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Mixing Pyrolyzed Forestry Bio–Fibers with Lignosulfonate to Develop "Biomass Charcoal Briquettes"

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To develop "Biomass Charcoal Briquette (BCB)", the forestry bio–fibers: wood/bamboo processing residues carbonized by pyrolysis were mixed with the pulping derivative, lignosulfonate (LS). The BCB was mixed with biomass charcoals (BC) and LS in predetermined density (PD) and mixing percent weight (wt%) with BC and LS. These were fabricated into BCB by cold/hot–pressing. The heating value of the BCB was evaluated for the potential of efficient conversion into biofuel, and the combustion emitted functional groups were analyzed by using TGA–IR to learn the characteristics of subsequent emissions. The BC yield decreased as the carbonization temperature and holding duration increased. The heating value and power consumption increased with carbonization temperature and holding duration. The H/C and O/C atomic ratios of charcoal approached to those of anthracite and lignite, respectively. The forestry bio–fibers with higher BC yield and heating value (1.6–1.7 times higher) was employed as the original materials for the development of BCB. The rebound degree (%) of BCB thickness developed by hot–pressing was lowered to 2.0–5.0%. The heating values of BCB by the extreme value theory, Dulong formula, and actual sampling point–selected were 22.22–23.57, 26.18–26.53, and 22.51–23.10 MJ/kg respectively. At the same PD, the BCB with a higher mixing percent weight with BC proportion had a higher heating value; for the same mixing percent weight, a higher PD represented a higher heating value. The energy yield of BC at the carbonization temperature of 300°C was 65.94% and the energy density was 1.65. According to TGA–IR, the functional groups emitted from the combustion of forestry bio–fiber, BC and LS in the air and nitrogen were subject to CO_2 peak.

Key words: Biomass Charcoal Briquettes (BCB), Heating Value, Lignosulfonate (LS), Pyrolysis, Thermogravimetric analysis–infrared spectroscopy (TGA–IR)

INTRODUCTION

Taiwan produces about 1 500 000 tons of the forestry bio–fibers: wood/bamboo processing residues annually which are recognized as biomass with great development potential. Generally, the optimal utilization of biomass is direct combustion, but the untreated material has some defects. These are high water content, poor powdering performance, and low energy density of the original material. Pretreatment with heat can solve these problems (Van der Stelt *et al*., 2011; Bazargan *et al*., 2014). The pyrolysis of biomass can reduce biomass processing residues. The obtained biochar has carbon fixation, and a high heating value (Lin *et al*., 2021). It can substitute coal for industry use (Bridgwater, 2007; Deev and Jahanshahi, 2012; Demirbas *et al*., 2016). The Lignosulfonate (LS) is one of the derivatives from papermaking black liquor of sulfite pulping after sulphonation treatment. It has surface activity and coherence (Van der Klashorst, 1989; Rodríguez *et al*., 1990), and can be used in adhesives, surfactants, and cement additives (Laurichesse and Avèrous, 2013).

According to the International Energy Agency (International Energy Agency, IEA), biomass energy is the fourth largest energy source in the world. The share of various sources in energy production is 10.3% by biomass, petroleum 31.3%, coal 28.6%, and natural gas 21.2% (IEA, 2016). Taiwan is short of energy and natural resources. It depends on a lot of imports. At present, the Taiwan government's key points of energy projects include four major areas. These areas in Ministry of Science and Technology (MOST) are active devotion to energy saving, energy storage, energy creation, and intelligent system integration (MOST, 2016). This is required to strengthen the development of the green energy industry. In the "preplanning work of destructor plant transformation into biomass energy center" planned by the Environmental Protection Administration (EPA) of Executive Yuan Taiwan, the agricultural and forestry processing residues are regarded as the target of material source for energy (Waste–to–energy).

To increase energy efficiency, the agricultural and forestry bio–fiber processing residues are treated with pyrolysis which is a newly developed concept. After pyrolysis, the weight, volume, and moisture of the products are reduced, leading to lowered transportation costs and increased heating value (MOST, 2016). This process also has the dual benefit of environmental protection and energy. The heating value is the heat generated by the complete combustion of substances. The magnitude

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of heat energy released from combustion can be estimated using the extreme value theory, Dulong's equation (Sheng and Azevedo, 2005; Channiwala and Parikh, 2002), and actual sampling point–selected (Lin *et al.*, 2021). The biochar derived from the pyrolysis of biomass has a higher heating value than the original material (Hernandez–Mena *et al.*, 2014; Chen *et al.*, 2015). The biomass or biochar was pressed into solid fuel e.g., biomass pellets (Kaliyan and Morey, 2008) and biomass fuel briquettes (Ward *et al.*, 2014; Lin *et al.*, 2021; 2022). Dinesha *et al.* (2019) report that the pellets/briquettes have better physical and thermal properties. These can be produced either by cold or hot–pressing. The advantages of cold pressing include rapid preparation and low energy consumption. The solid fuel prepared by hot–pressing is relatively stable properties but has a higher preparation cost (Pinate and Dangphonthong, 2018; Lin *et al.*, 2021).

To achieve "the Suitable Material and Applicability" of energy planning principle for biomass with suitable preparation method and conditions, and to contribute to the dual benefit of carbon footprint management of forestry and environmental protection, the forestry bio–fibers: wood/bamboo processing residues were carbonized by low–temperature pyrolysis in this study. Biomass charcoals (BC) were mixed with different proportions of LS and pressed into "Biomass Charcoal Briquette (BCB) " to evaluate the feasibility of using biomass energy. The forestry bio–fibers was prepared into charcoal and mixed with LS in different mixing percent weight in the "Cascade" concept to fabricate BCB with the "anchor effect". The physical, chemical and thermal properties of BCB were investigated. To know the optimal mixing percent weight and the optimum fuel briquette preparation conditions (Lin *et al.*, 2022), the extreme value theory, Dulong's formula (Sheng and Azevedo, 2005; Channiwala and Parikh, 2002), and actual sampling point–selected (Lin *et al.*, 2021) of BCB were used for multiple comparisons of heating value with the fuel used by the present power plants. The emitted functional groups were evaluated by Thermogravimetric analysis–infrared spectroscopy (TGA–IR) to realize the characteristics of pollution emissions as a reference for later processing. Also, aiming to convert the forestry bio–fibers into energy and increase energy efficiency. It is feasible to be used as the original materials of biomass energy.

