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The densification of bio-char: Effect of pyrolysis temperature on the qualities of pellets

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HIGHLIGHTS

- Pelletization of bio-char derived from biomass pyrolysis was investigated.
- The optimal pelletizing conditions for bio-char densification were 128 MPa pressure and 35% water content.
- Effect of pyrolysis temperature on densification of bio-char pellets was determined.
- The bonding mechanism of the pellets derived from bio-char pyrolyzed at different temperatures was studied.
- Pellets compacted from 550 to 650 °C bio-char showed superior qualities for application as renewable biofuels.

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ABSTRACT

The densification of bio-chars pyrolyzed at different temperatures were investigated to elucidate the effect of temperature on the properties of bio-char pellets and determine the bonding mechanism of pellets. Optimized process conditions were obtained with 128 MPa compressive pressure and 35% water addition content. Results showed that both the volume density and compressive strength of bio-char pellets initially decreased and subsequently increased, while the energy consumption increased first and then decreased, with the increase of pyrolysis temperature. The moisture adsorption of bio-char pellets was noticeably lower than raw woody shavings but had elevated than the corresponding char particles. Hydrophilic functional groups, particle size and binder were the main factors that contributed to the cementation of bio-char particles at different temperatures. The result indicated that pyrolysis of woody shavings at 550–650 °C and followed by densification was suitable to form bio-char pellets for application as renewable biofuels.

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1. Introduction

Bio-char is a notable climate-mitigation material that it can draw down CO_2 from atmosphere since its highly recalcitrant nature (Kuzyakov et al., 2009; Mohan et al., 2014; Nguyen et al., 2010), which is shown in the path of fixing carbon through photosynthesis and returning it to the atmosphere after utilization (Woolf et al., 2010). And production of bio-char, in combination with densification process has been suggested as a possible way to handle bio-char and enable wider employment (Bazargan et al., 2014; Haykiri-Acma et al., 2013; Kong et al., 2013). Because of the uniform shape and size of the products, high density and hardness, high carbon concentration and well pore structure, densified bio-char can be more suitable for transportation, storage and handling for use in standard combustion equipment, soil amendment and coke refining oven.

Recently, because of the rapid growth of energy demands and the dwindling reserves of fossil fuel, densified biomass fuel was sought by the Chinese government to replace coal in present firing plants without any significant modifications (Kambo and Dutta, 2014). The production capacity of pellets using agriculture wastes in China was 3 million ton in 2010, and aimed to increase to 10 million ton in 2015, furthermore reach to 50 million ton by the year of 2020 (TNE, 2011; TMA, 2007). As for woody biomass, takes a large proportion of the total biomass in China, should be treated and utilized to satisfy the ever-increasing energy market and mitigate the environmental burden. Bio-char can be produced from the anoxic thermal cracking of woody residues at large factories, on individual farms, and even in domestic fireplaces, making it available at every socioeconomic level (Woolf et al., 2010). Simultaneously, other bioenergy, such as syngas and bio-oil, are

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additional produced with bio-char in different proportions through pyrolysis technologies applied commercially. In this way, pyrolysis of woody biomass related with the densification of bio-char and upgraded application of the by-products, suggests splendid advantages pertaining to economic potential, energy security and environmental improvement. Consequently, the technology for bio-char densification urgently needs to be developed, demonstrated and proven.

