standard methods for performing these analyses due to wide range of reported values on thermochemical properties of biomass.

OBJECTIVE

The main objective of this study was to determine the thermochemical properties of straw, husk and rice husk char from Philippine rice cultivars NSIC Rc222 (inbred) and NSIC Rc132H (hybrid) as related to thermochemical conversion processes. These included heating value (HV), moisture, fixed carbon (FC), ash, volatile matter (VM) and weight percentages of carbon (C), hydrogen (H), oxygen (O), nitrogen (N) and sulfur (S).

METHODOLOGY

RICE BIOMASS COLLECTION

Straw, husk and rice husk char from rice cultivars NSIC Rc222 and NSIC Rc132H were the biomass considered in this study. Based on study of Launio (as cited by Bordey et al., 2016), the newly developed NSIC Rc222 is the topmost variety planted and adopted by farmers from the top rice-producing provinces in the Philippines, such as Isabela and Nueva Ecija. The tested high yielding ability, which is 10 tons per hectare as maximum yield and 6.1 tons per hectare as average yield, is the main reason of its popularity to farmers. Likewise, NSIC Rc132H or popularly known as SL-8H is the most preferred hybrid variety of farmers according to Mr. Leo C. Javier (*Project Leader of Thermosensitive Genic Male Sterile Hybrid Rice, Philippine Rice Research Institute, personal communication, April 2015)* which was consistent with the result of study of Launio (as cited by Bordey et al. 2016).

Samples of rice straw and husk of variety NSIC Rc 222 were obtained from the produce of the Philippine Rice Research Institute while that of NSIC Rc132H were from the produce of Bagong Buhay ng Mabini Multi-purpose Cooperative in Santo Domingo, Nueva Ecija, Philippines in the dry season of 2013. Husk samples were processed using multi-pass rice mill while rice husk char was obtained by gasifying rice husk samples in a batch-type, top-lit, updraft gasifier. Straw samples, on the other hand, were cut and threshed using hand sickle and axial-flow type rice thresher. Collected samples of rice straw were sundried until the stem had no visible green portion. Two samples with four kilograms per sample per rice biomass were secured using plastic sack and properly labeled and stored at place with room temperature prior to analysis.

PROPERTY DETERMINATION

All analyses were performed by SGS Philippines according to published ASTM standards. Samples were prepared according to Practice D2013 which pulverized the rice biomass to pass a 250-µm (No. 60 sieve). The total moisture (as received) of husk, straw and char was determined according to ASTM D3302/D3302M-12. This test method covers the measurement of the total moisture as these rice residues exist at the site, at the time and under the conditions they were sampled and was used for calculating other analytical results to "as received" basis. Proximate analysis was performed according to ASTM D3172-07a. This practice covers the determination of "as determined" moisture (ASTM D3173-11), VM (ASTM D3175-11), and ash (ASTM D3174-12). The moisture obtained in this analysis was used for calculating results of VM and ash to a dry basis. The FC was then calculated as the resultant of the summation of percentage ash and volatile matter subtracted from 100 according to ASTM D3172-07a. Furthermore, weight fractions of C, H, and N were determined according to test method ASTM D5373-14 while percentage of total S was according to Test Method ASTM D4239-14. The weight percentage of O was then obtained by subtracting from 100 the sum of C, H, N, S and

ash contents. Higher and lower heating values of rice biomass samples were determined according to ASTM 5865-13.

STATISTICAL ANALYSIS

Quantitative data were presented as mean values (n = 2). One-way analysis of variance (ANOVA) was undertaken to determine significant differences between the varieties. Significant difference was statistically considered at the level of p <0.05.

RESULTS AND DISCUSSION

MOISTURE CONTENT

The total moisture of husk, straw, and char from inbred and hybrid rice varieties ranged from 6.2% to 14.7% while the as determined moisture ranged from 4.6% to 8.2% (Table 1). Analysis showed significant difference on the moisture content between varieties of all the rice biomass tested. The total moisture indicates the moisture of the biomass at the time and the condition it was sampled while moisture as determined was used to determine results of VM and ash compositions to a "dry basis". With very low moisture contents, these rice residues can be considered as highly favorable feedstock for thermal conversion technologies. Biomass with low moisture, typically less than 50%, is more suited for thermal conversion technology according to McKendry, 2002. The effect of an increase in moisture decreases heating value of biomass (Demirbas, 2002) because large amount of energy would be used for vaporization of the fuel moisture during conversion (Mansaray and Ghaly, 1997). Differences in moisture could have resulted from using different collection, storage and drying procedures (Zhang et al., 2012). The obtained moisture (as determined) values for husk are lower than the values of 6.68 to 10.44% reported by Mansaray and Ghaly (1997) which were determined according to ASTM-D 3173-73. Similarly, the measured values for straw are lower than the values of 6.58 to 6.92% reported by Zhang et al. (2012) which were determined according to ASTM 2010.