MATERIALS ANDMETHODS

Test materials

1. The forestry bio–fibers: wood/bamboo processing residues: Japanese cedar (*Cryptomeria japonica* D. Don; JC) and Moso bamboo (*Phyllostachys pubescens*, MB), obtained from the wood working factory of National Chiayi University (NCYU), was all crushed into 4–8 mesh placed in a ventilated area for air–dried.
2. Lignosulfonate (LS): the byproduct of the sulfurous acid pulping process. LS is brown yellow, soluble in water and insoluble in organic solvents, and its average molecular weight is 8×10^3 g/moL.

Test method

Basic properties of wood/bamboo

1. Moisture content: refer to CNS 452 (2018) Wood–Determination of moisture content for physical and mechanical tests to measure moisture content (MC).
2. Ash determination: Huan–Shu–Jian–4216.0 method, as published by the EPA (2005).
3. Combustible content determination: Huan–Shu–Jian–4217.0 method, as published by the EPA (2005).
4. Chemical composition analysis: the ethanol–toluene extract was analyzed according to the wood ethanol–toluene extract testing method (CNS 4713); holocellulose quantification: testing method for the holocellulose of natural fiber material for pulp (CNS 6984); lignin quantification: testing method for the acid–insoluble lignin in wood and pulp (CNS 2721), the testing method for acid–soluble lignin in wood and pulp (CNS 12108), and the Klason lignin quantification method and acid–soluble lignin were used for determination.

Preparation of biomass charcoals

1. Absolute–dried weight 100 g of JC and MB was put in the closed container of the super–high temperature vacuum carbonization equipment (Chi–How Heating Co., Ltd.), respectively. The nitrogen (N_2) was admitted, where the gas flow was 200 mL/min, in order that the container was free of oxygen. The carbonization temperatures were 300, 400, 500, and 600°C, the heating rates were 10°C/min (Inguanzo *et al.*, 2002), the holding duration was 60 min (Lin *et al.*, 2021; 2022), the carbonization process was completed.
2. Biomass charcoals (BC), Japanese cedar charcoal (JCC) and Moso bamboo charcoal (MBC), yield (%) was calculated by BC yield (%) = (absolute–dried weight of BC / absolute–dried weight of BC) × 100 (Lin *et al.*, 2015a; 2015b).

Determination of properties of wood/bamboo, BC and LS

1. Elemental analysis (EA): element analysis method NIEA R409.21C, the carbon (C), hydrogen (H), nitrogen (N), and sulfur (S) contents of the BC and LS were determined using the elemental analyzer (Elemental Vario CHNS/O Analyzer and Thermal Conductivity Detecto, Germany), and oxygen (O) was calculated.
2. Krevelen analysis: the mixing percent weight of specimens (BC and LS, wt%) and coal samples (anthracite, lignite, bituminous coal, and subbituminous coal) were compared by van Krevelen's diagram, and presented as O/C and H/C atomic ratios.
3. Heating value analysis: referring to waste heating value testing method – bomb calorimeter method (EPA, 2007), the heating value computing equation

is:

(1) (End temperature – Initial temperature) × 2000 = Total heat release (cal)

(2) (Original nichrome wire weight – Residual nichrome wire weight) × 1400 = Total heat release of nichrome wire (cal)

(3) Total heat release – Total heat release of nichrome wire = Total heat release of BC

(4) Total heat release of BC / wood/bamboo weight = BC heating value (cal/g)

(5) 1 cal/g = 1 kcal/kg = 4186 J/kg = 4.186×10–3 MJ/kg, the heating value of each BC is represented by MJ/kg.

4. Thermogravimetric analysis (TGA): TGA is an established technique, used in the quantification of weight changes within a material, as a function of temperature or time (Hsu *et al.*, 2000). Throughout this, TGA was carried out using a Perkin–Elmer TGA, fully supported by computer–controlled software options from Perkin–Elmer Thermal Analysis Systems for control and data handling. The specimen JC, MB, BC, and LS after being oven dried at a temperature of 105°C for over 24 h, each weighing approximately 5.0 mg, were placed into an open experimental sample pan and suspended from a sensitive microbalance. A furnace surrounded the specimen to provide accurate heating ranging from 50 to 800°C, while the measurements were taken. In order to isolate the decomposition step, all runs were purged in the air and N_2 atmosphere, at the flow rate of 50 mL/min, with heating rate, at 10°C/min (Lin *et al.*, 2004; 2011; Lin and Murase, 2007).

Preparation of Biomass Charcoal Briquette

Preparation of Biomass Charcoal Briquette (BCB): BC, JCC and MBC, was crushed by a pulverizer into 60–80 mesh particles (Lin *et al.*, 2022). The BCB was prepared by adding water to the mixture of BC and LS, as a binder for water solubility and adhesion (Tejadoa *et al.*, 2007). The predetermined density (PD) of BCB were 0.6, 0.7, 0.8, 0.9 and 1.0 g/cm^3. The solidification molding conditions: gauge pressure 100 kgf/cm^2; BC/LS mixing percent weights: 90/10, 85/15, 80/20, 75/25, and 70/30 wt%. According to the pretest results, the water addition level was 1:4 (LS: water). BCBs' length, width, and thickness of 10×10×1.8 cm, holding duration: 5 min. The pre–BCB mat was then dried at 100°C for subsequent tests for BCB properties and heating value (Lin *et al.*, 2021).

