VARIATION OF CHEMICAL PROPERTIES, CRYSTALLINE STRUCTURE AND CALORIFIC VALUES OF NATIVE MALAYSIAN BAMBOO SPECIES

Syaiful Osman

Sr. Lecturer E-mail: syaifulosman@uitm.edu.my

Mansur Ahmad

Professor E-mail: mansur628@uitm.edu.my

Mohd Nazarudin Zakaria

Sr. Lecturer Faculty of Applied Sciences School of Industrial Technology Universiti Teknologi MARA Shah Alam, Malaysia E-mail: nazarudin@uitm.edu.my

Balkis Fatomer A. Bakar

Sr. Lecturer Faculty of Forestry and Environment Department of Wood and Fiber Industry Universiti Putra Malaysia Serdang, Malaysia E-mail: bfatomer@upm.edu.my

Falah Abu

Sr. Lecturer E-mail: falah@uitm.edu.my

Siti Hasnah Kamarudin

Sr. Lecturer E-mail: sitihasnahkam@uitm.edu.my

Shahril Anuar Bahari

Sr. Lecturer Faculty of Applied Sciences School of Industrial Technology Universiti Teknologi MARA Shah Alam, Malaysia E-mail: shahril721@uitm.edu.my

^{*} Corresponding author

Reza Hosseinpourpia*

Associate Professor Department of Forestry and Wood Technology Linnaeus University Växjö, Sweden E-mail: reza.hosseinpourpia@lnu.se

(Received February 2022)

Abstract. The chemical properties of four common Malaysian bamboo species locally known as Beting (*Gigantochloa levis*), Semantan (*Gigantochloa scortechinii*), Lemang (*Schizostachyum brachyladum*), and Akar (*Bambusa vulgaris*) were studied. Chemical analysis shows that the alkaline-extractive content of the Malaysian bamboo species ranged from 24.4% to 25.6%, ethanol–toluene extractive content for Malaysian bamboo species ranged from 4.0% to 7.2% and water extractive content ranged from 10.4% to 12.8%. The average value of holocellulose content for Malaysian bamboo was 64.5-70.7%, Klason lignin within 25.3-28.4%, cellulose content was between 28.5% and 33.8%, and α -cellulose content for all bamboo species was within the range of 40.7-47.9%. The crystallinity of bamboo samples was between 42.0% and 44.4%, indicating a semicrystalline structure. Heating value of bamboo ranged between 17.0 MJ/kg and 18.1 MJ/kg with *G. scortechinii* having the highest heating value. The Inductive Couple Plasma Atomic Emission Spectroscopy (ICP-ES) analysis showed that Potassium (K) and Calcium (Ca) were the major elements in the ash of all bamboo samples. This study demonstrates the potential of native bamboo species as an alternative sustainable raw material to wood for a wide range of applications.

Keywords: Bamboo, physicochemical, calorific value, spectroscopic analysis.

INTRODUCTION

Growing population and rapid industrialization contribute significantly to an increasing demand for forest-based materials and energy production. This emphasizes the importance of finding alternatives to the existing materials (Abdulkhani et al 2017). It is estimated that there are around 1400 bamboo species worldwide, whereas in Peninsular Malaysia, there are about 59 bamboo species that consists of 34 indigenous species and 25 species are cultivated (Wong 1995). Gigantochloa scortechinii is the most common species in Malaysia, with approximately 70% of the total clump extracted from the bamboo forest (Hisham et al 2005; Mohmod et al 2016). According to Malaysia National Forestry Inventory 4 (NFI4), the total number of clumps of Gigantochloa scortechinii and Gigantochloa levis in Peninsular Malaysia is 163,000 and 911,956 clumps, respectively with the total area of bamboo in Malaysia is around 0.6 million ha (Kuehl 2015; Anon 2018).

Comparatively, more studies have been conducted to analyze the properties of wood instead of bamboo using the same techniques as in this work (Ghavidel et al 2020, 2021). However, some studies on bamboo behavior are available as a basis for this study. The chemical characteristics of bamboo are one of the critical properties that must be understood to encourage and widen its applications. Liese (1985) claimed that the chemical properties of bamboo vary depending on species, growing conditions, age, and growth site of bamboo culms. Major constituents of bamboo are cellulose (38-50%), hemicelluloses (23-32%), and lignin (15-25%) that make-up to 90% of the total mass (Cao et al 2014).

It was shown previously that top location of bamboo culm shows significantly higher extractive and ash content compared with middle and bottom parts (Kamthai 2003). Bamboo nodes also contain more lignin and ash but less water-soluble extractives than internodes (Kamthai and Puthson 2005). Li (2004) studied the chemical composition of *Phyllostachys pubescens* bamboo at different ages and as a function of culm height. The author claimed that age and height of bamboo culm affect its chemical composition, as the hemicelluloses and α -cellulose content increased from the bottom to the top part of bamboo, but the changes in lignin

and ash content were statistically insignificant. The content of hemicelluloses, α -cellulose, and Klason lignin was higher in outer layer of bamboo than in the epidermis while the epidermis had a higher extractive content compared with the outer layer. The higher content of α -cellulose and Klason lignin is closely related to the fact that the outer layer contributes most to the mechanical strength of culm. Kumar and Chandrashekar (2014) found that Indian bamboo ash had relatively high percentages of silica and potassium and the contents of ash, volatile, and fixed carbon were varied significantly among different bamboo species. Physicochemical characterization of several commercially important Asian bamboo species (Bambusa nutons, Bambusa tulda, Bambusa arundinacea, Bambusa pallida, Bambusa bambus, Dendrocalamus strictus, and Dendrocalamus strictus teri) showed the alkali solubility variability between 26.1% and 28.3% in all bamboo species.

