

Biomass Characterization of Pigeon Pea (*Cajanus cajan*) Wood for Thermochemical Conversion

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ABSTRACT

*Physical, thermochemical, and compositional analyses were performed on pigeon pea (*Cajanus cajan*) wood to determine its overall biomass characteristics. Pigeon pea is a minor crop locally known as kadios, usually grown in backyards, marginal lands, and insignificant land portions in the Philippines. In this study, pigeon pea wood is identified as a new potential lignocellulosic bio-resource for producing renewable energy due to its several attractive agro-energy features. Proximate analysis showed that mean moisture content (MC) dry basis, volatile combustible matter (VCM), and ash contents of pigeon pea wood were 10%, 66%, and 12%, respectively, which fall within the range of recommended values for biomass feedstock. The fixed carbon (FC) content of pigeon pea wood is 22%, the highest value among common biomass materials. Ultimate analysis of pigeon pea wood reveals carbon (C) content of 41%, similar to its nitrogen (N) content. Its hydrogen (H) content is 6.17%, which falls on the upper limit for most agricultural biomass (5-6%). Pigeon pea wood thus showed the highest H/C and O/C molar ratios. Moreover, its heating value (HV) is 17.13 MJ/kg, which also falls within the mean range of the other biomass. It also contained 15-25% lignin, 30-50% cellulose, and 20-40% hemicellulose. Based on these results, it can be concluded that pigeon pea wood has potential biofuel properties as new feed or co-feed for thermochemical conversion processes (i.e., pyrolysis, torrefaction, and gasification).*

Keywords: Pigeon pea, biomass, characterization, pyrolysis, bioenergy, biofuel

INTRODUCTION

There is a rapidly increasing demand to utilize alternative renewable energy sources as a result of an increasing energy consumption, depleting fossil fuel reserves, and worsening environmental problems (Capunitan and Capareda, 2012; Imam and Capareda, 2012; Demirbas and Arin, 2002; Maguyon and Capareda, 2013). Among the

renewable energy sources, biomass is most commonly used in developing countries, with biomass-derived products being traded internationally (McKendry, 2002; Wu *et al.*, 2011).

In the Philippines' Republic Act No. 9513, also known as Renewable Energy Act of 2008, biomass is defined as non-fossilized biodegradable organic material originating from naturally occurring or

cultured plants, animals and micro-organisms, including agricultural products, by products and residues (<https://www.officialgazette.gov.ph>). As an alternative energy source, biomass offers several advantages: it is one of the largest sources of energy reserves in the world, approximately supplying about 14% of world's energy consumption (Saleji *et al.*, 2009; Pütün *et al.*, 2004); carbon dioxide neutral, low sulfur content, and easy to transport (Mahinpey *et al.*, 2009) and to cultivate in the fallow and marginal lands. These characteristics make biomass a prominent choice for renewable energy (Capunitan and Capareda, 2012; McKendry, 2002).

Biomass energy plays a vital role in the Philippines' energy supply. Nearly 30 percent of the energy for the 103 million Filipinos mainly uses biomass for household cooking by the rural poor. Biomass energy application accounts for around 15% of the primary energy use in the country. The Philippines has a land area of 30 million hectares, 47% of which covers agricultural land. The total area devoted to agricultural crops is 13 million hectares distributed among food grains, food crops, and non-food crops. Thus, the Philippines has abundant supplies of cheap biomass resources, offering much potential for clean energy generation (<https://bioenergyconsult.wordpress.com>). In fact, there is now a compelling need to tap this enormous volume of agricultural waste for bio-energy production. Biomass conversion technologies when developed in the Philippines may result in decreased dependence on imported oil, rural revitalization, and job creation.

One of the potential biomass sources for biofuels is the pigeon pea [*Cajanus cajan* (L.) Millsp.]. Pigeon pea is a minor crop locally known as *kadios* (Tagalog), *kardis* (Ilocano) or *karu* (Kapampangan), which is usually grown in backyards, marginal lands or on insignificant land portions. The potential of this crop for small and large scale production is thus very high (Mula and Saxena, 2010). It is abundant in the Philippines especially in Ilocos region, Cagayan Valley, Central Luzon, Bicol region, Laguna, Batangas, Western / Central / Eastern Visayas, Zamboanga and Misamis Oriental (Saxena *et al.*, 2010). Pigeon pea is a versatile crop, wherein all of its parts can be utilized either as food (pods,

seeds and leaves), feed/forage/fodder (pods and leaves), folk medicine (leaves, pods, seeds, roots), fertilizer (dried leaves/hulls), fencing material (stalk), fuelwood, soil erosion agent, and others. Moreover, production areas for pigeon pea is not solely as feedstock for thermochemical process, since the biomass produced after its part have been utilized (i.e., stem/stalk, hull, shavings, leaves, etc.) can be tapped as feedstock, and it is a value-added to its vast potential. Such uses/benefits may compensate economically in the long run.

Full biomass utilization for energy and chemical production encompasses thermochemical, biochemical, and agro-chemical processes. Of these, thermochemical conversion, particularly pyrolysis, has gained interest among researchers in recent years, in an attempt to produce a wide range of fuels and other products from biomass materials (Capunitan and Capareda, 2012). Pyrolysis is an old-age yet attractive technology, which involves thermal decomposition of biomass in the absence of oxygen to produce solid, liquid, and gaseous products (McKendry, 2002; Capunitan and Capareda, 2012; Demirbas and Arin, 2002; Maguyon and Capareda, 2013).