| Rice Biomass | Moisture | Variety | |
|--------------|--------------------------------|--------------------|-------------------------|
| | | NSIC Rc222(inbred) | NSIC Rc132H (Hybrid) |
| Husk | Total Moisture, %(as received) | 12.70 _b | 13.30 _a |
| | Moisture, % (as determined) | 8.20a | 7.40 _b |
| Straw | Total Moisture, %(as received) | 14.70 _a | 13.10 _b |
| | Moisture, % (as determined) | 5.00 _b | 5.90 _a |
| RH char | Total Moisture, %(as received) | 6.20 _b | 6.85 _a |
| | Moisture, % (as determined) | 4.60 _b | 5.15 _a |

Table 1. Moisture of husk, straw and char from inbred and hybrid varieties.

Means with the same letter within the row are not significantly different

PROXIMATE COMPOSITION

The VM content of straw showed the highest value among the rice biomass tested. The measured values were 65.5% for inbred and 62.15% for hybrid which difference was statistically significant. VM content of char, however, showed the lowest range of value with 2.95% (inbred) to 3.70% (hybrid). This could be due to the fact that char already undergone gasification prior to analysis thus most of its VM were already driven off during the process. The FC which remained after devolatilization was also highest on char. It significantly varied from 21.4 to 27.4% compared to 16.4 to 17.25% FC of husk and straw. Furthermore, the ash which is the residue left after the biomass is completely burned was highest on char. It significantly varied from 68.90% to 75.65%. These values, compared to 25.0% and 19.3% average values obtained from husk and straw, respectively, were three to four times higher. The measured values of VM are lower than the values of 65.47% to 68.37% for straw and 63.0% to 70.2% for husk reported by Lim et al. (2012), Yuan et al. (2012) and Mansaray and Ghaly (1997).

| | | Variety | |
|--------------|---------------------------|--------------------|-------------------------|
| Rice Biomass | Proximate Composition (%) | NSIC Rc222(Inbred) | NSIC Rc132H (Hybrid) |
| Husk | Volatile Matter | 57.70 _a | 58.50 _a |
| | Fixed Carbon | 17.25 _a | 16.40 _a |
| | Ash | 25.05 _a | 25.10 _a |
| Straw | Volatile Matter | 65.45 _a | 62.15 _b |
| | Fixed Carbon | 17.15 _a | 16.70 _a |
| | Ash | 17.40 _b | 21.15 _a |
| RH char | Volatile Matter | 2.95 _a | 3.70 _a |
| | Fixed Carbon | 21.40 _b | 27.40 _a |
| | Ash | 75.65 _a | 68.90 _b |

Table 2. Proximate composition of husk, straw and char from inbred and hybrid varieties (dry basis).

Means with the same letter within the row are not significantly different

Proximate analysis of a fuel determines the VM, ash and FC. The volatiles burn as a gas product in the flame whereas FC burns slowly and without flame. Both properties provide a measure of the ease to ignite and burn the biomass which is related with the ease in gasification or oxidation process. The ash, on the other hand, is the incombustible solid mineral matter in the fuel. According to McKendry (2002), the available energy of the fuel is reduced proportionately dependent on magnitude of ash content. The chemical composition of the ash can present significant operational problems such as slogging, fouling, sintering and corrosion (McKendry 2002 and Cuiping et al., 2004). At higher temperature ash fuses or softens and forms clinker that entraps combustible matters and prevents proper air distribution (Patel and Gami, 2012). Non-slogging reactors are usually controlled to operate below the ash-softening temperature by varying the fuel and air inputs (Mansaray and Ghaly, 1997).

ULTIMATE COMPOSITION

Ultimate analysis of a fuel gives its elemental composition such as carbon, nitrogen, hydrogen, oxygen and sulfur. It is important in estimating theoretical air required for complete combustion, heating value and formation of pollutant emissions (Suarez et al, 2000). The weight fraction of Total C from rice biomass varied from 21.64% (char) to 40.83% (straw), O

from 2.0% (char) to 36.3% (straw), H from 0.43% (char) to 4.99% (straw), N from 0.23 (husk) to 0.68% (straw), and S from 0.02 (husk) to 0.10% (straw). Results showed that these chemical elements are richer in straw than husk. Furthermore, based on values obtained from char, gasification of husk decreases the concentration of O, Total C and H which heating value strongly depends. The low values of S and N obtained for all rice biomass tested were in the range reported by several authors (Suarez et al. 1999, Jenkins et al. 1998 and Lim et al. 2012) which indicated that combustion of these residues will not significantly contribute sulfur oxide (SO_x) and nitrogen oxide (NO_x) emissions which both considered as air pollutant. On the two varieties tested, significant difference was observed in all ultimate composition of straw except sulfur of husk and total carbon of char.