Currently, the densification of biomass, torrefied biomass and even hydrothermal bio-char have been studied extensively (Han et al., 2013; Lam et al., 2014; Larsson et al., 2012; Liu et al., 2014; Reza et al., 2014). The densification of lignocellulose biomass was confirmed to impart dense, uniform and durable properties, which significantly influence the transportation, handling and storage characteristics of the product. Peng et al. (2013a,b) demonstrated that torrefaction and densification technology was an effective method to form torrefied wood pellets of superior quality, compared with the raw controlled pellets. Furthermore, Reza et al. (2012, 2014) pelletized hydrothermal carbonized loblolly pine char into pellets which exhibited favorable properties, such as enhanced hydrophobicity, abrasion resistance and density, compared with the pellets produced from raw pine or dry torrefied pine. Both the torrefaction and hydrothermal followed by densification were promising methods for upgrading biomass, while the hydrothermal carbonized pellets showed considerably superior physicochemical properties when compared to the raw and torrefied pellets (Kambo and Dutta, 2014). Since volatiles, especially N-containing volatiles, were evaporated and carbon was concentrated during anaerobic pyrolysis (Winter et al., 1999), the resulted bio-char was a considerable fuel with high energy content and renewable combustion properties. With different physical, chemical and fuel properties of pyrolytic bio-char compared to biomass, torrefied biomass and hydrothermal char (Hu et al., 2015; Chen et al., 2012), the compacting of bio-char showed different densification behavior, densification results and forming mechanism, while the studies focused on this were quite limited. Bio-char can be pelletized into bio-briquettes with satisfactory characteristics, not only inherited from bio-char but also enhanced by densification process, in terms of volume and energy density, compressive strength and combustion properties with the addition of binders (Haykiri-Acma et al., 2013). The $Ca(OH)_2$ and lignin used as binders reduced the disruptive force and enhanced the bonding force during bio-char densification process (Kong et al., 2013; Hu et al., 2015). Bazargan et al. (2014) pointed out that without binders or the addition of water, the resultant bio-char pellets were so weak that they could not be ejected integrally from the equipment after being formed. Jiang et al. (2014) and Tumuluru et al. (2011) proved that raw materials and compacting conditions significantly influenced the densification process and the properties of the pellets. However, there is a lack of research focused on the densification of bio-char and optimization of the compacting conditions to form high-quality pellet fuels, especially for bio-chars derived from different pyrolysis temperatures. Despite that temperature was proved to be an important factor that determined the properties of the resulted char residues and influenced the conversion and utilization of pyrolytic products (Chen et al., 2012).

Therefore, this study focused on the pelletization of bio-chars derived from different pyrolysis temperatures (mainly from 250 to 650 °C). Process optimization in relation to the compacting conditions of compressive pressure and water addition content was initially explored. Subsequently, densification of different bio-char mixtures were carried out and qualities pertaining to volume density, compressive strength, energy consumption and moisture adsorption properties of the resulted pellets were investigated in an effort to explain the influence of the pyrolysis temperature on pelletization. The bonding mechanism of different bio-char pellets was elucidated based on SEM images of the surface of pellets and the characteristics of bio-char particles. The significance of the current research compared to the previous studies is that we try to illustrate the effect of pyrolysis temperature on the qualities of bio-char pellets and reveal the mechanism of bio-char densification, which no papers have been published in this area as far as we concern. The results may be the guidance for bio-char densification technology and helpful to the pyrolytic conversion and efficient densification utilization of biomass.

2. Methods

2.1. Materials and binder

The woody shavings obtained from a local furniture factory were sheared and crushed, followed by drying in an oven at 105 °C for 24 h. Then the woody bio-char preparations were carried out in a fixed-bed tubular reactor with a moving silica sample-carrier. The sample-carrier was the quartz ark, purchased from Shenshi Chemical instrument Co., Ltd, China, with the size of 60 mm in length and 30 mm in width. A flow of nitrogen (99.99%, 0.8 L/min) was used as the carrier gas to prevent the oxidation reaction. The reactor was pre-controlled at the experimental temperature before pyrolyzing woody shavings. Samples were retained for 30 min at the corresponding temperature to obtain complete pyrolyzed residues. The detailed pyrolysis process is explained in a previous report (Chen et al., 2012). After pyrolysis, the residual bio-char was ground in a blade mill (XY-1000A, Songqing Hardware Company, China) for 3 min, which was followed by the particle size analysis (MS2000, Malvern Instruments Ltd., U. K.). Five kinds of bio-chars, derived from pyrolysis of the woody samples at different temperatures (250–650 °C), were included to illustrate the effect of pyrolysis temperature on the densification results.