Among the potential benefits derived from pigeon pea is that about 15-20 tons/ha of fuel wood from pigeon pea crop can provide energy @ 4,000 kcal/kg (ICRISAT, 2013). Moreover, previous studies were focused on production of char, briquettes, compact solid fuels, etc. To date, detailed characterization and thermochemical conversion of pigeon pea grown in the Philippines are sparsely studied.

Characterization of indigenous biomass or lignocellulosic biomass (LCB) will play a strong and positive role in bioenergy production. The source of new raw materials for a sustainable biofuel production is crucial for popularizing the use of biofuel at the domestic level. This may then result in a more focused or localized future activities on biofuel production at the village level and will promote utilization of emerging indigenous biomass for harnessing bioenergy. Moreover, the qualitative and quantitative characterization of biomass components is necessary from its application perspectives. This could be achieved only when a

complete characterization of biomass is done prior to any thermochemical and biological processes. Hence, systematic characterization of biomass is indispensable in biofuels production.

In this study, we sought to provide complete characterization of pigeon pea wood biomass as an alternative source of renewable energy. A process flow for biomass preparation was developed in order to systematically characterize the biomass in terms of its physical, thermochemical and compositional properties.

METHODOLOGY

Preparation of Pigeon Pea Wood Samples

The flowchart of the biomass material preparation is shown in Figure 1. Pigeon pea (ICP 7035 variety) wood samples were collected from PSAU pigeon pea plantation area located (Lat15°12'53", Long. 120°42'0") at PAC Magalang, Pampanga. The pigeon pea were planted in a marginalized hilly/upland rainfed area with a clay loam soil type, moderately flat to rugged terrain (20% slope) at an elevation of 70m MSL. The raw material was selected according to a set of criteria based on practice, namely: taking only samples of good condition, from a single location only and the main stem/branch with at least 2-5 cm in diameter to fit the hammer mill. It was taken manually at the base of the plant by using a sharp cutting tool or a bolo.

The dried pigeon pea wood samples were reduced into smaller size (8 cm long, 2-5 cm diameter) using a stationary circular saw (Makita, 5 hp, 60 Hz, and 1750 rpm), operated at 33.34 kg/hr with a power consumption of 0.17 kW-hr. This was further size-reduced using a fabricated hammer mill (@10hp, 60hz) at 5.60 kg/hr with a power consumption of 2.68 kW-hr, for two passes. Moreover, the milled pigeon pea sample was sieved using the U.S.A. standard testing sieve in combination with Ro-Tap testing sieve shaker (Model B, serial no. 4949). The U.S.A. testing sieve set consisted of number 10, 12, 18, 20, 30 and 40 to obtain particle sizes of 0.5 to 2.5 mm.

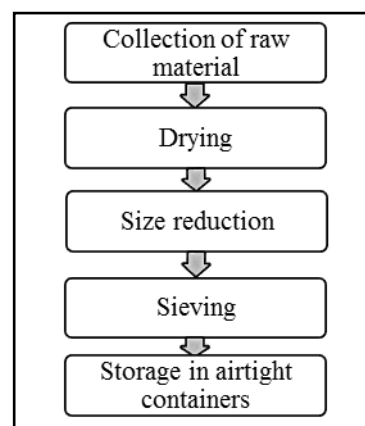


Figure 1. Flow chart of pigeon pea biomass material preparation

The standard procedure for sieving was based on ANSI/ASAE S319.4 (R2012). The sieved samples were stored in polyethylene bags with desiccant.

Pigeon Pea Wood Characterization

The standard test methods for biomass characterization developed by the ASTM were used to determine the physical, thermochemical and compositional properties of pigeon pea, as illustrated in Figure 2.

Physical Properties

The physical properties as cited hereunder, were evaluated. Parameters gathered were replicated three to five times.

In the particle sieve analysis, the parameters calculated to describe the particle size distribution were the fineness modulus (FM), the particle size in terms of its geometric mean diameter (d_{gw}) and geometric standard deviation (S_{gw}), surface area (A_t), and the number of particles (N_t).

The FM indicates the uniformity of grind of the resulting product as derived by Henderson and Perry (1976), with the following equation:

$$FM = \frac{\sum f_i M_i}{100}$$

Equation 1

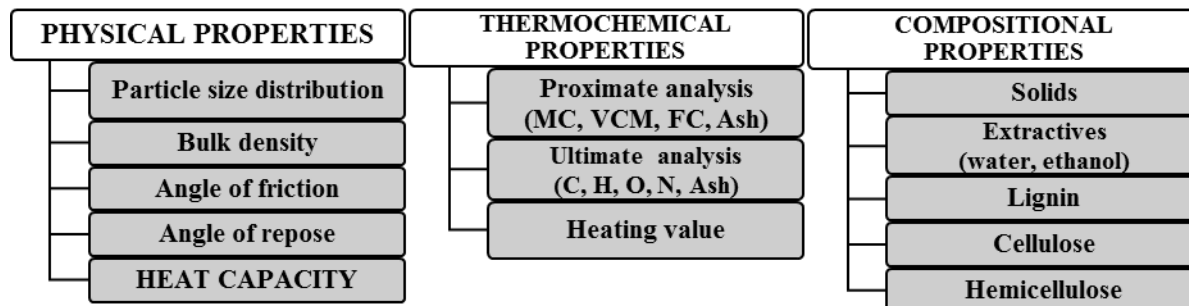


Figure 2. Characterization of pigeon pea wood

where: f_i = percentage of material retained in each sieve

M_i = multiplier corresponding to each sieve

The calculation formulas for d_{gw} , S_{gw} , A_t , and N_t , derived by Pfof and Headley (1976) and Sokhansanj and Yang (1996) were based on ANSI/ASAE S319.4 (R2012).