| Rice Biomass | Ultimate Composition (%) | Variety | |
|--------------|--------------------------|--------------------|----------------------|
| Rice Biomass | Olumate Composition (%) | NSIC Rc222(inbred) | NSIC Rc132H (Hybrid) |
| Husk | Total Carbon | 37.50 _a | 37.25 _a |
| | Hydrogen | 4.48_{a} | 4.50 _a |
| | Oxygen | 32.7 _a | 32.9 _a |
| | Nitrogen* | 0.28 | 0.23 |
| | Sulfur | 0.03 _a | 0.02 _b |
| Straw | Total Carbon | 40.85 _a | 38.90 _b |
| | Hydrogen | 4.99_{a} | 4.81 _b |
| | Oxygen | 36.3 _b | 34.4 _a |
| | Nitrogen* | 0.47 | 0.68 |
| | Sulfur | 0.06 _a | 0.10 _b |
| RH char | Total Carbon | 21.65 _b | 27.95 _a |
| | Hydrogen | 0.43 _a | 0.48_{a} |
| | Oxygen | 2.0 _a | 2.3 _a |
| | Nitrogen* | 0.27 | 0.33 |
| | Sulfur | 0.05 _a | 0.06 _a |

Table 4. Ultimate composition of rice biomass from inbred and hybrid varieties (dry basis).

Means with the same letter within the row are not significantly different *unduplicated analysis

HEATING VALUE

The heating value (HV) of a material is an expression of the energy content. The HV is an important thermal property for modeling thermochemical conversion system for biomass (Sheng and Ezevedo, 2005). HV can be reported in terms of higher (HHV) or lower (LHV) heating value. HHV is the total energy content released when water vapor resulting from

combustion is condensed, thus realizing the latent heat of vaporization. Whereas LHV is the energy released when water vapor remains in gaseous state. Based on the results, the HHV of rice biomass, as affected by variety, significantly varied from 7.56 to 15.89MJ/kg while the LHV varied from 7.02 to 13.94MJ/kg.

| Rice Biomass | Heating Value, MJ/kg | Variety | |
|--------------|----------------------|--------------------|----------------------|
| Rice Diomass | meaning value, MJ/kg | NSIC Rc222(inbred) | NSIC Rc132H (hybrid) |
| Husk | Higher HV | 14.72 _b | 14.58 _a |
| | Lower HV* | 12.44 | 12.42 |
| Straw | Higher HV | 15.89 _a | 15.31 _b |
| | Lower HV* | 13.94 | 13.27 |
| RH char | Higher HV | 7.56 _a | 9.86 _b |
| | Lower HV* | 7.02 | 9.14 |

| Table 4. Higher and lower heating | y values of rice biomass | from inbred and h | vbrid varieties. |
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Means with the same letter within the row are not significantly different *unduplicated analysis

Among the rice biomass tested, straw showed the highest HV and char showed the lowest which is consistent with the fact (Mansaray and Ghaly, 1999) that decreases in ash content result in higher energy content of the fuel (Figure 1). Char properties are affected by many factors including carbonization temperature (Wang et al., 2014). According to Maiti et al. (2006) the optimum temperature for carbonization to obtain a char having moderately high heating value was found as 400° C.



Figure 1. High heating value (HHV) versus ash content of rice biomass

CONCLUSION

Thermochemical properties of rice biomass from varieties NSIC Rc222 and NSIC Rc132H were determined. These included heating value, proximate and ultimate compositions as related to the design and exploitation of thermochemical conversion systems. The total moisture content of the rice biomass ranged from 6.2 to 14.7%. Proximate analysis of two main rice residues (husk and straw) indicated high volatile content ranging from 57.7 to 65.5% and low FC and ash contents ranging from 16.3 to 17.2% and 17.4 to 25.1%, respectively. Conversely, rice husk char contained low volatiles ranging from 3.0 to 3.7% and high FC and ash contents ranging from 21.4 to 27.4% and 68.9 to 75.65%, respectively. The weight fractions of carbon, oxygen and hydrogen in husk and straw ranged from 37.27 to 40.83%, 32.7 to 36.3% and 4.47 to 4.99%, respectively. On the other hand, the weight fractions of carbon, oxygen and hydrogen in rice husk char ranged from 21.64 to 27.94%, 2.0 to 2.3% and 0.43 to 0.48%, respectively. The high and low heating values varied from 14.71 to 18.30MJ/kg.

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