Although the decline in wood supply does not apply to all countries (Ekstrom 2022), however, deforestation is still a major problem, as more countries are beginning to make greater efforts to conserve forests. For example, in Sabah, one of the states in Malaysia with a vast area of tropical forest, the timber trade in Sabah has been declining because of various conservation efforts, and this trend is expected to continue for the next 20 yr. Bamboo-based sector and timber industry can complement each other to cater demand from population increase. In addition, there is also a need to promote sustainable materials and to preserve tropical forests (The Malaysian Reserve 2022).

Since there are numerous potentials uses for various bamboo species nationally and worldwide, ranging from pulp and paper to panel manufacturing, chemical and bioenergy industries, it is advisable to understand its chemical properties, which are influenced by culm height. Therefore, the main objective of this study was to comprehensively investigate certain chemical properties of four native Malaysian bamboo species through chemical composition analysis, Fourier Transform IR (FTIR) spectroscopy, elemental analysis, X-ray structure analysis (XRD), and oxygen bomb calorimeter (OBC). This information will contribute to a better understanding of the mentioned native bamboo species to expand their application as an economically viable and alternative renewable material.

MATERIALS AND METHODS

Raw Materials

Four native Malaysian bamboo species; Semantan (G. scortechinii), Beting (G. levis), Lemang (S. brachyladum), and Akar (B. vulgaris) with age of 3 yr old were collected from a local source in Peninsular Malaysia, with an approximate height of 180 cm from top to bottom. Samples were air-dried upon arrival and sectionized as shown in Fig 1 indicating the bottom, middle and top part of bamboo. Nodes and internodes sections are also indicatedOuter skin was removed using hand spoke, the bamboo specimens were then cut into smaller pieces and ground using Wiley milling machines (Thomas Scientific, Swedesboro, NJ), and then sieved subsequently screened using a vibrating screening machine. Grounded bamboo particles, 40 mesh in size (Fig 2) were then stored in airtight containers for further analysis. Prior to each analysis, bamboo particles were oven-dried at 70°C for 24 h.

Characterization of Bamboo Species

Specific gravity, acidity, and buffering capacity. Acidity (pH) of bamboo species was determined according to TAPPI-T509 (2006).



Figure 1. (a) Entire bamboo culm (bottom, middle, and top) with positioning of nodes and internodes; (b) schematic image of longitudinal section of bamboo specimen.



Figure 2. Ground bamboo specimen (40 mesh) used for analysis.

Buffering capacity (β) was calculated as the number of milliequivalents (N \times m) required to change the pH to 3.5 as shown in Eq 1.

Buffering capacity
$$(\beta) = \frac{n}{\Delta pH}$$
 (1)

Where, *n* is the number of moles of acid or base added per liter of solution. The Δ pH is calculated by subtracting the initial pH from final pH.

Determination of extractive content. Extractive content of bamboo species was determined using hot water, alkaline, and ethanol-toluene extraction methods. For hot-water extractive content, 2 g of oven-dried particles were placed in a 250 mL Erlenmeyer flask and topped up with 100 mL distilled water. The flask was then placed in a shaking water bath at 95°C for 5 h. The specimens were then removed and filtered by vacuum suction, washed with hot distilled water, and ovendried at $103 \pm 5^{\circ}$ C for 24 h. For each bamboo species, the sample size was equivalent to *G. scortechinii* = 25, *G. levis* = 24, *S. brachyladum* = 23, and *B. vulgaris* = 24.

The alkaline-extractive content was determined according to ASTM D1109—84 (2013) using 1% NaOH solution. For each bamboo species, the sample size was equivalent to 25. Ethanol–toluene

extractive content was assessed according to standard ASTM D1107—96 (2013) by ethanol–toluene ratio of 2:1 (v/v) through Soxhlet extraction. The extractive content after each extraction method was calculated by following Eq 2:

Extractive content
$$(\%) = [(W1 - W2)/W1] \times 100$$
(2)

where, *W*1 and *W*2 are weight of oven-dried samples before and after extraction, respectively.

Analysis of cellulose, holocellulose, and α -cellulose content. Measurements of extractive free specimens were performed according to ASTM D1103-60 (1977), ASTM D1104-56 (1978), Li (2004), Pettersen (1984), and Bodirlau et al (2007) and the cellulose/holocellulose and α -cellulose content was calculated by using Eq 3. Each bamboo species was measured six times.

$$cellulose/holo cellulose/\alpha cellulose content (%) = \left[\frac{W2 - W1}{W3}\right] 100$$
(3)

where, *W*1 is the oven-dried weight of crucible, *W*2 is the oven-dried weight of residue and crucible, *W*3 is the weight of oven-dried extractionfree sample before analysis.

Lignin content determination. Klason lignin content of extraction-free bamboo species was assessed according to ASTM D1106-96 (2001) and using Eq 4. Each bamboo species was measured in sample size as follows; *G. scortechinii* = 26, *G. levis* = 24, *S. brachyladum* = 25, and *B. vulgaris* = 23.

% Klason lignin =
$$\left[\frac{W1}{W2}\right] \times 100$$
 (4)

where, W1 and W2 are the respective oven-dried weight of samples after and before measurement.

Ash content analysis and elemental analysis of bamboo. Ash contents were analyzed for lower (bottom section in Fig 1) and upper (combination of middle and top sections in Fig 1) parts along the bamboo height. Ash content was determined based on the method outlined by ASTM D1102—84 (2013) and each bamboo species were analyzed with the respective sample number of 40 samples for each bamboo species.

The elemental composition of bamboo ash, was evaluated by Inductive Coupled Plasma Optical Emission Spectroscopy (ICP-OES) (Model Optima 5300 DV—Perkin Elmer, Shelton, CT).

Fourier Transform IR (FTIR) spectroscopy. FTIR analysis was performed to determine the functional chemical groups present in the bamboo species using FTIR Spectroscopy (NICOLET 6700 model, Thermo Scientific Inc., Madison, WI) equipped with an attenuated total system (ATR) system and processed with OMNIC software. The oven-dried (60° C for 24 h) bamboo particles were placed in contact with the ATR on the crystal plate. IR spectrum of bamboo specimens was recorded between the wavelengths from 850 cm^{-1} to 3700 cm^{-1} in transmission mode.