The bulk density is the ratio of the mass of biomass particles to the total volume of biomass particles including the pore space volume between and within the biomass particles (Bhagwanrao and Singaravelu, 2014 and Cai *et al.*, 2017). The standard method for measuring bulk density (ASTM E873-82 R2013) was observed.

The BD was computed using the following formula:

$$BD = \frac{\text{weight of the sample}}{\text{Volume of the sample}} \quad \text{Equation 2}$$

Moreover, the bulk density for the unsieved as well as the sieved biomass were obtained.

The angle of friction is that angle with which a pile of biomass slides when raised horizontal (Capareda, 2014). The angle of friction apparatus was used. The biomass sample was placed on top of the apparatus, which was raised at a certain angle until it started to slide. This angle of friction formed was measured using a Vernier protractor (Mantua Metal Products Co., N.J., USA). This procedure was done for five times for steel and wood (along and across the grains).

The angle of repose is the steepest angle of descent or the slope relative to the horizontal plane when a biomass material is poured on a horizontal surface and can remain stable without slumping. This angle is technically defined as the internal angle between the surface of the pile and the horizontal plane, which can be 0° to 90° (Pascale, 2014; Cai *et al.*, 2017; and Capareda, 2014). This parameter was determined based on the standard method stated in ASTM C1444-00. The angle of repose formed was captured using a high-resolution camera and was determined using ImageJ software.

Pigeon pea wood samples in powder form which passed through mesh number 40, was submitted for specific heat capacity analysis. This sample was analyzed using a differential scanning calorimeter or DSC (Universal V4.5A TA Instruments, Q20 v24.10 Build 122). The DSC was located at the UPLB Nanotechnology Laboratory, Institute of Chemistry.

The heat capacity of the material is defined as the ratio of the amount of heat energy transferred by the material to the resulting increase in temperature of this material. It is given in units of joules per kelvin. Since heat capacity is an extensive property, specific heat capacity is more practical to use, since this is the heat energy per unit mass at a given temperature (Capareda, 2014). Heat capacity (c_p) can be computed by dividing the heat flow by the heating rate. The heat flow is the heat supplied (q) per unit time (t), while heating rate is the temperature increase (DT) per unit time. Moreover, the heat supplied is also known as the enthalpy of the transition (DH). The derivation was computed using Equation 3:

$$\frac{\frac{q}{t}}{\Delta T} = \frac{q}{\Delta T} = \frac{\Delta H}{\Delta T} = c_p \quad \text{Equation 3}$$

Moreover, Dupont *et al.* (2014) in their study on heat capacity measurement of various biomass types and pyrolysis residues, gave the following equation:

$$C_p = 5.340T - 299 \quad \text{Equation 4}$$

where, T is the absolute temperature, in K.

This equation was used to measure the theoretical biomass heat capacity and then it was compared with that of the experimental value.

Thermochemical Properties

The thermochemical properties were determined through proximate, heating value, and ultimate analysis. The proximate analysis consisted of determining the VCM, ash and FC contents, following the standard procedure (ASTM D1762). The VCM refers to the part of the biomass that is released when the biomass is heated at 925 ± 10 °C for 7 min (McKendry, 2002). While ash consists of the mineral and inorganic matter in a biomass (Vassilev *et al.*, 2010). Ash technically refers to the solid residue of biomass, produced by thermochemical conversion at 575 ± 10 °C for 3hr. It is an integral part of plant material with a wide range of elements (Singh *et al.*, 2017). Moreover, FC content is the biomass remaining after the release of volatile matter, excluding the ash and MC (Singh *et al.*, 2017). This is a calculated value, obtained by subtracting VCM and ash values from 100%.

The heating value analysis consisted of getting the gross calorific value (GCV) of the biomass material. This was determined according to standard procedure (ASTM D3286). The ultimate analysis consisted of the elemental values of C, H, oxygen (O), N, sulfur (S), and others. The O content was a calculated value, obtained by subtracting the C, H, and N values from 100%.

For these analyses, pigeon pea wood samples (in powder form which passed through mesh number 40), were submitted to the Standards and Testing Division, Industrial Technology Development Institute, Department of Science and Technology (DOST).

Compositional Properties

The compositional properties consisted of the lignin, cellulose, and hemi-cellulose contents of the pigeon pea wood. Pigeon pea wood samples (in powder form which passed through mesh 40) were submitted to the Chemistry Section, Material Science Division of the Forest Products Research and Development Institute.

The lignin content was obtained following the standard modified procedure (TAPPI T222). As for the amount of holocellulose in wood, it was determined by subtracting from 100% the following parameters, namely: the % total extractives from alcohol-cyclohexane (TAPPI T204 om-88-modified) and hot water soluble (TAPPI T207 om-93), % lignin, and % ash contents (TAPPI 211 om-85).