The apparent propellant effect of binders on the densification of bio-char was investigated in our former study (Hu et al., 2015). Alkaline lignin, as a by-product in paper manufacturing industry, and also rich in some rigid nutshells such as walnut shell and some woody plants, was found to be an outstanding binder in terms of densification beneficial and properties promoting (Hu et al., 2015). Hence, the alkaline lignin in analytical grade, purchased from Sigma–Aldrich Co., Ltd, USA, was used as the binder for bio-char pelletizing in this study.

2.2. Characterization of bio-char

The ultimate analysis of experimental samples were carried out in a CHNS/O elementary analyzer (Vario MICRO cube, Elementar, Germany) to explore the change trend of the relative elements via the rising pyrolysis temperature. Proximate analysis was performed based on the standard of the Proximate Analysis of Solid Biofuels (GB/T 28731-2012) using a muffle furnace (KSL-1200X, Kejing Materials Technology Co., Ltd, China). The true density of lignin and char materials was measured in a true density determinator (AccuPyc 1330, USA). The lower heating value of the char particles was determined using an oxygen bomb calorimeter (Parr 6300, USA). The chemical construction of the char derived from the variant temperatures was analyzed using a VERTEX 70 Fourier transform infrared (FTIR) spectrometer (Bruker, Germany). Seventy milligram of KBr (Merck, spectroscopy grade) was introduced to dilute the absorption of bio-char (approximately 0.7 mg) and the mixture was pressed into a tablet, which was then followed by the infrared spectrum analysis. The detailed test method was shown in Chen et al. (2014).

Table 1
Properties of lignin and pyrolyzed sawdust samples.

	Lignin	Woody shavings and bio-char					
Pyrolysis temperature (°C)	–	Raw[b]	250	350	450	550	650
Char yield (%)	–	–	88.96	31.41	23.79	21.21	19.17
Particle mean size (mm)	0.08	0.64	0.23	0.09	0.08	0.07	0.05
Bulk density (kg/m^3)	543.51	171.37	271.69	320.18	283.14	285.21	286.86
True density (kg/m^3)	–	1389	1348	1360	1490	1606	1736
LHV (MJ/kg)	19.31[a]	22.46	23.42	25.99	27.95	29.16	29.40
Saturated moisture uptake content (wt.%)	–	15.43	9.34	7.91	8.74	8.47	7.20
Proximate analysis, dry, wt.%							
Volatile	58.9[a]	83.88	81.31	35.43	23.05	12.28	8.37
Ash	36.9[a]	2.11	2.32	3.50	4.85	6.78	7.36
Fixed carbon	4.2[a]	14.01	16.37	61.07	72.10	80.93	84.26
Elemental analysis, dry, wt.%							
C	48.3[a]	48.53	50.40	61.77	74.22	84.68	88.10
H	4.9[a]	5.90	5.68	4.98	3.77	2.62	1.74
N	0.1[a]	0.11	0.10	0.16	0.22	0.24	0.29
S	3.1[a]	1.96	1.48	1.14	0.82	0.74	0.66
O (by difference)	6.7[a]	41.39	40.02	28.45	16.12	4.94	1.85

[a] Xin et al. (2013).
[b] “Raw” means the raw woody shavings dried at 105 °C.

Table 1 showed the properties of raw woody shavings, woody bio-char and lignin samples. As the pyrolysis temperature increased, the charcoal yield, lower heating value, true particle density, fixed carbon and carbon content of bio-char were all increased, while particle mean size, volatile, hydrogen and oxygen content decreased. These results were also suggested by Apaydın-Varol and Pütün (2012) and Chen et al. (2012). The charcoal yield was reduced dramatically from 88.96% to 19.17% as the temperature increased from 250 to 650 °C due to the devolatilization and thermal cracking reaction. As pyrolysis produced the homogeneous species products, the shrinkage and fracture of large particles into small and regular particles resulted in a decrease of the particle size, while the true density increased. Because of the removal of oxygen-containing volatiles and the increased degree of carbonization during pyrolysis, the carbon content increased and brought about the higher heating values of bio-char with the rising temperature (Chen et al., 2012). Fig. S1 (in the Supplementary data) depicted the molar ratio of H/C via O/C of the raw and pyrolyzed woody samples in a Van Krevelen diagram. The Van Krevelen diagram, drafted with the element compositions shown in Table 1, provides an insight into the effect of temperature on the elemental changes of the products. It clearly showed that oxygen and hydrogen were removed selectively when woody shavings were torrefied or pyrolyzed. Moreover, the linear regression relationship was found in Fig. S1 between H/C and O/C via the increased treating temperature with the coefficient of determination (R^2) of 0.9917, revealed good linear correlation between the molar H/C ratio and the molar O/C ratio. And the slope of the linear regression was 1.87, indicating that the impact of carbonization on the H/C ratio was higher than on the O/C ratio, and this was consistent with the results of Du et al. (2014). The decomposition, cracking and then extraction of hydrogenated and oxygenated components from biomass could be responsible for the diminishing of H and O with H_2, CH_4, CO and CO_2 evolving out as gas products.