In terms of cold pressing preparation, after mixing according to the preset BC/LS mixing percent weights of 90/10, 85/15, 80/20, 75/25, and 70/30 wt%, the water was added for BCB. The BCB mat was placed in a 10×10×1.8 cm mold and a multistage pressing was used. The pressure was kept for 1 min during each press and the pressure was relieved for 30 s. The process was repeated four times. When the target dimension of 1.8 cm thickness was reached the pressure was kept for 5 min. The BCB was taken out immediately after holding and placed at room temperature for 10 min. The length, width, thickness, and weight were recorded.

In terms of hot–pressing preparation, the mold was placed in the hot–press. The upper/lower plate temperature was set at 100±5°C for 20 min preheating. The BCB mat was placed in the mold. A multistage pressing was used which was similar to the cold pressing procedure. The BCB was taken out after holding and placed at room temperature for 10 min, the length, width, thickness, and weight were also recorded.

Determination of properties of Biomass Charcoal Briquette

1. Rebound degree: the percent of dimensional change in length, width, and thickness directions of BCB was measured. Dimensional rebound degree (%) = [(dimension after rebound – dimension before a rebound)/dimension before rebound] × 100.
2. Heating value of BCB: estimation of the extreme value theory, deduction of Dulong formula, determination of the heating value of the actual sampling points–selected was evaluated. The calculations of the energy yield, energy density, and heating value effect were performed.

   (1) Estimation of the extreme value theory: BCB estimated heat value formula = (BC heating value × proportional absolute–dried weight of BCC) + (LS heating value × proportional absolute–dried weight of LS);

   (2) Deduction of Dulong formula (Sheng and Azevedo, 2005; Channiwala and Parikh, 2002): the percent weight, as derived from elemental analysis, was substituted into Dulong formula to calculate the high heating value (HHV), and the equation was: HHV (MJ/kg) = 33.68 × C + 144.4 × {H–(O/8)} + 9.428 × S;

   (3) Heating value determination of an actual specimen of BCB: the heating values at 10 points in the upper, middle, and lower parts of BCB were measured by an adiabatic calorimeter (1341 Plain Jacket Calorimeter), the average and standard deviation were calculated, and the heating value distribution of the BCBB was investigated. The internal and external heating values of the BCB were evaluated (Lin *et al.*, 2021).
3. Energy yield and Energy density (Bergman *et al.*, 2005): Energy Yield = Yield of Mass × [Heating value of Torrefied (MJ/kg)/ Heating value of Feedstock (MJ/kg)]×100; Energy Density= Energy Yield (%) / Torrefied Yield (%).

Thermogravimetric analysis with infrared spectrometry

TGA, as described in previous section, is a quantitative technique that does not identify evolved compounds. To understand the evolved species produced by the thermal decomposition of the specimens, an analysis was carried out using a TGA (Perkin–Elmer Pyris 7 TGA model), linked to a secondary method of analysis, the Fourier–Transform Infrared Spectroscopy (using a

Perkin–Elmer FTIR), which was able to identify the evolved species during the TGA measurements. The TGA and FTIR (TGA–IR) were connected using a transfer line with a continuous scanner in a gaseous cell. The infrared spectrometric (IR) response data was recorded by a personal computer. The spectrum time based version 2.0 software (2000, Perkin–Elmer, Inc.) obtained and analyzed the evolved species as they occurred. The specimens, weighing about 5.0 mg each, were placed in an experimental sample open pan and suspended from a sensitive microbalance in the Pyris 7 TGA model. The conditions were set the same as for the Perkin–Elmer TGA 1, described above, regarding heating and flow rates. The evolved species analysis was performed on the TGA–IR, and their IR spectra was then investigated by spectrum version 5.3 (2005, Perkin–Elmer, Inc.). However, the IR response obtained for various evolved species using the TGA–IR appeared about 10 s later, when compared to the traces of the TGA tests. To investigate the criteria and limitations of both TGA–IR and TGA for each particular analysis, and to ensure accurate results, it was necessary to carefully calculate and compare the results obtained between the decomposition temperature (obtained from the TGA) and the decomposition time of the evolved species from the IR response (obtained from the TGA–IR) (Lin and Murase, 2007).

Statistical analysis

This study conducted different carbonization temperatures; same carbonization temperature and different holding durations; same density and different mixing percent weight; same mixing percent weight and different densities; where the heating values of BC were represented by average (standard deviation), Statistical Product and Service Solutions (SPSS) was used for Duncan's multiple range analysis, various treatments were represented by ($\rho<0.05$), and different English letters represent significant difference.

RESULTS AND DISCUSSION

Basic Properties of wood/bamboo, and LS

A higher MC produces burning of the material less likely. The heating value increases as the MC decreases (Szymajda and Łaska, 2019). The MCs in wood and bamboo were 10.36 and 10.48%, respectively. The MC in LS was 6.36%. The LS had the highest ash content (17.4%), the bamboo took second place (4.16%), and the wood has the lowest ash content (0.82%). The combustible contents in wood/bamboo and LS were 88.84/85.36, and 76.10%. These were equivalent to the combustible content in the raw material of sawdust biofuel, 86.57–87.92% (Chen *et al.*, 2011). The ethanol–toluene extract contented in wood/bamboo was 3.41–4.23% whereas the holocellulose and lignin contented in wood/bamboo were 64.68 and 32.41%/68.60, and 25.81%, respectively. The amount of ethanol–toluene extract content represents the content byproducts such as resin, rubber, and tannin in the test material; a higher value contributes to increase in the heating value (Lin *et al.*, 2021). The holocellulose and lignin are natural high molecular compounds composed of C, H, and O elements, and the main source of biomass heat value. Both contents are the key factor in the heating value (Todaro *et al.*, 2015).