The alpha cellulose content was determined following this procedure. Sodium hydroxide soluble sample (17.5%) was added to half gram of holocellulose extractive. This was stirred at 20°C for 40 min and was filtered after 5 min. The filtrate was discarded while the residue was added with 20 mL of 10% acetic acid. It was washed acid-free with a liter of boiling water and was filtered again. The resulting filtrate was discarded while the residue was dried at 105°C for 48 hours. Percentage alpha cellulose was calculated. The sodium hydroxide soluble extractive used was determined by the standard procedure set by TAPPI T212 om-88. The hemicellulose was obtained by subtracting the % cellulose (by weight) from the % holocellulose (by weight).

Experimental Design

For all the parameters, a simple mean and standard deviation were used, with 3 to 5 replications each.

RESULTS AND DISCUSSION

Pigeon Pea Wood Preparation

The scientific classification of pigeon pea is kingdom (Plantae), division (Magnoliophyta), class (Magnoliopsida), order (Fabales), family (Fabaceae), genus (*Cajanus*), species (*C. cajan*) and binomial name is *Cajanus cajanifolius* (Linnaeus) Millspaugh (Mula and Saxena, 2010). The variety (ICP 7035) of the pigeon pea used in this study was among the gene pool of the International Crop Research Institute in Semi-Arid Tropics. Varietal assessment of ICP 7035 was conducted at PSAU, in which said variety thrived well in the region.

Proper drying and size reduction of the pigeon pea wood prior to characterization is a very important aspect to increase its surface area. The initial MC was determined using a moisture meter (R&D Instruments, MT-10), specifically intended for wood and worked on the principle of electric resistance. Sun drying was done for 10 to 14 days to attain the equilibrium moisture content (EMC) at an average temperature of 29°C and relative humidity (RH) of 67% with an evaporation rate of 74 mm/hr. Moreover, the following formula was used to determine the final weight of the sample:

$$m_i(1 - MC_i) = m_f(1 - MC_f)$$

Equation 5

where: MC_i = initial MC, dry basis.
 MC_f = final MC, dry basis.

Physical and Thermochemical Properties

The physical properties of pigeon pea wood is presented in Table 1. The pigeon pea wood has an

Table 1. Physical and thermochemical properties of pigeon pea wood

PHYSICAL CHARACTERISTICS	EXPERIMENTAL VALUE	PHYSICAL CHARACTERISTICS	EXPERIMENTAL VALUE
Moisture Sorption (%)		Angle of Friction	
Initial Moisture Content	51.54±3.78	Steel Surface	39°10'±0°34'
Final Moisture Content	9.93±0.42	Wood Surface Along Grains	58°04'±2°23'
Bulk Density (kg m ⁻³)		Wood Surface Across Grains	60°26'±0°26'
Mixture	163±5.70	Angle of Repose	42°0.2'±1°33'
0.5 mm particle size	150±3.54	Flow Index	2 to 4
1.5 mm particle size	138±8.37	Flowability Grade	Low Flowing
2.5 mm particle size	132±11.51	Specific Heat (kJ·kg ⁻¹ K ⁻¹)	0.89
Proximate Analysis		Ultimate Analysis	
Moisture Content (%)	9.89±0.37	Carbon (C)	41.1±0.54
Volatile Comb. Matter (%)	65.9±0.15	Hydrogen (H)	6.17±0.20
Ash Content (%)	12.3±0.28	Nitrogen (N)	0.854±0.03
Fixed Carbon Content (%)	21.8±0.41	Oxygen (O)	51.9±0.70
Heating Value (MJ/kg)	17.13 ± 0.40	(by difference)	

average initial MC of 51.54±3.78%, which was determined using a moisture meter (R&D Instruments, MT-10). The final MC of 9.93±0.42% dry basis, falls within the range of the recommended MC (less than 10 to 15%) for biomass (Kumar *et al.*, 2010; and Isahak *et al.*, 2012). A moisture sorption study of biomass is important for biomass harvest, handling, transport, and storage. Therefore, proper drying and storage operations are required to preserve the quality of biomass feedstocks. The EMC is a key parameter to characterize the water sorption behavior of biomass (Bridgwater and Boocock, 2013). The EMC of biomass depends on its composition, porosity, microstructure and specific surface area (Lin *et al.*, 2016).

As to the parameters for particle sieving analysis, the FM of pigeon pea wood was computed to be 4.19 using Equation 1. While, the average particle size ($d_{gw} \pm S_{gw}$) is 1.0226±0.68 mm, the total surface area is 472,533.00 cm² and has 1,438,421,330 particles. The particle size is very relevant for the thermochemical conversion technology selection process. In general, particle sizes of ground biomass

have a log-normal distribution, which indicates that the number of smaller biomass particles is considerably greater than that of larger particles. Moreover, lignocellulosic biomass is irregular in shape, which resulted in difficulties in accurate dimension measurements of length, width, and thickness. Accurate characterization for biomass particle size and shape is essential for designing the handling, storage, and processing facilities (Cai *et al.*, 2017).

The mean bulk density of the pigeon pea biomass (milled but unsieved) was $163 \pm 5.70 \text{ kg m}^{-3}$. While the samples that were sieved with particle sizes of 0.5, 1.5 and 2.5 mm were 150 ± 3.54 , 138 ± 8.37 and $132 \pm 11.51 \text{ kg m}^{-3}$, respectively (Table 1). Pigeon pea wood is below the average BD of wood (300 to 550 kg m^{-3}), charcoal (200 to 300 kg m^{-3}), and hardwood chips (280 to 480 kg m^{-3}), but falls within that for cereal grain straws (15 to 200 kg m^{-3}), and that of lignocellulosic biomass (900 kg m^{-3}), the values of bulk density as reported by various authors (Lata and Mande, as cited by Capareda, 2014; Cheng, 2009; and Jose and Bhaskar, 2015). Hence, the low bulk density of pigeon pea wood suggests that densification may be required for efficient transport and storage. This physical property is a key in designing the logistic system for biomass handling and transport. It depends on the biomass particle size and shape, MC, particle density, and surface characteristics (Bhagwanrao and Singaravelu, 2014; and Cai *et al.*, 2017).