2.3. Densification process

In this work, the pellets were prepared using a 200 kN universal material testing machine (CMT5205, MTS, China) fitted with a load sensor and displacement transducer with the resolutions of ±0.01 N and ±0.1 μm, respectively. A steel pellet-mold was used to compress the samples at a regular cylindrical shape with the velocity of 5 mm/min to the desired final applied compressive pressure. The mold was then held for 3 min at final displacement for the specified relaxation and cohesion. More details on the densification unit and the test procedure are referred to the previous report (Hu et al., 2015).

Before pyrolyzed bio-char was compressed, lignin and bio-char were mixed sufficiently. Then water was added into the solid mixture and followed by the thoroughly stir. The mass ratio of lignin and bio-char was 1:10, and water content was altered to find the optimum water adding condition. In each run, 3 g of bio-char powder, along with proportional amounts of lignin and water, was filled into the mold cylinder to make a single pellet of 20 mm in diameter and 12–20 mm in height. The woody shavings derived bio-chars pyrolyzed at different temperatures were named as T-char, and the compacted pellets were referred as T-pellet, where T indicates the pyrolysis temperature. Firstly, different compaction conditions of pressure (32–224 MPa) and water content (0–40%) were applied to investigate the optimal process conditions for the pelletization of bio-char. And then compaction of bio-chars derived from different pyrolysis temperatures (250–650 °C) were carried out to explore the effect of pyrolysis temperature on the qualities of bio-char pellets.

2.4. Qualities of bio-char pellets

Considering that density, hardness and moisture uptake rate are the most important properties of pellets to be considered in terms of the logistics treatment efficiency and the upgrading application ability (Peng et al., 2013a), the quality of the bio-char pellets was evaluated in terms of volume density, compressive strength, moisture adsorption properties and energy consumption during the compaction process in this study.

The volume density was measured based on the mass, height, and diameter of the pellets after compaction. Compressive strength was analyzed in the universal material testing machine unit (CMT5205, MTS, China) with a cylinder metal rod (diameter of 5 mm). After one week of storage at 25 °C and relative humidity of 30%, the testing was carried out to show the strength after the pellets had been stored. The compressive force applied was perpendicular to the cylindrical axis of pellets. The rod was dropped at a speed of 2 mm/min until each pellet started to break or fracture. The maximum force at which each sample could withstand before falling apart was recorded to calculate the ultimate compressive strength (Hu et al., 2015; Kambo and Dutta, 2014;

Nielsen et al., 2009). The moisture adsorption behavior of the pellets derived from different bio-chars were measured using a humidity equipment (HWS-150, Sumsung Laboratory Instrument Company Ltd., China) at a constant temperature of 30 °C and relative humidity of 70%. The pellets were dried at 105 °C for 24 h before testing, and subsequently placed in the incubator for water adsorption. The mass of the pellets was measured every 30 min for the first 4 h and followed by every 120 min until the mass reached constant. The energy consumption was obtained by integrating the force–displacement curve during compaction process. Each experiment run was performed in triplicate and error bars were used to show the deviation of each value.