Yield and heating value of BC

The yield of JCC was 30.12–38.67%, that of MBC was 26.57–33.57% which was a little lower than JCC. The yield of BC decreased as the carbonization temperature and holding duration increased. The yield of charcoal is caused by pyrolysis which produces the volatile matter and tar of wood/bamboo dissipate as gas and liquid (Elyounssi *et al.*, 2012; Oyedun *et al.*, 2012). Meanwhile, the yield of BC from increases pyrolysis opportunity of original materials as the holding duration increases (Lin *et al.*, 2021). In terms of BC yield at a carbonization temperature of 300°C with non–holding duration (0 min) had differences (Table 1). The heating value increased with the increase of carbonization temperature and holding duration. This means that carbonization can increase the heating value. The heating value of JCC increased from 15.54 to 25.62–28.89 MJ/kg (1.6–1.8 times of JC). For BMC, the value increased from 15.30 to 24.46–28.60 MJ/kg (1.7–1.8 times of MB). The heating values of BC prepared at different carbonization temperatures were analyzed at 95% significance level. The heating values of different carbonization temperatures were significantly. Considering energy conservation, this study selected the preparation conditions with a higher BC yield. The heating value was increased by about 1.6–1.8 times with minimum power consumption, i.e. carbonization temperature 300°C and retention time 0 min, for developing BCB.

Elemental analysis of wood/bamboo, LS, and BC

The percent composition of C, H, O, N, and S of the material is known by elemental analysis. The elementary composition of biomass is used for estimating the heating value (Friedl *et al.*, 2005). The C content in each biomass was 45.70–50.50%, H was 5.30–6.70%, O was 34.90–42.00%,. The N and S contents were lower than 1.70 and 0.20%, respectively. The wood/bamboo elemental analyses had similar trends in this study. The LS has a higher S content because it contains a sulfur–bearing sulfonic group (Tejado *et al.*, 2007). As the pyrolysis process generates H_2O tar, C–O and C–H bond rupture (Hu *et al.*, 2000). The C contents in JCC and MBC were increased to 72.36 and 77.14%. They are close to 73.50% of biomass fuel briquettes and coals (Ward *et al.*, 2014; Lin *et al.*, 2021; 2022). It is said that the H and O contents are decreased relatively while the N and S contents are relatively increased (Results no showed in Table).

Van Krevelen analysis wood/bamboo, and BC

After carbonization, the H/C and O/C atomic ratios of wood/bamboo decreased from 0.14/0.81 and 0.14/0.76 to 0.06/0.30 and 0.06/0.21 respectively (Fig. 1). The H/C, O/C of anthracite and lignite are 0.38, 0.05, and 1.00, 0.30, respectively (Prins *et al.*, 2007). The H/C of JCC and MBC was similar to anthracite and the O/C was similar to lignite. In Taiwan, the coals used for power generation is mainly bituminous coal / sub–bituminous coal (Taipower, 2005), and their H/C and O/C are 0.74 and 0.08 / 1.08 and 0.22, respectively (Lin *et al.*, 2021). The JCC and MBC had a lower H/C atomic ratio than bituminous and sub–bituminous coals, but a higher O/C. Wood/bamboo has; therefore, the potential to be effectively transformed by carbonization into one of the combustible materials.

Thermogravimetric analysis of wood/bamboo, LS, and BC

The cellulose, hemicellulose, and lignin have different pyrolysis temperatures. This temperature difference is attributed to the short molecular chain and nonstationary structure of many branches of hemicellulose, which induce better thermal reaction (Stefanidis *et al.*, 2014). Cellulose is a highly linear polymer formed of d–glucose which has higher thermal stability. The lignin has an aromatic ring with a highly cross–linked structure. It is less likely to be pyrolyzed than hemicellulose and cellulose (Quan *et al.*, 2016). Figure 2 shows the pyrolysis results of various specimens in N_2.

Table 1. Yield, heating value and power consumption of wood/bamboo and biomass charcoals

Specimen $^{1)}$	Yield (%)	Heating value (MJ/kg)
JC	–	15.54 (0.57) $^{A2)}$
MB	–	15.30 (0.43) ^{A}
LS	–	15.43 (0.51) ^{A}
JCC–300–0	40.00 (0.37) $^{E3)}$	25.62 (0.85) $^{I4)}$
JCC–300–60	38.67 (0.69) ^{F}	25.17 (0.41) $^{IQ5)}$
JCC–300–120	37.91 (0.82) ^{F}	26.44 (0.11) ^{I}
JCC–400–60	36.59 (0.44)	25.92 (0.42) ^{R}
JCC–400–120	34.24 (0.29)	26.79 (0.25)
JCC–500–60	32.74 (0.27)	27.57 (0.19) ^{S}
JCC–500–120	32.26 (0.15)	28.89 (0.58)
JCC–600–60	30.97 (1.02)	27.28 (0.34) ^{S}
JCC–600–120	30.12 (0.29)	27.70 (0.47)
MBC–300–0	35.05 (0.69) $^{e3)}$	24.46 (0.56) $^{i4)}$
MBC–300–60	33.57 (0.16) ^{f}	25.18 (0.36) $^{ijq5)}$
MBC–300–120	33.28 (0.13) ^{f}	26.44 (0.86) ^{j}
MBC–400–60	32.77 (0.71)	25.51 (0.11) ^{q}
MBC–400–120	29.29 (0.20)	26.66 (0.43)
MBC–500–60	28.19 (0.23)	27.96 (0.18) ^{r}
MBC–500–120	27.99 (0.30)	28.06 (0.33)
MBC–600–60	26.75 (0.09)	27.74 (0.01) ^{r}
MBC–600–120	26.57 (0.36)	27.80 (0.07)

$^{1)}$ JC: Japanese cedar (*Cryptomeria japonica* D. Don/, JC) ; MB: Moso bamboo (*Phyllostachys pubescens*, MB); LS: Lignosulfonate; JCC: Japanese cedar charcoal; MBC: Moso bamboo charcoal, MBC; specimen–carbonization temperature (°C)–holding duration (min);