X-ray Diffraction (XRD) relative. Crystallinity index of bamboo specimens was analyzed using XRD method on a PANalytical Xpert Pro (X'pert Pro Panalytical, Netherlands) with Cu K α , 1.54Å radiation source). Measurement was performed at an energy of 45 kV, an electric current of 40 mA in the scan ranges from 10° to 90° at a scan speed of 6°/min. Relative crystallinity of different bamboo fibers was calculated based on Segal method (Segal et al 1959; Yueping et al 2010; Yun et al 2016; Bakar and Kamke 2020) as shown in (Eq 5):

$$CrI = \left[\left(I_{002} - \frac{I_{am}}{I_{002}} \right) \right] \times 100\%$$
 (5)

where, Crystallinity index is the relative crystallinity (%), I_{002} is the maximum intensity of the peak between 20° and 25° (crystalline), and $I_{\rm am}$ is the lowest intensity between 15° and 22.7° (amorphous).

Calorific value determination. Calorific values of bamboo species were determined using IKA OBC Model C5000 (Cole-Parmer, Chicago, IL).

A crucible containing 0.5 g of the specimen was lit in a combustion chamber. The pressure was set at 30 bars, and specimens were ignited at 298K in oxygen. 1 cm³ of water was added to the decomposition vessel during analysis. Calorific values of bamboo were expressed in Joule per gram (J/g). Six samples were used for each bamboo species

Statistical analysis. Analysis of two-sample *T*-test was performed to compare sections (nodes and internodes) and locations (lower and upper) of the bamboo culm. One way analysis of variance (ANOVA) followed by Tukey test was used for multiple comparisons when comparing top, middle, and bottom locations of the bamboo culm to compare mean with a 95% confidence interval (P < 0.05).

RESULTS AND DISCUSSION

Specific Gravity, pH and Buffering Capacity

Specific gravity (SG) is ratio of density of a material to the density of water (Haygreen and Bowyer 1989). The average SG of all bamboo species ranged from 0.70 to 0.85 (Table 1), which is in the same range as previous studies (Ahmad and Kamke 2005; Kamruzzaman et al 2008; Yu et al 2008; Kaur et al 2016). For each bamboo species, there is statistically significant difference along the culm height for G. scortechinii bamboo (F =25.19, P = 0.00) and B. vulgaris bamboo (F =9.35, P = 0.002), at 95% confidence interval. In contrast, no significant differences were found for *G. levis* bamboo (F = 0.62, P = 0.551) and *S. bra*chyladum bamboo (F = 2.91, P = 0.088). High SG of bamboo becomes a disadvantage when considered it for a specific application such as composite products where the recommended SG range is below 0.5 (Ahmad and Kamke 2005). However, other applications such as energy utilization and high-density feedstock are preferable as they contain more energy per unit volume (Kumar and Chandrashekar 2014).

The pH of the internode section of *G. scortechinii*, *G. levis*, *S. brachyladum*, and *B. vulgaris* were slightly acidic (Table 1). This is similar to other bamboo species such as *Dendrocalamus asper*

	SG*			рН				
Bamboo species	T*	M*	B*	T*	M*	B*	I*	N*
G. scortechinii	$0.70^{a^{**}}$	0.75 ^{a**}	0.83 ^{a**}	4.58 ^{a**}	4.55 ^{a**}	4.58 ^{a**}	4.79 ^{a**}	4.3 ^{b**}
G. levis	(0.02) 0.78 ^{c**}	(0.05) 0.74 ^{b**}	(0.03) $0.77^{a^{**}}$	(0.46) 5.07 ^{a**}	(0.43) 5.25 ^{a**}	(0.15) $4.82^{a^{**}}$	(0.29) 5.33 ^{a**}	(0.27) 4.8 ^{b**}
S. brachyladum	$(0.08) \\ 0.82^{a^{**}}$	(0.03) $0.85^{a^{**}}$	(0.06) 0.77 ^{b**}	(0.26) 5.29 ^{a**}	(0.57) 5.24 ^{a**}	(0.25) 5.03 ^{a**}	(0.40) 5.18 ^{a**}	(0.14) $5.2^{a^{**}}$
B. vulgaris	(0.07) $0.85^{a^{**}}$ (0.01)	(0.05) $0.85^{a^{**}}$ (0.01)	(0.03) $0.80^{a^{**}}$ (0.04)	(0.22) 4.62 ^{a**} (0.42)	(0.21) 4.64 ^{a**} (0.50)	(0.27) 4.63 ^{a**} (0.36)	(0.23) 4.88 ^{a**} (0.24)	(0.28) $4.3^{b^{**}}$ (0.30)

Table 1. SG and pH value of bamboo.

SG, Specific gravity T, Top; M, Middle; B, Bottom; I, Internodes; N, Nodes.

** Results are expressed as mean and standard deviation (in parentheses) based on 71, 24, and 75 measurements for pH analysis, acid buffer capacity, and SG, respectively. Values that do not share a superscript letters (^{a,b}) within the same row are significantly different based on grouping information using Tukey Method, P < 0.05. Two-sample *T*-test was conducted to compare internodes and nodes, P < 0.05.

and *Dendrocalamus strictus* (Ahmad and Kamke 2003; Malanit et al 2009). pH values of the selected native bamboo species in this study were comparable to common wood species such as *Populous* spp., *Pinus sylvetris, Shorea* spp., and *Tsuga canadiensis* with a value of 5.8, 5.1, 4.7, and 5.5, respectively (Wegener 1989).

Buffer capacity varied among species and by internode and node (Fig 3). Compared with other bamboo species, *G. levis* required the greatest



Figure 3. Buffering capacity of various bamboo species at internodes (I) and nodes (N) positions.

amount of acid (mL) to reach pH 3.5. Compared with the nodes, internodes required a higher amount of acid to change the pH of the bamboo species to 3.5. This is especially true for the species *G. levis* and *B. vulgaris*. Buffering capacity of native bamboo in this study ranged from 0.3 to 0.5 milliequivalents, higher than that of Calcutta bamboo (Ahmad and Kamke 2005) and some woody species such as *Populus* spp. (aspen, cottonwood), *Pseudotsuga menziesi* (douglas fir), *Tsuga canadensis* (eastern hemlock), and *Quercus alba* (white oak) (Wegener 1989).