Simultaneously, scanning electron microscopy (SEM) was carried out to study the bonding performance by observing the cementation of the surface. Before SEM analysis, the samples were dried at 105 °C for 24 h. A thin layer was carefully cut off from the surface of the pellet using a surgical blade. Then the underside of the intact surface layer was attached to a metal stub with conductive carbon paste. The top side of the surface layer was sputter coated with gold for 300 s in a sputter coater (SCD 050, Bal-Tec, Liechtenstein). Finally, SEM images were recorded using the scanning electron microscope (Quanta 200, FEI Company, Netherlands) operating at 20 kV. Multiple images were observed for each pellet and the best representative image was chosen for each pellet.

3. Results and discussion

3.1. Optimization of process conditions for pelletization of bio-char

3.1.1. Effect of pressure

The effect of compressive pressure on volume density, compressive strength and energy consumption in pelletization of bio-char and lignin mixture is shown in Fig. 1. In this study, the pressure applied ranged from 32 to 224 MPa when bio-char derived pyrolysis temperature, water content and lignin content were controlled at 450 °C, 20% and 10%, respectively. As shown in Fig. 1, the volume density of bio-char pellets varied from 643.32 to 700.35 kg/m^3 at applied pressures of 32–224 MPa. And it was increased linearly when the pressure was less than 128 MPa and subsequently changed mildly when the applied pressure exceeded 128 MPa. Simultaneously, the compressive strength initially increased with the rising pressure, and a subsequent decrease was occurred in strength for pressure above 128 MPa. Energy consumption increased approximately linearly with the increased applied pressure. The pellet formed at 128 MPa exhibited the greatest strength (0.85 MPa) and a relative high density of 693.26 kg/m^3, indicating that higher pressure brings about denser pellets with less voids and higher volume density, which benefited for the transportation and handling processes. And the highest compressive strength in 128 MPa showed the best resistance of pellets to breakage or damage, which would result in cost reductions during logistics treatment.

It is accepted that high pressure brings about better connection of the particles and therefore reduces the gaps and voids between the material particles (Tumuluru et al., 2011; Stelte et al., 2011a). A higher volume density indicates a smaller percentage of internal voids (gaps) and the improved cohesive character of the pellets, which relates to the compressive strength. Accordingly, in this study, higher pressure decreased the volume of pellets and offered better bonding opportunity which formed denser pellets and enhanced the compressive strength at pressures lower than 128 MPa, but no obvious influence on the volume density and the decrease of compressive strength occurred with a further increase in the pressure. It seems therefore reasonable that the pressure of 128 MPa is likely a threshold for volume density and compressive strength. The change trend of volume density and compressive strength of pellets are different with the pressure below and above 128 MPa. Since with the recalcitrant nature of bio-char particles, the further increase of pressure means the approximate of the limit and cannot result in a desired higher volume density and better compressive strength in this study. Yaman et al. (2000) declared that unwanted fractures occurred when the load applied exceeding the optimum briquetting pressure. The "sudden dilation" of pellets at pressure exceeding 128 MPa reduced the compressive strength.

Pressure is an important factor for pelletization in the woody pellets industry. It is a common and direct method to increase the molecular connection and promote the coherence of the adjacent particles. However, the attempt to increase the pressure excessively in an effort to elevate the volume density and promote the strength of woody char pellets is futile. What is more, this practice increases the consumption of energy. In the present study, a compressive pressure of 128 MPa was indicated as the optimal briquetting pressure, resulting in considerable volume density and the highest compressive strength.

3.1.2. Effect of water content

Fig. 2 shows the effect of water content on the pellet characteristics at a pelletizing pressure of 128 MPa, lignin content of 10%, and the bio-char derived pyrolysis temperature of 450 °C. It needs to be pointed out that with less than 15% water content, the resulted pellets were so weak that they could not be ejected from the mold after densification. When the water content was 15%, the bio-char particles formed into pellets successfully, but they

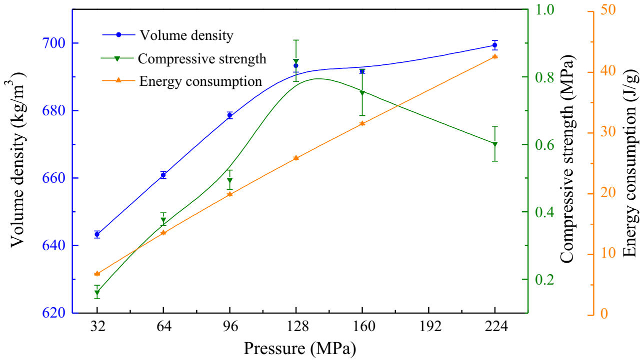

Fig. 1. The effect of pressure on the qualities of woody char pellets (bio-char obtained at 450 °C, densified with 20% water and 10% lignin addition).