$^{2)}$ Mean (standard deviation) by Duncan's multiple range tests at 5% significant level with English words AB for the heating value of JC, MB, and LS;

$^{3)}$ Duncan's multiple range analysis at 5% significant level with English words EF/ef for the 300°C carbonization temperature with different yields of JCC and MBC;

$^{4)}$ Duncan's multiple range analysis at 5% significant level with English words IJK/ijk for the 300°C carbonization temperature with different holding durations of JCC and MBC;

$^{5)}$ Duncan's multiple range analysis at 5% significant level with English words QRS/qrs for the yields of JCC/MBC at 300°C carbonization temperature and 60 min of holding duration

The weight loss before 100°C was derived from the volatilization of moisture. The LS had three cracking points. The temperature interval of main weight loss was 151.10–391.87°C and the weight loss in this interval was 39.33%. MB had two cracking points. The temperature interval of weight loss was 215.42–399.72°C and the weight loss was 61.92%. JC, JCC, and MBC had only one cracking point. The temperature intervals of weight loss were 238.68–394.58, 363.12–687.69, and 329.03–646.91°C, respectively. The weight losses were 37.38, 22.69, and 29.96%, respectively. The initial temperature (151.10°C) of the weight loss interval of LS was lower than that of the other specimens. It is maybe because the bond rupture of ether in its structure requires less energy (Kawamoto, 2017).

The tail section of the TGA curve becomes stable, which indicates that the pyrolysis residue is constantly decomposed in a relatively extensive temperature interval (Munir *et al.*, 2009). The pyrolysis in nitrogen (oxygen–free environment) generates more char (Demirbaş, 2001). As the residue of char combustion increased the char reached its highest values 59.08–64.89%. The LS was at 40.02% for second place. The wood/bamboo was at the lowest 17.33–19.76%. The JCC and MBC had higher pyrolysis temperatures than JC and MB, but lower weight loss. The JCC and MBC combusted in different environments (N_2) had a higher first pyrolysis temperatures than their original materials (JC and MB), but lower weight loss (Results no showed in Fig).

Dimensional rebound degree of BCB prepared by cold/hot–pressing

Solid biofuel is particle–like or massive solid fuel fabricated from crushed and dried biomass. Its fuel density

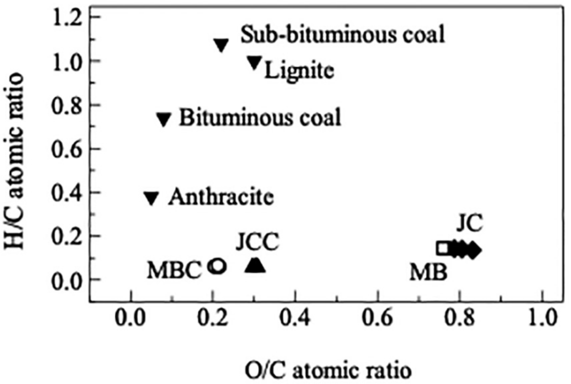

Fig. 1. Van Krevelen's diagram of wood/bamboo and biomass charcoals
Note: JC, MB, JCC, and MBC see Table 1

is enhanced, physical and thermal properties are improved, and it is easy to be transported and used (Dinesha *et al.*, 2019). The wood biomass charcoal briquettes (WBCB) and bamboo biomass charcoal briquettes (BBCB) prepared by cold pressing had lower dimensional rebound degree of length and width than thickness which was 0.40–2.10%, of thickness was 9.06–34.40%. The hot–pressing can improve the dimensional rebound degree of the composite board and enhance its stability (Rominiyi *et al.*, 2017). Afterward, the BCB pressed by hot–pressing to improve its dimensional rebound degree.

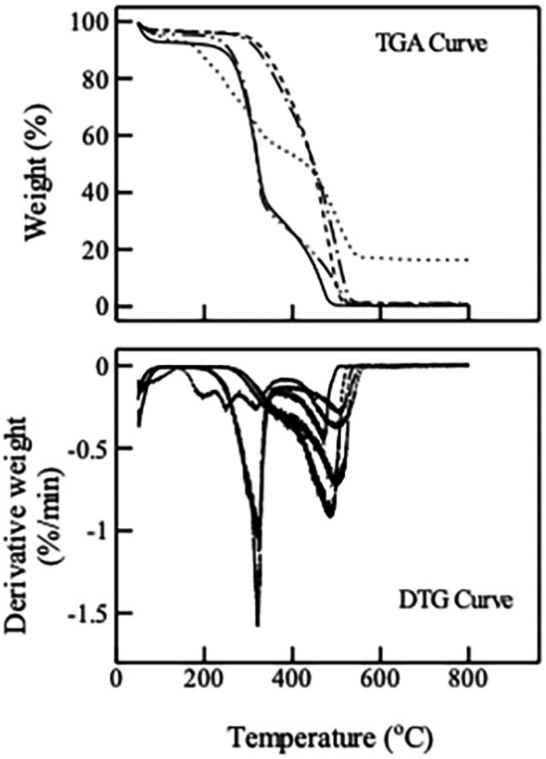

Fig. 2. TGA and DTG curves in air of wood/bamboo, lignosulfonate and biomass charcoals

Legends ——— : JC; —··— : MB; ······· : JCC; ----- : MBC; —·— : LS

Notes: JC, MB, JCC, and MBC see Table 1

The moisture addition level of BC and LS was adjusted to 1: 2. As the moisture addition level was lowered, the agglomeration failed. It was preliminarily formed into a BCB mat by pre–pressing. The obtained BCB was dried at 40°C for 24, 48, 72, 96, and 120 h and hot–pressed for 5 min. To know the feasibility of BCB drying uniformity, the MC was determined. The dimensional rebound degree of length and width of BCB prepared by hot–pressing of the BCB of mixing percent weight 80/20 wt% and PD 0.8 g/cm^3 dried for different periods was 1.10–2.20%, that of thickness was 5.84–8.23%. It is lower than the dimensional rebound degree of thickness (9.06–34.40%) of cold pressing. The dimensional rebound degree decreased as the drying time increased (Table 2).