Analysis of Chemical Composition

Extractive contents of the studied bamboo species are presented in Fig 4(a). Extractives in bamboo are a minor fraction that consists of nonstructural organic and inorganic components (Qi et al 2013). The respective alkaline soluble content (%) for G. scortechinii, G. levis, S. brachyladum, and B. vulgaris bamboo species were 25.6%, 24.4%, 24.9%, and 24.7%, respectively (Fig 4[a]). No statistically significant difference was found along the culm height of G. scortechinii bamboo (F =0.34, P = 0.719), G. levis bamboo (F = 0.84, P = 0.462), S. brachyladum bamboo (F = 0.63, P = 0.549) and B. vulgaris bamboo (F = 2.25, P = 0.152) (ANOVA, $\alpha = 0.05$). Also, the differences between the nodes and internodes section were statistically insignificant. Kaur et al (2016) reported that alkaline extractives of six Indian



Figure 4. (a) Graphical representation of extractive content, (b) chemical composition for all varieties of bamboo species studied. Number of specimens, n for Alkaline extractive = 96, alcohol extractive = 99, hot-water extractive = 96, holocellulose = 48, α -cellulose = 43, cellulose = 24, Klason lignin = 98, ash = 168, and calorific value = 24.

bamboo species ranged from 26.1% to 28.3%, which is slightly higher than the values obtained in this study (24.7-25.6%). High alkaline-extractive content suggests that the bamboo samples should be properly stored after harvesting to avoid degradation (Kaur et al 2016).

Ethanol-toluene extractive content showed that the respective average values for *G. scortechinii*, *G. levis*, *S. brachyladum*, and *B. vulgaris* were 5.5%, 7.0%, 4.5%, and 3.7% (Fig 4[a]). The values for nodes specimens of *G. scortechinii*, G. levis, S. brachyladum, and B. vulgaris were 4.1%, 4.7%, 3.1%, and 5.4%, respectively. There was no statistically significant difference found between nodes and internodes for all bamboo specimens. Hot-water extractive content indicated that the average values for G. scortechinii, G. levis, S. brachyladum, and B. vulgaris were 11.8%, 12.8%, 11.0%, and 10.4%, respectively. The differences between height and types of bamboo species were not statistically significant. This was also true for the nodes and internodes of S. brachyladum and B. vulgaris samples. However, the differences between hot-water extractive content of internodes and nodes for G. scortechinii and G. levis bamboo samples were statistically significant (P-value equivalent to 0.000 and 0.001, respectively, at 95% confidence interval). The ethanol-toluene content and hot-water extractive content in this study ranged from 4.1% to 7.2% and 10.4% to 12.8%, respectively, which is slightly higher than the values previously reported for bamboo species. Ethanol and hot-water extractive content of bamboo samples from the literature ranged between 3.15% and 5.99% and 5.26% and 12.6% (Li 2004; Kaur et al 2016).

Chemical compositions of native bamboo samples are shown in Fig 4(b). The average holocellulose content ranged from 64.50% to 70.65%. Along bamboo's culm height, only G. scortechinii showed a significant difference in the average value. The magnitude of difference between nodes and internodes was not significant in all bamboo species. The average respective values of α -cellulose ranged between 40.73% and 47.86%. These values were higher for internodes than nodes, with the difference being significant in G. levis and B. vulgaris bamboo. Comparison between all bamboo species indicated a significant difference in terms of α -cellulose (F = 5.07, P = 0.005) at a 95% confidence interval. In this study, the value of holocellulose was found within 64.49-70.54%, which was lower than the value determined by Kumar and Chandrashekar (2014) for different Indian bamboo species.

Klason lignin content of *G. scortechinii*, *G. levis*, *S. brachyladum*, and *B. vulgaris* was 25.91%, 27.30%, 25.30%, and 28.39%, respectively. No

Table 2. Cellulose to lignin (C/L) ratio of different bamboo species.

C/L ratio
1.16
1.14
1.12
1.18

significant differences were found in the culm height of bamboo samples. However, a comparison between internodes and nodes showed a significant difference in *G. levis, S. brachyladum*, and *B. vulgaris* samples. The lignin content of selected Malaysian native species consistent with that of Indian native bamboo species previously reported, ranging from 20% to 32.5% (Li 2004; Wahab et al 2013; Kumar and Chandrashekar 2014; Kaur et al 2016). Depending on intended application, high lignin content in bamboo samples might be favorable, eg for biorefinery or energy purposes.

Cellulose to lignin (C/L) ratio ranged from 1.12 to 1.18 (Table 2); lower than the value for most hardwoods (Bodirlau et al 2007). C/L ratio is a significant criterion in biochemical conversion process of biomass and the utilization of biomass for pulping.

FTIR Spectroscopy

FTIR transmittance band assignment and spectra of native bamboo samples are shown in Fig 5 and Table 3. The broad band at around 3300 cm^{-1} may be associated with expanding and contraction vibration of OH, which could be related to the presence of alcoholic and phenolic hydroxyl groups involved in hydrogen bonds (Ghaffar and Fan 2013). The prominent band at around $2890 \,\mathrm{cm}^{-1}$ is associated with CH can also be observed. Typical assignments of bands at around 1600 cm^{-1} , 1500 cm^{-1} , and 1430 cm^{-1} are related to skeletal vibration of the aromatic ring from lignin, C=Cstretching vibration in the aromatic structure of lignin, and CH bending in plane, respectively (Ghaffar and Fan 2013). The vibration at around $1240\,\mathrm{cm}^{-1}$ can be attributed to the presence of guaiacyl type lignin in bamboo (Chen et al 2014).