The angle of friction of pigeon pea wood on steel and wood along and across the grain surfaces is $39^\circ 10' \pm 26'$, $58^\circ 4' \pm 2^\circ 23'$ and $60^\circ 26' \pm 34'$, respectively. The steel surface had lower resistance to friction, followed by the wood along the grain. The angle of friction on wood across the grain was highly resistant to friction. This supports Capareda (2014), who stated that if the surface is smooth, it can be observed that the biomass slides at a lower angle than when the surface is rough. This parameter is also important in the design of conveying systems and hopper for biomass fuel bins. Proper use of this angle of friction prevents bridging from biomass feed bins or conveying systems.

The angle of repose (Φ) of the pigeon pea biomass is $42^\circ 0.2' \pm 1^\circ 33'$ (Table 1). The angle of repose and flow index are among the parameters reported to characterize flowability (Lumay *et al.*, 2012). Based on the flowability grades under different ranges of angle of repose (Sudhagar, 2015 and Lam and Sokhansanj, 2014), pigeon pea wood possessed a flow index of 2 to 4 with a grade of “low flowing.” The flow of properties of biomass feedstock plays an important role in the design of the equipment for biomass material storage, particularly for biomass conveying systems of silos and hoppers, transportation, storage and handling (Miao *et al.*, 2014; Cai *et al.*, 2017; and Capareda, 2014).

The result of DSC analysis on pigeon pea wood showed the enthalpy of transition (ΔH) to be 351.3 J-g^{-1} with a change in temperature (ΔT) of 394.95 K . Using Equation 3, the specific heat capacity of pigeon pea biomass is $0.89 \text{ kJ-kg}^{-1} \text{ K}^{-1}$. Moreover, Dupont *et al.* (2014) provided an empirical equation to calculate the average biomass heat capacity, which yielded $1.81 \text{ kJ-kg}^{-1} \text{ K}^{-1}$ using Equation 4. Comparing these values, the experimental value of pigeon pea biomass has lower specific heat capacity. Specific heat, which is an indication of the heat capacity of a material, is another important thermal property of biomass often required for thermodynamic calculations (Dupont *et al.* 2014). It depends on the moisture content (MC) of biomass and temperature (Cai *et al.*, 2017). According to Capareda (2014), this parameter is now being used in the modeling of some biomass processes.

Thermochemical Properties

The proximate analysis of pigeon pea wood is shown in Table 1. Pigeon pea wood was also compared with some of the common biomass in terms of their proximate and heating value analysis (Table 2).

Pigeon pea wood has an MC of $9.89 \pm 0.37\%$. High MC decreases the combustion yield of a biomass (García *et al.*, 2013). Thermal conversion technologies can also use feedstocks with high MC but the overall energy balance for the conversion process is adversely impacted. On this basis, woody and low MC herbaceous plant species such as pigeon pea are the most efficient biomass sources

for thermal conversion to liquid fuels, such as methanol (McKendry, 2002).

The VCM and ash contents of pigeon pea wood are $65.90 \pm 0.15\%$ and 12.30 ± 0.28 , respectively (Table 1). These values fall within the mean value or range of other common biomasses (Table 2). According to McKendry (2002), biomass typically has a high volatile matter than coal (less than 20%). The presence of volatile matter in biomass influences the fuel reactivity. Moreover, Singh *et al.*, (2017) stated that ash content affects the combustion rate in biomass sample and the percentage composition varies according to the type of biomass (i.e., wood has 0.5%, and agricultural crop residues have 5-10%), except for paddy and rice straw as seen in Table 2. Capareda (2014) also stated the importance of this component, that is, high-ash-content biomass will tend to form slag and may cause fouling problem in many thermal conversion conveying parts.

The FC content of pigeon pea wood is 21.80 ± 0.41 (Table 1). This is the highest value among the common biomass (Table 2). According to Capareda (2014), FC is also important in thermal conversion. Carbon is the prime element useful for making liquid biofuels, and if matched with H will generate hydrocarbon fuels.

Furthermore, according to Cai *et al.* (2017), proximate analysis results can be illustrated using a ternary graph. This graph is a barycentric plots on three variables which sum to a constant and graphically depict the ratios of the three variables as positions in an equilateral triangle. In Figure 3, pigeonpea wood is located quite far from the rest of the biomasses and it has the highest FC. Likewise for the paddy straw, which has the highest ash content. The rest of the biomasses have quite the

Table 2. Proximate and heating value analysis of pigeon pea wood and common biomass

BIOMASS	MC (%)	VCM (%)	Ash (%)	FC (%)	HV (MJ/kg)	REFERENCES
Pigeon pea wood	9.89	65.90	12.30	21.80	17.13	This study
Wood	20.00	82.00	1.00	17.00	18.60	McKendry (2002)
Paddy straw	7.30	60.80	22.60	16.60	17.89	Lee <i>et.al.</i> (2013)
Bagasse	13.20	81.70	2.40	15.90	18.28	Lee <i>et.al.</i> (2013)
Sorghum biomass	12.80	75.00	8.50	16.50	75.00	Capareda (2014)
Corn stover	9.90	78.50	6.30	15.20	78.50	Capareda (2014)
Rice Straw	8.70	67.40	17.90	14.70	67.50	Capareda (2014)
Woodchips (softwood)	10.00	87.20	0.30	12.50	19.40	Capareda (2014)