There was no significant difference in the dimensional rebound degree of thickness of 72, 96, and 120 h drying according to Duncan's multiple range analysis. The thickness rebound degree after hot–pressing of plywood was 2.0–5.0% (Sheldon and Walker, 2006). However, the dimensional rebound degree of thickness after hot–pressing of BCB was larger than 5% in this test. The dimensional rebound degree was improved by increasing the hot–pressing time. The BCB mat of 80/20 wt% and PD 0.8 g/cm^3 was dried at 40°C for 72 h. The preparation was prepared using different hot–pressing periods. Afterward, the WBCB and BBCB were hot–pressed for 5, 10, 20, 25, and 30 min. The dimensional rebound degrees of length and width of the hot–pressed BCB were lower than 2%, that of thickness was 1.36–5.88%. The dimensional rebound degree decreased as the hot–pressing time increased. The dimensional rebound degree of thickness of the pressed by hot–pressing for 20–30 min was lower than 5%, and there was no significant difference. The BCB mat prepared by hot–pressing was preloaded for 5 min to form a BCB which was dried at 40°C for 72 h. The dried BCB was hot–pressed at 100°C for 20 min. The dimensional rebound degrees of wood/bamboo BCB hot–pressed in different preparation conditions are shown in Table 2. The dimensional rebound degree of thickness of WBCB and BBCB was lower than 5%. The thickness rebound degrees of WBCB in different preparation conditions

Table 2. Dimentional rebound degree of hot–pressed wood/bamboo biomass charcoal briquettes [1] with different preparation conditions

BC [2]	Prepartion conditions [3]		Rebound degree (%) [4]		
	PD(g/cm^3)	BC/LS(wt%)	length	Width	Thickness
WBCB	0.7	80/20	0.50 (0.02)	0.80 (0.01)	3.92 (0.02) $^{a5)}$
	0.8	80/20	1.20 (0.01)	1.10 (0.02)	4.10 (0.02) ^{b}
		75/25	1.00 (0.01)	0.80 (0.00)	4.01 (0.01) ^{c}
BBCB	0.7	80/20	0.30 (0.02)	0.20 (0.01)	2.00 (0.03) ^{e}
	0.8	80/20	0.60 (0.02)	0.60 (0.01)	2.12 (0.02) ^{f}
		75/25	0.40 (0.01)	0.50 (0.02)	2.07 (0.03) ^{f}

[1] Biomass charcoal briquettes :BCB dried at 40°C for 72 h and hot–pressed at 100°C for 20 min;

[2] BC: biomass charcoal; WBCB: wood biomass charcoal briquettes; BBCB: bamboo biomass charcoal briquettes;

[3] PD: predetermined density; BC/LS (wt%): mixing percent weight with BC and LS;

[4] BCB was taken out after holding and placed at room temperature for 10 min, the dimensional rebound degree were measured;

[5] Duncan's multiple range analysis at 5% significant level with English words abc/efg for the thickness rebound degree of WBCB/BBCB

were different. There was no significant difference in BBCB of PD 0.8 g/cm^3 and different mixing percent weights.

Energy properties

Comparison of heating value analysis of BCB

The BCB heating value was evaluated by estimation of extreme value theory, deduction of Dulong's equation (Sheng and Azevedo, 2005; Channiwala and Parikh, 2002), and determination of actual sampling point–selected (Lin *et al.*, 2021). The heating value analysis of BCB pressed by adjusting hot–pressing preparation conditions is shown in Table 3. The heating value of WBCB pressed in different preparation conditions estimated by extreme value theory was higher than that of BBCB. The heating value of JCC–300–0 was higher than that of MBC–300–0. The heating values of WBCB and BBCB estimated by Dulong's equation were 26.18 and 26.53 MJ/kg, respectively. These values were higher than the estimated values of extreme value theory and actual sampling point–selected. It is might be because the heat loss in the combustion process is not deducted from the heat generation of elements in Dulong's equation. The heating values of two BCBs of the actual sampling point–selected were 22.56–23.10 and 22.51–23.02 MJ/kg, respectively. There were significant differences in different preparation conditions. This means that in the case of the same BC/LS wt% and different densities, the BCB with a higher density has a higher heating value; in the case of the same density and different BC/LS wt%, a higher BC proportion has a better heating value (Lin *et al.*, 2021; 2022).

Energy yield, energy density of BC

The energy yield is the mass–energy (MJ/kg) transformation percentage of precursor and solid product when the biomass is converted into a solid product by conversion technology. The energy density is the energy content per unit volume (Bergman *et al.*, 2005). The energy yield of JCC/MBC decreased as the carbonization temperature and holding duration increased. The carbonization temperature of 300°C for JCC and MBC had the highest energy yield, which was 62.63–65.94% and 55.25–57.51%, respectively. The energy density of JCC and MBC increased with the increase of carbonization temperature and holding duration. This means that the carbonization can increase the energy density of biomass. Additionally, the energy density of JCC and MBC at a carbonization temperature of 300°C was 1.62–1.70 and 1.60–1.73, respectively (Results no showed in Table). It is higher than the energy density of SDRC combusted in a nitrogen environment (1.59 and 1.57) (Lin *et al*, 2021). This means that the JCC/MBC of this study has better energy properties.

Functional groups of Combustion Emission Gas

Figure 3 shows the functional groups emitted from LS, wood/bamboo, and BC heated from room temperature to 800°C in Air and N_2, respectively. The pyrolysis time interval of each spectrum was 400 s. Figures 3 (A), (B), (C), (D), and (E) on the left side of the figure are the spectra of samples combusted in air. Figures 3 (a), (b), (c), (d), and (e) on the right side are the spectra in N_2.