The intensity of FTIR bands was used to evaluate the ratio between aliphatic and aromatic absorption, syringyl/guaiacyl (S/G) ratio, and phenolic OH group and CO group contents, as described previously (Bodirlau et al 2007). Table 4 shows that the absorbance ratio of S/G in Malaysian bamboo is almost similar to each other regardless of species. This ratio is one of the key parameters



Figure 5. ATR-FTIR spectrum of all different bamboo species.

Wavenumber (cm ⁻¹)					
G. levis	G. scortechinii	S. brachyladum	B. vulgaris	Corresponding chemical bonds	References
3340.2	3334.5	3333.9	3332.7	O–H, expanding and contracting vibration	Yueping et al 2010; Chen et al 2014; Ghaffar 2016
2893.0	2893.0	2895.0	2893.5	C–H, expanding and contracting vibration	Yueping et al 2010; Chen et al 2014; Ghaffar 2016
1603.4	1603.6	1604.0	1603.1	Skeletal vibration of aromatic ring from lignin	Yueping et al 2010; Ghaffar 2016
1506.5	1506.2	1514.3	1509.1	C=C stretching vibration in aromatic structure of lignin	Chen et al 2014
1423.1	1423.8	1423.1	1421.6	C-H, bending in plane	Yueping et al 2010; Chen et al 2014
1318.1	1318.1	1323.8	1323.5	O–H, bending vibration in plane	Yueping et al 2010
1236.0	1235.0	1238.0	1238.0	Acyl-oxygen CO–OR stretching vibrations in hemicelluloses, C–O of guaiacyl unit stretching vibrations in lignin	Chen et al 2014
1160.0	1152.3	1158.0	1160.0	C–O from <i>p</i> -coumaric ester group, typical for H, G and S lignin	Yueping et al 2010; Ghaffar 2016
1030.1	1030.1	1031.6	1027.0	Aromatic C–H in plane deformation, symmetri- cal C–O stretching	Ghaffar 2016
899.7	894.0	894.0	895.0	C–H deformation in cellulose; C–H stretching out of plane due to β-linkage	Ghaffar 2016

Table 3. Corresponding chemical bonds to their associated bands.

in biomass material as it influences the delignification process and the recalcitrance of sugar release (Yoo et al 2018). Content of phenolic OH groups and aliphatic to aromatic absorbance ratio

Table 4. Ratio of aliphatic to aromatic signals, S/G (syringyl/guaiacyl) ratio, the content of phenolic OH groups, and C–O groups.

	Aliphatic to aromatic absorbance ratio signal (A ₂₈₉₃ /A ₁₅₀₆)	S/G ratio (A ₁₃₂₃ /A ₁₅₀₆)	Content pf phenolic OH groups (A ₁₃₂₃ /A ₁₅₀₂)
G. levis	0.90	1.03	0.96
G. scortechinii	0.96	1.01	0.98
S. brachyladum	0.95	1.02	0.98
B. vulgaris	0.97	1.01	0.98

is also similar for all bamboo species. Phenolic OH groups are important because they enable sulfonation, cleavages of major interunit ether linkages in both acidic and alkaline conditions, and oxidative delignification reaction (Lai and Guo 1991).

Crystalline Structure of Native Bamboo Species

Crystalline character of lignocellulosic materials influences their acid/enzymatic hydrolysis behavior (Rambo and Ferreira 2015). The XRD of four Malaysian native bamboo samples are illustrated in Fig 5. The existence of two peaks (16° and 23°) at different diffraction angles indicates the



Figure 6. XRD Diffraction of native bamboo species.

semicrystalline structure of bamboo samples. The diffraction peaks at about 16° and 23° can be associated with cellulose I and IV, both exhibiting monoclinic structure (Poletto et al 2014; Mayandi et al 2015).

Crystallinity index of the sample is computed with Eq 5 by removing the intensity approximately at 16° , leaving the crystalline to total material ratio (Fig 6). This technique approximates the crystalline percentage in the sample and neglect other criteria as peak overlap, crystallite size, orientation, and paracrystallinity (French and Santiago Cintrón 2013). Therefore, this method provides relative crystallinity index for comparison purposes within this study.

The crystallinity index of the bamboo species indicated that the crystallinity of different bamboo samples was almost identical, ranging from 42.0% to 44.4% (Table 5). These values are lower than the crystallinity index of *Neosinocalamus affinis* sample (Yueping et al 2010) and higher than Moso bamboo (Yun et al 2016). Generally, the crystallinity of bamboo is significantly lower than flax, banana, sisal, kapok, pineapple leaf and

Table 5. Crystallinity index (%) of bamboo samples.

Bamboo species	002 Crystal plane angle (2θ)	I ₀₀₂	001 Crystal plane angle (2θ)	I _{am}	Crystallinity index (%)
G. scortechinii	22.1	1724	15.4	958	44.4
G. levis	22.1	1503	15.7	854	43.2
S. brachyladum	22.2	1845	15.7	1070	42.0
B. vulgaris	21.7	1213	15.8	688	43.3

Table 6. Degree of crystallinity (DC) of some other lignocellulosic materials.

Sample type	DC (%)	References
Bamboo (Neosinocalamus	52.5	Yueping et al 2010
affinis) Jute	53.8	
Flax	67.4	
Bamboo (Moso)	38.3	Yun et al 2016
Banana rachis	80.9	Deepa et al 2015
Sisal	91.3	
Kapok	86.5	
Pineapple leaf	92.3	
Coir	84.5	

DC, Degree of crystallinity.

coir (Table 6). This is a favorable characteristic as it indicates low recalcitrance of lignocellulosic biomass to improved sugar access (Chin et al 2017), thus, increasing accessibility to xylans and



Figure 7. Ash content and calorific value of bamboo species at different culm positions. Number of specimens, n for ash = 168 and calorific value = 24.