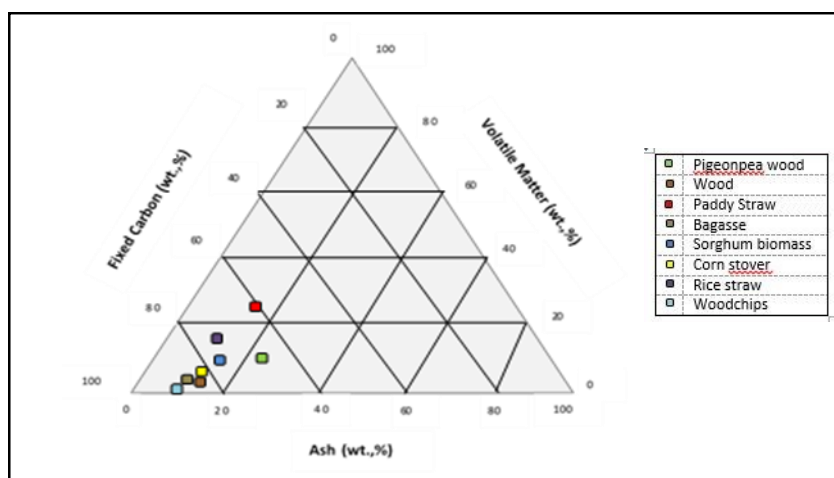


Figure 3. Ternary graph showing the proximate analysis of pigeon pea wood in comparison with other common biomass materials.

same position in the graph and were grouped together and have similar proximate content.

A biomass that is suitable for a thermochemical process feedstock should have high VCM and low ash content. Such biomass readily releases more volatile compounds during heating while leaving a solid product with less ash and higher FC, thus improving its heating value and making it a more valuable product (Capunitan and Capareda, 2012). Vassilev *et al.*, (2010) also mentioned that the VCM and FC can influence the biological conversion process of the fuel. Pigeon pea wood had a combination of high O content and high organic VCM, indicating a potential of producing large amounts of inorganic vapors during combustion (consistent with Figure 3).

The ultimate (elemental) analysis of pigeon pea wood is presented in Table 3. These elements determine the fuel efficacy and are the major component of biomass (Singh *et al.*, 2017). Pigeon pea wood was compared with some of the common agricultural biomass (Table 3). The C content

of some agricultural biomass ranged from 38 to 52% and that pigeon pea wood which has 41.07% C falls in the middle values. Capareda (2014) stated that the C content of the biomass material is always correlated to the HV, which also mean that there is an increase in the energy density accordingly. Moreover, the C and H contents of biomass are two most significant elemental properties when it comes to its further conversion into liquid fuel. However, the widespread reduction in the elemental H may be detrimental to the future use of the biomass for liquid fuel production; thus, it is essential to use appropriate temperature when upgrading biomass.

The H content for most agricultural biomass is around 5 to 6% (Table 3), whereas that of the pigeon pea wood fall on the upper limit. As for its N content, pigeon pea wood fall in the middle values, similar with that of the C content. While in terms of the O content, pigeon pea wood had the highest O content as compared with other biomass, suggesting that the former is highly oxygenated.

The fuel efficacy not only depends on the proximate and ultimate analysis of biomass, but also on the atomic ratio of H:C and O:C (Singh *et al.*, 2017). According to Capareda (2014), two

Table 3. Ultimate analysis of pigeon pea wood and some common agricultural biomass

BIOMASS	C(%)	H(%)	N(%)	O(%)	REFERENCES
Pigeon pea wood	41.07	6.17	0.85	51.90	This study
Wood (average)	51.60	6.30	0.00	41.50	McKendry. (2002)
Paddy straw	48.75	5.98	1.99	43.28	Lee, et.al. (2013)
Bagasse	51.71	5.32	0.33	42.64	Lee, et.al. (2013)
Sorghum biomass	38.10	5.60	0.90	46.70	Capareda (2014)
Corn stover	40.00	5.90	1.30	46.20	Capareda (2014)
Rice Straw (TX)	39.90	6.00	1.30	24.70	Capareda (2014)
Woodchips (softwood)	46.10	6.60	0.20	46.60	Capareda (2014)

important parameters that maybe calculated from the ultimate analysis are the atomic hydrogen-to-carbon (H/C) ratio (which are almost always 1.0) and oxygen-to-carbon (O/C) ratio. These ratios are important to thermal conversion systems. Figure 4 presents these ratios for different agricultural biomass, plotted in a Van Krevelen diagram, and is concentrated on the upper portion of the diagram. Moreover, the H/C molar ratios of these biomasses are quite high, with pigeon pea and rice straw having the highest H/C molar ratios. Also, pigeon pea wood registered the highest O/C molar ratio. According to Singh *et al.*, (2017), the lower the ratio, the higher is the energy content. The material with a relatively low O/C ratio has more energy density and higher high heating value This is consistent with the higher chemical energy contained in C-C bonds than in C-O bonds. This diagram also shows the correlation between the calorific value and atomic ratio.