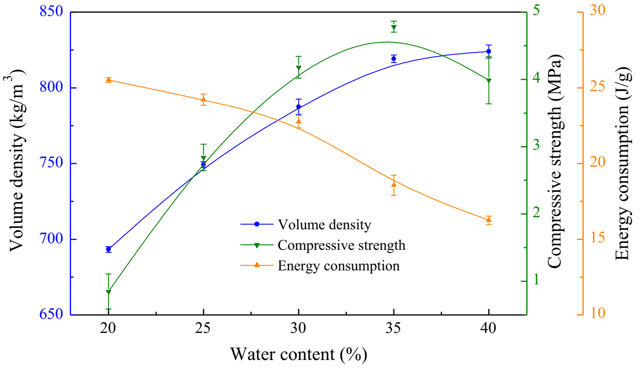

Fig. 2. The effect of water addition content on the qualities of woody char pellets (450 °C bio-char with pressure of 128 MPa and lignin addition content of 10%).

fractured easily and the strength of the pellets could therefore not be measured. Consequently, the water content showed here ranges from 20% to 40%. From Fig. 2, it can be observed that the compressive strength initially increased from 0.85 to 4.78 MPa, with the water content increasing straightly and got the maximum value at water content of 35%, then it decreased. The volume density of pellets also increased linearly prior to 35% water content, and was stable at approximately 820 kg/m^3 when the added water content was 35–40%. The energy consumption used for shaping the bio-char into pellets decreased from 25.51 to 16.25 J/g when more water was added, corresponding with the water content changing from 20% to 40%.

The addition of water into the bio-char during the densification process can act as a lubricant and therefore reduce the frictional resistance between particles and densification equipment (Han et al., 2013). The increased water content initially leads to an increase in briquette strength due to the enhanced van der Waal's forces by increasing the contact area of the particles, promoted solid bridge formation and developed capillary binding pressure (Tumuluru et al., 2011). Therefore, a minimum amount of water is needed for the curing of formed particles to supply enough interfacial contact and develop the coherence force (Jiang et al., 2014; Serrano et al., 2011). In this study, it was clearly shown that a minimum water content of 20% was needed to form woody bio-char pellets with 10% of lignin at the pressure of 128 MPa. While the superfluous water increases the compression resistance and the pellets formed are semi-solid, which would increase the handling and treatment costs. Densification at optimal water content could result in an enhanced hydrogen bond and improved bonding character. Furthermore, it is assumed that at the optimal water content, multilayer water molecules transformed into monolayer water molecules at the pellet surface (Han et al., 2013). However, water content exceeding 35% would lead to relative sliding between the particles, consequently destroying the monolayer structure and reducing the interfacial bonding force (Jiang et al., 2014). This is assumed the reason for the decreased compressive strength at 40% water content, as observed in Fig. 2.

3.2. Pelletization of bio-chars derived from different pyrolysis temperatures

Fig. 3 shows the volume density, compressive strength and energy consumption of the bio-char pellets as a function of pyrolysis temperature at the densification condition of 128 MPa, water addition content of 30% or 35% and lignin content of 10%. As seen in Fig. 3a, the volume density of 250-pellet was 881.17 kg/m^3 with the water addition content of 35%, and it was reduced with the pyrolysis temperature increased from 250 to 450 °C. However, the density of the pellets increased significantly, probably from 819.15 to 1105.28 kg/m^3 at 35% water content, when the temperature was further increased from 450 to 650 °C. Compressive strength was also decrease initially and subsequently increase with the increasing temperature, reaching a lowest point at the pyrolysis temperature of 350 °C (3.07 MPa for 35% water content). It is noteworthy that the compressive strength of 250-pellet was higher than that of 350-pellet and 450-pellet, but much less than that of 550-pellet and 650-pellet, as indicated in Fig. 3b. Meanwhile, energy consumption during compacting process initially increased with the increasing temperature from 250 to 450 °C, and then decreased when the temperature exceeded 450 °C, as shown in Fig. 3c. A similar trend was observed with the water content at 30% and 35% for the density, strength and energy consumption of bio-char pellets, indicating that compared with water content, the pyrolysis temperature (or raw bio-char materials) had a more pronounced effect on the properties of the resultant pellets.