		Inorganic elements (mg/kg)						
Bamboo species	Al	Ca	Cu	Fe	К			
G. scortechinii	12.16 ^{a*}	1022.8 ^{a*}	5.81 ^{a*}	87.42 ^{a*}	1917.2 ^{a*}			
	(9.96)	(565.2)	(2.38)	(55.48)	(1213.5)			
G. levis	10.21 ^{a*}	1195.5 ^{a*}	2.84 ^{b*}	103.39 ^{a*}	1243.7 ^{a*}			
	(8.04)	(320.0)	(1.14)	(49.26)	(1296.0)			
S. brachyladum	18.20^{a^*}	1127.6 ^{a*}	1.92 ^{b*}	110.17 ^{a*}	1077.9^{a^*}			
-	(13.94)	(363.2)	(1.20)	(58.53)	(122.2.8)			
B. vulgaris	18.26 ^{a*}	1179.8 ^{a*}	5.79 ^{a*}	110.12 ^{a*}	845.9 ^{a*}			
	(11.48)	(307.2)	(3.13)	(47.71)	(922.3)			
	Mg	Mn	Na	Si	Zn			
G. scortechinii	421.6 ^{ab*}	76.69 ^{b*}	98.01 ^{a*}	236.46 ^{a*}	42.27 ^{a*}			
	(195.4)	(82.59)	(76.84)	(233.18)	(41.32)			
G. levis	465.1 ^{ab*}	95.12 ^{b*}	107.67 ^{a*}	238.27 ^{a*}	78.57 ^{a*}			
	(164.1)	(61.48)	(75.14)	(217.97)	(76.34)			
S. brachyladum	312.3 ^{b*}	187.05 ^{a*}	206.56 ^{a*}	163.02 ^{a*}	60.10^{a^*}			
	(88.6)	(108.61)	(153.06)	(87.61)	(54.92)			
B. vulgaris	648.0 ^{a*}	69.32 ^{b*}	128.59 ^{a*}	400.14 ^{a*}	76.61 ^{a*}			
	(312.5)	(58.12)	(70.20)	(339.45)	(110.04)			

Table 7. Elemental composition of bamboo ashes.

Means that do not share a superscript letters (^{a,b}) within the same column are significantly different based on grouping information using Tukey Method, P < 0.05.

* Results are expressed as mean and values in parentheses represent standard deviation based on three measurements for each element.

glucans during enzymatic hydrolysis process, ie during bioethanol production.

Calorific Value and Inorganic Compositions of Native Bamboo Species

Ash content values ranged from 5.43% to 8.50% (Fig 7[a]). Comparison along the culm height of bamboo (upper and lower sections) illustrated that the difference was not significant at 95% confidence interval. However, significant difference was found among the bamboo species (F = 4.78, P = 0.003). The ash content of current bamboo species ranged from 5.43% to -8.5%, which are higher than the values previously reported from Indian bamboo samples, ie the ash content of Indian native bamboo samples ranged from 0.4% to 3.0% (Kumar and Chandrashekar 2014). Table 7 indicates the ash compositions in Malaysian native bamboo samples. Results indicated that K, Ca, Mg, Si, Na and Fe are the main elements of ash in the bamboo samples. Potassium (K) was the major element among all bamboo species (846 mg/kg-1917.2 mg/kg) and the highest amount was found in G. scortechinii bamboo

Mean calorific values of G. scortechinii, G. levis. S. brachyladum, and B. vulgaris were 18.06 MJ/ kg, 17.50 MJ/kg, 17.00 MJ/kg, and 17.97 MJ/kg, for both internodes and nodes respectively (Fig 7[b]). The differences among bamboo species were statistically significant (ANOVA, $\alpha =$ 0.05, F = 10.70, P = 0.000). Comparison between nodes and internodes suggested that the magnitude of differences was not significant. The low calorific value of S. brachyladum could be due to high ash content (8.09%) and low lignin content (25.33%) compared with other bamboo species. These results are consistent with Kumar and Chandrashekar (2014) who reported high ash content and low lignin content may contribute to lower calorific value. High SG of bamboo (0.7-0.85) with calorific value values between 17.06 and 18.06 MJ/kg indicates that the current native Malaysian bamboo species have great energy potential, although relatively high ash content of some species, eg S. brachyladum, may negatively affect its heating value.

Traces of mineral ions in lignocellulosic materials may affect their use for future applications. Inorganic elements in ash do not burn to generate heat, and are, therefore, a hindrance in energy utilization. The content of potassium (K) was the highest in all bamboo species (846-1917.2 mg/kg) and the highest amount was found in G. scortechinii bamboo. The second highest element was calcium (Ca), with an average value of 1022-1180 mg/kg. Potassium (K) is among the major alkali element in most lignocellulosic materials (Mlonka-Medrala et al 2020) with an average concentration of 21-70% in ash composition of bamboo (Kumar and Chandrashekar 2014: Samadhi et al 2018). During combustion process, potassium (K) and sodium (Na) are responsible for lowering the ash melting point. This can cause clinkers problems that can jam the furnace. Slugging and fouling can also occur when ash is vaporized and condensed in the boiler, leading to hard formation on heat transfer surfaces (Clarke and Preto 2011). Alternately, calcium (Ca) and magnesium (Mg) will increase the melting point of ash. Lignocellulosic materials with higher amounts of calcium such as wood are preferred over the material with a higher alkali metal. They pose fewer fouling problems than herbaceous materials such as straws and grass (Miles et al 1996; Kumar and Chandrashekar 2014). Bamboo has similarity with wood biomass materials in terms of desirable fuel characteristics such as low alkali index and low ash content. Although its heating value is considerably lower than some wood species, it is still higher than straws, grasses, and most agricultural residues (Chin et al 2017).

CONCLUSIONS

Experiments were conducted to determine the physicochemical properties of four Malaysian bamboo species. The four bamboo species showed a similar range of values in all the experiments tested, especially in SG, chemical compositions, FTIR spectra, crystallinity, and elemental analysis. However, the node showed greater variability in pH, buffering capacity, α -cellulose, and lignin content. Culm height had only influenced some bamboo species for SG values. In manufacturing, the minimum variability could lead to maximum utilization of raw material. Nodes could be

excluded from certain composite products because they exhibited greater variability.