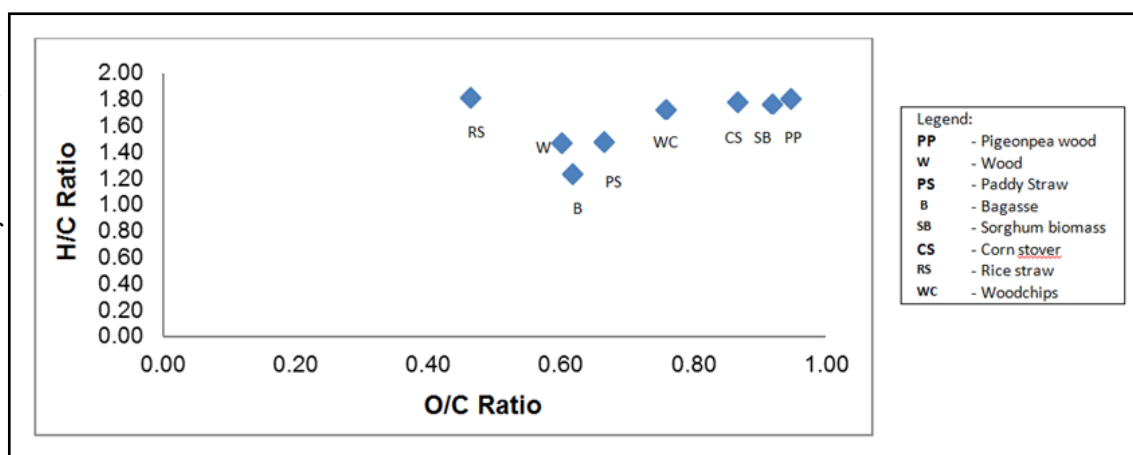


Figure 4. The Van Krevelen diagram of the different biomasses

Moreover, in pigeon pea wood, the contents of low-energy C-H and C-O bonds are found to be relatively high, whereas the contents of high-energy bonds (C-C bond) are relatively low. Indeed, relatively lower O/C and H/C ratios in biomass mean greater energy content or high energy densification (higher HHV). This simply suggests that lower temperature input may be needed to convert most of the pigeon pea biomass to energy in the form of bio-oil during actual pyrolysis (for example, lower pyrolysis temperature to effectively break these chemical bonds in pigeon pea to produce bio-oil as compared to other biomass feedstock containing low O/C ratio).

The heating value of any fuel is the energy released per unit of mass per unit volume of the fuel when it is completely burnt (ASABE, 2011). The higher high heating value refers to the condition where water is condensed out of the combustion products. Higher heating value represents the gross calorific value (Singh *et al.*, 2017). The heating value or the gross calorific value, which is the most important biomass characteristics, gives the amount of the energy in the biomass. The heating value of the biomass highly depends on the MC present in the biomass (Capareda, 2014).

The heating value content of pigeon pea wood is 17.13 ± 0.40 MJ/kg (Table 1), which fall also on the mean range or value of the biomasses (Table 2). According to Cai *et al.*, (2017), woody biomasses have slightly higher high heating value than herbaceous biomasses, that is 18.5 to 22.5 MJ/kg, and about 15.5 to 19.5 MJ/kg, respectively.

Chemical Compositional Properties

Result of the compositional properties show that pigeon pea wood contained $34.26 \pm 0.29\%$ cellulose, $34.83 \pm 0.68\%$ hemicellulose, and $17.99 \pm 0.22\%$ lignin (Table 4). In the use of diverse biomass resources for conversion, a vital step is the

compositional analysis based on the macro-components, namely: cellulose, hemicellulose and lignin (Capareda, 2014). Compositional analysis is also one of the most critical parameter for biomass fuel analysis (Singh *et al.*, 2017). Cellulose is a linear polysaccharide consisting of hundreds or thousand β (1 $\rightarrow$ 4) linked D-glucose units. It is the structural component of the cell wall of biomass. Hemicellulose is a polymer composed of groups of complex carbohydrates such as sugars and starch (Capareda, 2014). Lignin is a complex, large molecular structure containing cross-linked phenolic polymers (Cai *et al.*, 2017). Lignin is a very important component of biomass as binder of the cellulosic compounds and as mortar that keeps the cellulosic blocks rigid (Capareda, 2014). Other biochemical components of biomass include also extractives, lipids, proteins, simple sugars, starches, water, hydrocarbons, ash, and other compounds.

Moreover, pigeon pea wood falls within the range of the cellulose, hemicellulose and lignin composition of plant biomass (average), that is, 30-50% cellulose, 20-40% hemicellulose and 15-25% lignin (Singh *et al.*, 2017). When compared with other typical lignocellulosic biomass, pigeon pea wood has lower cellulose content than hardwood, softwood and corn stalk. In terms of hemicellulose content, pigeon pea wood has higher value than sorghum and rice straws. For its lignin content, pigeon pea wood is also lower than hardwood and softwood. Other LCB have similar values with pigeon pea wood.

Table 4. Chemical composition analysis of pigeon pea wood and other typical lignocellulosic biomass.