Figure 3 (A) the peak of LS–Air occurred at 800s which was located at 2921–2851 cm^{-1}, imcluding the C–H stretching of CH_2 with the peaks occurring at 3400–3600 cm^{-1} and 2296, 2356 cm^{-1} at the 1200s. It corresponded to the OH group and CO_2 peak. The CO_2 peak increased gradually at 1600–2800s, meanwhile the CO resulted from imperfect combustion is found at 2100 cm^{-1} (Lin *et al.*, 2004; El–Hendawy, 2006). Figure 3 (a) the peak of LS–N_2 also occurred at 800s the C–H stretching of $CH_{2,}$ but the CO_2 peak at the 1200s was smaller (Guo and Bustin, 1998).

Figure 3 (B) the peak of JC–Air occurred in the 1600s. The peak of 2300–2400 cm^{-1} was higher. Mainly the CO_2 peak and C=O were stretching and the CO peak was found at 2100 cm^{-1} (Lin *et al.*, 2004; El–Hendawy, 2006). The peak decreased slowly at 2400–3600s. The stretching of aliphatic C–O occurred at 4000 and 1000–600 cm^{-1}. There were some functional groups like the C–H group, carbonyl, and benzene ring. Figure 3 (b) the peak of JC– N_2 occurred at the 1600s which was the C–H stretching at 2921–2851 cm^{-1}. The N–H stretching of the OH group and NH_2 was found at 3400–3600, 3545, and 3509 cm^{-1} (Guo and Bustin, 1998). The CO_2 peak of 2296 and 2356 cm^{-1} was lower than that of JC–Air at 1600–3600s.

Figure 3 (C) smaller peak of JCC–Air occurred at 1200 s. The main peak occurred at 1600–2800 s which was the CO_2 of 2296 and 2356 cm^{-1}, and the C=O stretch-

Table 3. Heating value of WBCB and BBCB by calculating with the methods of extreme value theory, Dulong's fomula and actual sampling point–selected

BC1)	Preparation conditions		extreme value theory (MJ/kg)	Dulong's equation (MJ/kg)	Actual sampling point–selected (MJ/kg)
	PD(g/cm^3)	BC/LS(wt%)2)			
WBCB	0.7	80/20	23.54	26.50	22.88 (0.03) a3)
	0.8	80/20	23.57	26.53	23.10 (0.05) b
		75/25	23.13	26.25	22.56 (0.02) c
BBCB	0.7	80/20	22.64	26.43	22.83 (0.04) e
	0.8	80/20	22.69	26.46	23.02 (0.09) f
		75/25	22.22	26.18	22.51 (0.05) g

1), 2) and 3) see Table 2 2), 3) and 4)

ing at 2352 and 2380 cm^{-1}. The stretching of C=O occurred at 972 and 962 cm^{-1}. 890 and 726 cm^{-1} corresponded to NO_2 bending vibration. The –CH_2– vibration was generated at 710–718 cm^{-1} (Lin *et al.*, 2004; El–Hendawy, 2006). Figure 3 (c) JCC–N_2 had no apparent peak, a weak CO_2 peak was found only at 1600 s.

Figure 3 (D) the peak of MB–Air occurred at 1200 s which was the C–H stretching of 2921–2851 and 2980 cm^{-1}, and the CO_2 peak at 2296 and 2356 cm^{-1}. There was the stretching of the OH group and aliphatic C–O at 3400–3600 and 1000–600 cm^{-1} (Guo and Bustin, 1998). Figure 3 (d) the peak of MB–N_2 occurs at 400s. The apparent peak occurred in the 1600–2000s. The OH group, C=O stretching and C–H stretching of CH_2, and