Additionally, the indication of SG showed a value >0.7, indicating that the four bamboo species are suitable for producing composite materials that minimize the increase of SG in the final products such as oriented strand board (OSB), laminated veneer lumber (LVL), plywood and gluedlaminated lumber (glulam). Chemical nature of the four bamboo species is critical for the selection of an adhesive system. Acidity values through pH and buffer capacity are among the principal factors was addressed. The four bamboo species are more on acidic conditions and exhibit a high buffer capacity, thus relating it to the certain formulation to maximize the quality of adhesive system. The properties of the four bamboo species studied are comparable to those of other bamboo species. This suggests that the use of bamboo for the production of bioresin production in the wood industry is possible and could solve the problem of supply of certain bamboo species.

REFERENCES

- Abdulkhani A, Alizadeh P, Hedjazi S, Hamzeh Y (2017) Potential of soya as a raw material for a whole crop biorefinery. Renew Sustain Energy Rev 75:1269-1280.
- Ahmad M, Kamke FA (2003) Analysis of Calcutta bamboo for structural composite materials: Surface characteristics. Wood Sci Technol 37:233-240.
- Ahmad M, Kamke FA. (2005) Analysis of Calcutta bamboo for structural composite materials: Physical and mechanical properties. Wood Sci Technol 39:448-459.
- Anon. (2018) Rattan and Bamboo. Forestry Department of Peninsular Malaysia. https://www.forestry.gov.my/ index.php/en/buluh-dan-rotan
- ASTM D1102—84 (2013) Standard test method for ash in wood. http://www.astm.org/cgi-bin/resolver.cgi?D1102-84(2013)
- ASTM D1103-60 (1977) Method of test for Alphacellulose in wood.
- ASTM D1104-56 (1978) Method of test for holocellulose in wood.
- ASTM D1106-96 (2001) Standard test method for acidinsoluble lignin in wood.
- ASTM D1107—96 (2013) Standard test method for ethanol-toluene solubility of wood. http://www.astm. org/cgi-bin/resolver.cgi?D1107-96(2013)
- ASTM D1109—84 (2013) Standard test method for 1% sodium hydroxide solubility of wood. http://www.astm. org/cgi-bin/resolver.cgi?D1109-84(2013)

- Bakar BFA, Kamke FA (2020) Comparison of alkali treatments on selected chemical, physical and mechanical properties of grape cane fibers. Cellulose 27(13):7371-7387.
- Cao X, Peng X, Sun S, Zhong L, Sun R (2014) Hydrothermal conversion of bamboo: Identification and distribution of the components in solid residue, water-soluble and acetone-soluble fractions. J Agric Food Chem 62: 12360-12365.
- Chen C, Luo J, Qin W, Tong Z (2014) Elemental analysis, chemical composition, cellulose crystallinity, and FT-IR spectra of toona sinensis wood. Monatsh Chem 145(1): 175-185.
- Chin KL, Ibrahim S, Hakeem KR, San H'ng P, Seng HL, Mohd AML (2017) Bioenergy Production from bamboo: Potential source from Malaysia's perspective. Bio-Resources 12(3):6844-6867.
- Clarke S, Preto F (2011) Biomass burn characteristics. http://www.omafra.gov.on.ca/english/engineer/facts/11-033.htm.
- Deepa B, Abraham E, Cordeiro N, Mozetic M, Mathew AP, Oksman K, Faria M, Thomas S, Pothan LA (2015) Utilization of various lignocellulosic biomass for the production of nanocellulose: A comparative study. Cellulose 22(2):1075-1090.
- Ekstrom H (2022) The large softwood timber surplus in the US south is likely to diminish over the next decade, resulting in regional increases in sawlog prices. https:// finance.yahoo.com/news/large-softwood-timber-surplusus-205100534.html.
- French AD, Santiago Cintrón S (2013) Cellulose polymorphy, crystallite size, and the Segal crystallinity index. Cellulose 20(1):583-588.
- Ghaffar SH (2016) Aggregated understanding of characteristics of wheat straw node and internode with their interfacial bonding mechanisms. Brunel University London, London, UK.
- Ghaffar SH, Fan M (2013) Structural analysis for lignin characteristics in biomass straw. Biomass Bioenerg 57: 264-279.
- Ghavidel A, Hosseinpourpia R, Gelbrich J, Bak M, Sandu I (2021) Microstructural and chemical characteristics of archaeological white elm (*Ulmus laevis* p.) and poplar (*Populus* spp.). Applied Sciences (Switzerland) 11(21): 10271.
- Ghavidel A, Hosseinpourpia R, Militz H, Vasilache V, Sandu I (2020) Characterization of archaeological European white elm (*Ulmus laevis* spp.) and Black Poplar (*Populus nigra* L.). Forests 11(12):1-13.
- Haygreen JG, Bowyer JL (1989) Forest products and wood science: An introduction. 2nd edition. Iowa State University Press, Ames, IW.
- Hisham, HN, Othman S, Rokiah H, Mohmod AL, Ani S, Mustafa MT (2005) Characterization of bamboo *Gigantochloa scortechinii* at different ages. J Trop For Sci 18(4):236-242.