TRIAL	CELLULOSE (Per Weight %)	HEMICELLULOSE (Per Weight %)	LIGNIN (Per Weight %)	REFERENCE
Pigeon pea	34.0 – 34.6	34.2 – 35.5	17.8 – 18.2	This study
Hardwood stem	40 – 50	24 – 40	18 – 25	Capareda, 2014
Softwood (Pine)	45.0 – 50.0	25.0 – 35.0	25.0 – 35.0	Cai et.al., 2017
Sugarcane Bagasse	25.0 – 45.0	28.0 – 32.0	15.0 – 25.0	Cai et.al., 2017
Sorghum Straw	32.0 – 35.0	24.0 – 27.0	15.0 – 21.0	Cai et.al., 2017
Corn Stalk	35.0 – 39.6	16.8 – 35.0	7.0 – 18.4	Cai et.al., 2017
Rice Straw	29.2 – 34.7	23.0 – 25.9	17.0 – 19.0	Cai et.al., 2017
Grasses	25.0 – 40.0	25.0 – 50.0	10.0 – 30.0	Cai et.al., 2017

In biochemical or thermochemical conversion processes, the performances of cellulose, hemicellulose and lignin are different (Cai *et al.*, 2017). The ethanol yield from biomass is directly related to cellulose, hemicellulose and other sugars present in the feedstock. Comparing cellulose and hemicellulose, lignin concentration in the biomass makes the entire process difficult as it blocks the microbial fermentation although it may be useful for other purposes (Singh *et al.*, 2017). Also, lignin hinders the cellulosic bioethanol production (Welker *et al.*, 2015 and Cai *et al.*, 2017). The high lignin and/or high ash content in a biomass is unfavorable for bioethanol production (Singh *et al.*, 2017). According to Capareda (2014), lignin is component that is perhaps most difficult to convert biologically, and must be removed from the biomass matrix to improve the process efficiency. Accurate compositional analysis of lignocellulosic biomass enables evaluation of conversion yields and process economics, particularly in bioethanol conversion processes (Cai *et al.*, 2017).

SUMMARY AND CONCLUSION

In summary, the potential of pigeon pea wood as feedstock in thermochemical conversion was given emphasis. Sustainable production of biofuel requires a continuous abundant supply of feedstock as well as efficient conversion processes. Pigeon pea wood, available in large quantities in the Philippines, represents a new resource that is suitable for further expanding the current supply of local feedstock. To better understand the potential and suitability of pigeon pea wood as feedstock for thermochemical conversion process, properly prepared pigeon pea wood samples were characterized in this work through dedicated experiments. Correlating the physicochemical characterization data to thermochemical conversion is beneficial to better understand the mechanism of applied conversion processes and empirically describe the expected products under various operating conditions. Prior characterization of pigeon pea wood biomass is thus, an important tool to accurately predict, for example, yields and properties of products including char, liquids, and volatiles through modelling studies, supplemented by experimental data.

In this work, pigeon pea wood properties such as proximate, elementary chemical compositions, and HV were examined for its potential for pyrolysis. Pyrolysis is a complex process due to several transformations that produce a large number of product species. Aside from operating conditions, factors such as biomass processing, composition, MC, and particle size can influence the efficiency of the pyrolysis process. It is found that pigeon pea wood had lower ash content (12%) than straw samples, suggesting higher low heating value and suitability of pigeon pea wood to thermal conversion conveying parts.

Pigeon pea wood biomass generally falls within the range of the cellulose (30-50%), hemicellulose (20-40%), and lignin (15-25%) composition typically found in lignocellulosic biomass as reported in previous studies. Notably, however, pigeon pea wood had significantly lower lignin mass fractions than softwood (pine) as reported in the literature. It is thus, expected that pigeon pea wood will yield lower heating value than most pinewood biomass. Indeed, the heating value of the pigeon pea wood (17.13 MJ/kg), which is similar to that of rice straw and corn stover, but is lower than that of the wood. Furthermore, the higher cellulose content of pigeon pea wood as compared to sugarcane bagasse, sorghum straw, rice straw, and grasses (the hemicellulose content of pigeon pea wood is highest among other biomass), as well as lower lignin content is favorable to improve the rate of deconstruction of biomass during pyrolysis. This is due to the fact that both cellulose and hemicellulose degrade at lower temperatures than lignin, which degrades at considerably higher temperatures. The higher contents of H and O (51.90%) than C (41.07%) of pigeon pea wood samples strongly suggest that its energy value as compared to conventional oil is lower because of the lower energies associated in C-O and C-H bonds as compared to C-C bond. The lower N content in pigeon pea wood (0.85%) suggests that it will potentially produce less toxic nitrogen oxide species during pyrolysis. These characteristics proved advantageous for pyrolysis and far less recalcitrant to destruction than traditional lignocellulosic biomass feedstocks.

Based on the analysis of these important parameters, it can be concluded that pigeon pea wood biomass can be used as residual resource for production of biofuels through pyrolysis, an energy-efficient thermochemical conversion process. Moreover, pigeon pea wood has a good potential as a new feed or co-feed for thermochemical conversion processes (i.e., pyrolysis, torrefaction, and gasification) for biofuels production in the Philippines, comparable to other established sources of lignocellulosic biomass.

RECOMMENDATIONS

The following recommendations are provided based from the results of the study:

1. Pigeon pea can be pyrolyzed to determine the factors that can optimize its yield and its effects on the chemical composition of its products;
2. Pigeon pea wood can be considered as a new feed or co-feed for thermochemical conversion processes (i.e., pyrolysis, torrefaction, and gasification) for biofuels production
3. Assess the financial viability of pigeon pea as a potential feedstock for biofuel; and
4. Pigeon pea hull can also be considered for characterization.

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