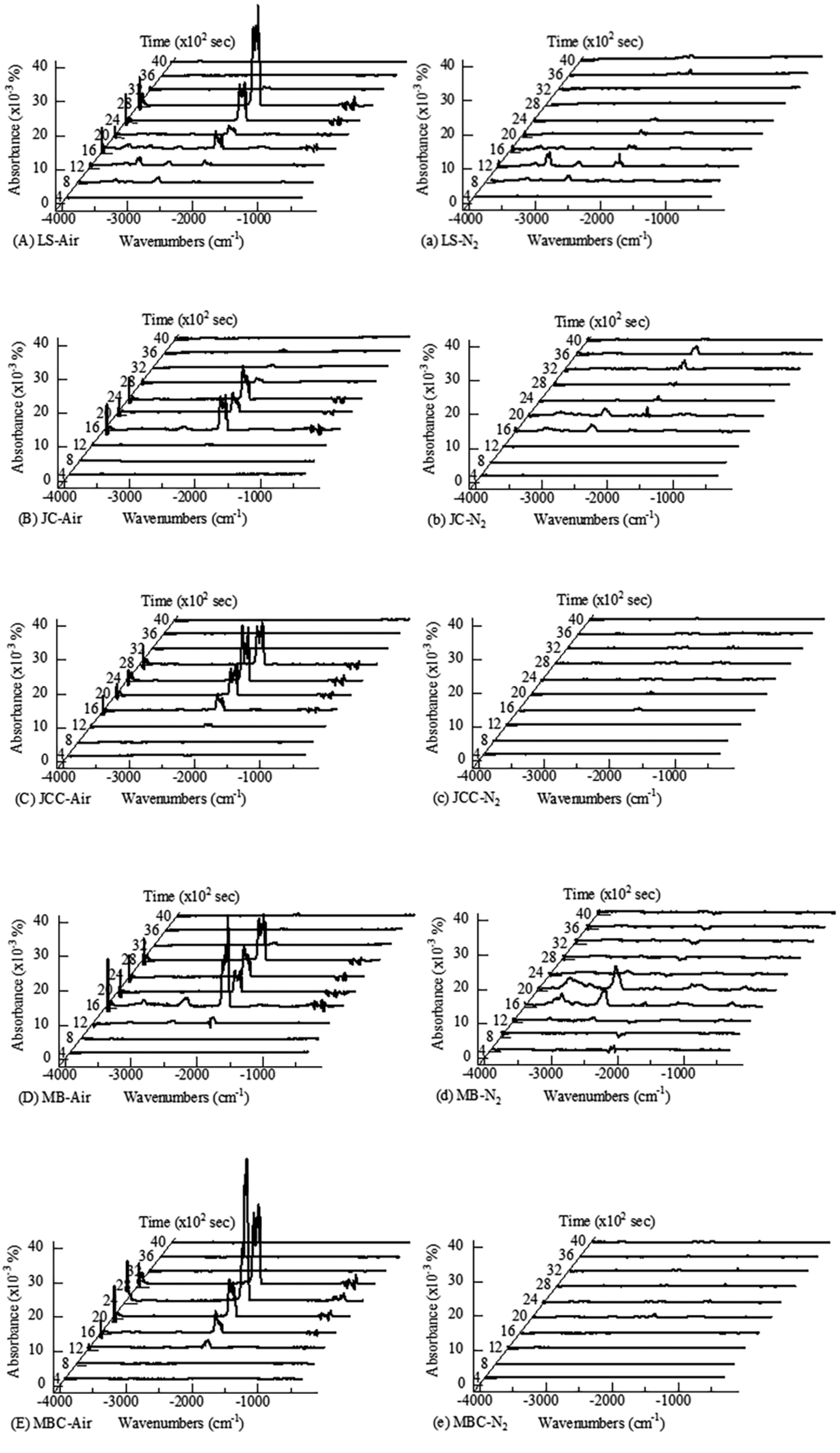

Fig. 3. TGA–IR spectra of wood/bamboo, lignosulfonate and biomass charcoals in air and N_2

aromatic C–H existed in 3500–4500 and 3200–2850 cm^{-1} (Varsányi, 1974).

Figure 3 (E) the peak of MBC–Air occurred at 1200 s which was located at 2300–2100 cm^{-1}, these were mainly the peaks of CO_2 and CO. The value increased with pyrolysis time. The maximum value occurred at 2400 s. There were OH group and C=O at 4000 and 1000–600 cm^{-1} (Guo and Bustin, 1998; Lin *et al.*, 2004). Figure 3 (e) MBC–N_2 had no apparent peak and Figure 3 (c) JCC–N_2 only had a weak CO_2 peak.

The TGA–IR peak of JC/MB and BC in the air was more apparent than that in N_2, and the main peaks were CO_2 and CO peaks which were located at 2300 and 2100 cm^{-1}, respectively. There were weak absorption peaks at 4000 and 1000–600 cm^{-1} which were the stretching of aliphatic C–O. The CO_2 peak of JCC and MBC in the air was higher than that of JC and MB. It has resulted from continuous pyrolysis and combustion of charcoal (Munir *et al.*, 2009).

CONCLUSION

The BC prepared at different carbonization temperatures was mixed in different percent weight of LS to develop the BCB. The results of transformation into biofuel were investigated by heating value analysis. The BC yield of JCC/BMC decreased as the carbonization temperature and holding duration increased. The BC yield of JCC/BMC carbonized at 300–600°C was 26.54–40.00%. The heating value increased with the increase of carbonization temperature and holding duration. The heating value of JCC/BMC was 24.46–28.60 MJ/kg. The heating value of JCC/BMC was increased by 72.36 and 77.14% after carbonization. It was close to 73.50% of commercial coals. The H/C and O/C atomic ratios of BC approach to anthracite and lignite. According to the TGA of purification in N_2, the maximum weight loss of JC/MB occurred at temperature 200–400°C, for BC it occurred at 330–690°C, and for LS it occurred at 150–400°C. The BC had the maximum char, the LS took second place, the JC/MB had the minimum chars, which were 59.08–64.89, 40.02, and 17.33–19.76%, respectively. The cold pressed BCB had better forming but poor dimensional rebound degree. After improvement by hot–pressing the dimensional rebound degree of length and width was 0.30–1.20% while the dimensional rebound degree of thickness was 2.00–4.10%. The preferred preparation conditions of hot–pressing were: moisture addition level of BC and LS was 1: 2, and the pre–BCB mat was preloaded in a mold for 5 min and formed into BCB mat. It was then dried at 40°C for 72 h, hot–pressed at 100°C for 20 min. The heating values of BCB evaluated by estimation of extreme value theory, deduction of Dulong's equation and actual sampling point–selected were 22.22–23.57, 26.18–26.53, and 22.51–23.10 MJ/kg, respectively. These were equivalent to 23.43 MJ/kg of sub–bituminous coal for power generation in Taiwan. The functional groups emitted from the combustion of JC/MB, LS, and BC in air and N_2 were mainly CO_2 with the peak of 2300 cm^{-1}, CO with the peak of 2100 cm^{-1}, the OH group, C=O stretching and $-CH_2-$ vibration occurred at 4000, 3400–3600 and 1000–600 cm^{-1}. The forestry bio–fibers: wood/bamboo processing residues were able to be reduced by pyrolysis and transformed into charcoal with a higher heating value. It is feasible to develop the mixture of charcoal (BC) and the derivative (LS) of pulping wastes into "Biomass Charcoal Briquette (BCB)".

AUTHOR CONTRIBUTION

Han Chien Lin designed the study and wrote this paper. Chia–Hsuan Liao performed the course/experiments and evaluated data with the statistical analysis. Sheau–Horng Lin provided the equipment – adiabatic calorimeter and guided the experiment of heating value. Noboru Fujimoto supervised the work. The authors assisted in editing of the manuscript and approved the final version.

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