- Kamruzzaman M, Saha SK, Bose AK, Islam MN (2008) Effects of age and height on physical and mechanical properties of bamboo. J Trop For Sci 20(3):211-217.
- Kamthai S (2003) Alkaline sulfite pulping and ECFbleaching of sweet bamboo (*Dendrocalamus Asper Backer*). Kasetsart University, Bangkok.
- Kamthai S, Puthson P (2005) The physical properties, fiber morphology and chemical compositions of sweet bamboo (*Dendrocalamus Asper Backer*). Witthayasan Kasetsat Witthayasat 39(4):581-587.
- Kaur, PJ, Kardam V, Pant KK, Naik SN, Satya S (2016) Characterization of commercially important Asian bamboo species. Eur J Wood Wood Prod 74(1):137-139.
- Kuehl Y (2015) Resources, yield, and volume of bamboos of Bamboos BT - Bamboo: The Plant and its Uses (W. Liese & M. Köhl (eds.); pp. 91-111). Springer International Publishing, Switzerland
- Kumar R, Chandrashekar N (2014) Fuel properties and combustion characteristics of some promising bamboo species in India. J For Res 25(2):471-476.
- Lai YZ, Guo XP (1991) Variation of the phenolic hydroxyl group content in wood lignins. Wood Sci Technol 25(6):467-472.
- Li X (2004) Physical, chemical, and mechanical properties of bamboo and its utilization potential for fiberboard manufacturing. LSU Master's Theses. 866, Louisiana State University. https://digitalcommons.lsu.edu/ gradschool_theses/866.
- Malanit P, Barbu MC, Frühwald A (2009) The gluability and bonding quality of an Asian bamboo (*Dendrocalamus Asper*) for the production of composite lumber. J Trop For Sci 21(4):361-368.
- Mayandi, K, Rajini N, Pitchipoo P, Sreenivasan V, Jappes JW, Alavudeen A (2015) A comparative study on characterisations of *Cissus quadrangularis* and *Phoenix reclinata* natural fibres. J Reinf Plast Compos 34(4): 269-280.
- Miles TR, Baxter LL, Bryers RW, Jenkins BM, Oden LL (1996) Alkali deposits found in biomass power plants, Vol 1. NREL Report, Golden, CO.
- Mlonka-Medrala A, Magdziarz A, Gajek M, Nowińska K, Nowak W (2020) Alkali metals association in biomass and their impact on ash melting behaviour. Fuel 261: 116421.
- Mohmod AL, Othman AR, Husain H, Mustafa MT (2016) Bamboo as a commodity: It is a dream or a possibility. *In* Proceedings of ASEAN Bamboo Symposium, 27-29 September 2016, Kuala Lumpur, Malaysia. Published by Forest Research Institute Malaysia (FRIM), Kepong, Malaysia.
- Pettersen RC (1984) The chemical composition of wood. Page 57-126 *in* R Rowell ed. The Chemistry of Solid Wood. Advances in Chemistry Series No. 207. ISBN 0-84120796-8. Washington 1984: American Chemical Society

- Poletto M, Ornaghi Júnior HL, Zattera AJ (2014) Native cellulose: Structure, characterization and thermal properties. Materials (Basel) 7(9):6105-6119.
- Qi J, Xie J, Hse CY, Shupe TF (2013) Analysis of *phyllostachys pubescens* bamboo residues for liquefaction: Chemical components, infrared spectroscopy, and thermogravimetry. BioResources 8(4):5644-5654.
- Rambo MKD, Ferreira MMC (2015) Determination of cellulose crystallinity of banana residues using near infrared spectroscopy and multivariate analysis. J Braz Chem Soc 26(7):1491-1499.
- Bodirlau R, Spiridon I, Teaca CA (2007) Chemical investigation of wood tree species in temperate forest in East Northern Romania. BioResources 2(1):41-57.
- Samadhi T, Narcia F, Amril H (2018) Preliminary evaluation of potassium extraction from bamboo ash. *in* MATEC Web of Conferences Volume 156, The 24th Regional Symposium on Chemical Engineering (RSCE 2017), 15-16 Nov 2017, Semarang, Indonesia. https:// doi.org/10.1051/matecconf/201815603027. Published by EDP Sciences, Les Ulis, France.
- Segal L, Creely JJ, Martin AE, Conrad CM (1959) An empirical method for estimating the degree of crystallinity of native cellulose using the X-ray diffractometer. Textile Res J 29(10):786-794.
- TAPPI-T509 (2006) Hydrogen Ion Concentration (Ph) of Paper Extracts (Cold Extraction Method).
- The Malaysian Reserve (2022) Sabah Timber Trade on a Decline for next 20 Years. https://themalaysianreserve. com/2017/03/31/sabah-timber-trade-on-a-decline-fornext-20-years/ (18 April 2022).

- W. Liese, Bamboos-Biology, Silvics, Properties, Utilization. Eschborn: Deutsche Gesellschaft f
 ür Technische Zusammenarbeit, 1985.
- Wahab R, Mustafa MT, Sudin M, Mohamed A, Rahman S, Samsi HW, Khalid I (2013) Extractives, holocellulose, α-cellulose, lignin and ash contents in cultivated tropical bamboo *Gigantochloa brang*, *G. levis*, *G. scortechinii* and *G. wrayi*. Curr Res J Biol Sci 5(6): 266-272.
- Wegener DFG (1989) Wood: Chemistry, ultrastructure, reactions. Walter de Gruyter, Berlin [etc.].
- Wong KM (1995) The bamboos of peninsular Malaysia. Forest research institute Malaysia, Published by Forest Research Intitute Malaysia (FRIM) in collaboration with Forest Research Centre, Forestry Department, Sabah, Malaysia.
- Yoo CG, Dumitrache A, Muchero W, Natzke J, Akinosho H, Li M, Sykes RW (2018) Significance of lignin S/G ratio in biomass recalcitrance of *Populus trichocarpa* variants for bioethanol production. ACS Sustain Chem Eng 6(2):2162-2168.
- Yu HQ, Jiang ZH, Hse CY, Shupe TF (2008) Selected physical and mechanical properties of moso bamboo (*Phyllostachys pubescens*). J Trop For Sci 20(4):258-263.
- Yueping W, Ge W, Cheng H, Tian G, Zheng L, Qiao QF, Zhou X, Han X, Gao X (2010) Structures of bamboo fiber for textiles. Textile Res J 80(4):334-343.
- Yun H, Li K, Tu D, Hu C (2016) Effect of heat treatment on bamboo fiber morphology crystallinity and mechanical. Wood Res 61(2):227-234.