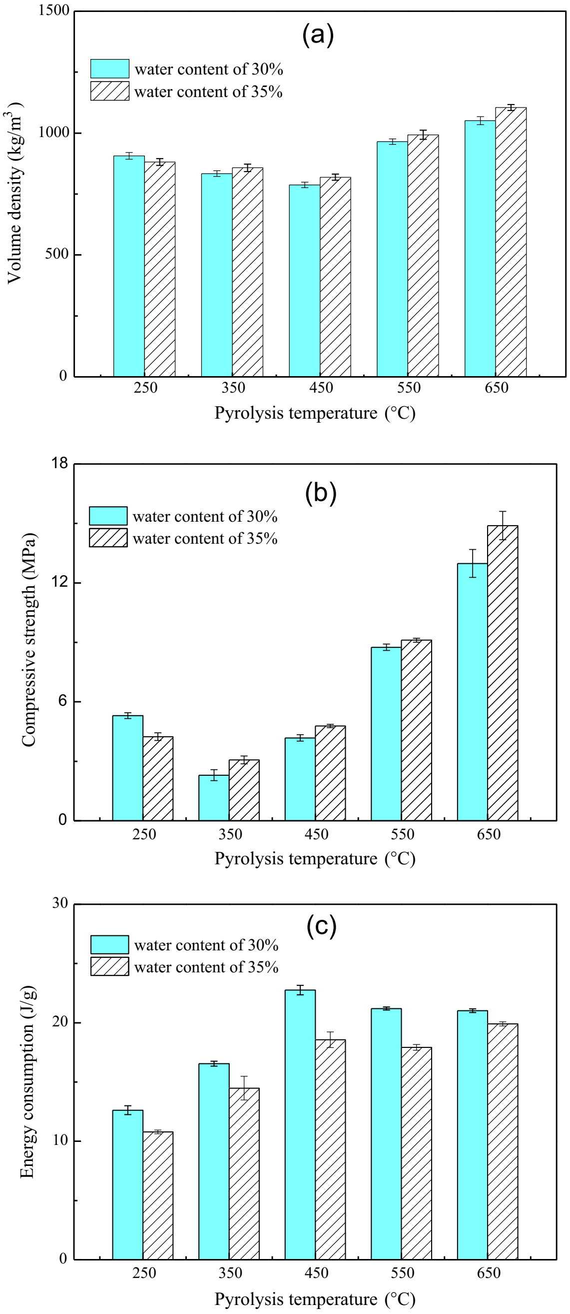

Fig. 3. The qualities of bio-char pellets compacted from bio-chars pyrolysis at different temperatures: (a) volume density, (b) compressive strength, and (c) energy consumption. (Pelletizing pressure of 128 MPa, lignin content of 10% and water addition content of 30% or 35%).

The moisture adsorption properties of the various bio-char pellets were measured in a humidity chamber with 70% relative humidity at 30 °C over 26 h. Fig. 4 plotted the moisture uptake rate of bio-char pellets formed at 128 MPa, 10% lignin and 35% water addition content with bio-chars obtained at pyrolysis temperatures of 250–650 °C. It clearly showed that all the pellets reached moisture saturation in 20 h. And 250-pellet had the highest saturated moisture uptake content of about 12 wt.%. While no significant difference was observed among the other pellets, given the saturated moisture uptake content between 10.26 and 11.14 wt. %, as shown in Fig. 4. Compared with the moisture adsorption of raw woody shavings and bio-char particles showed in Table 1,

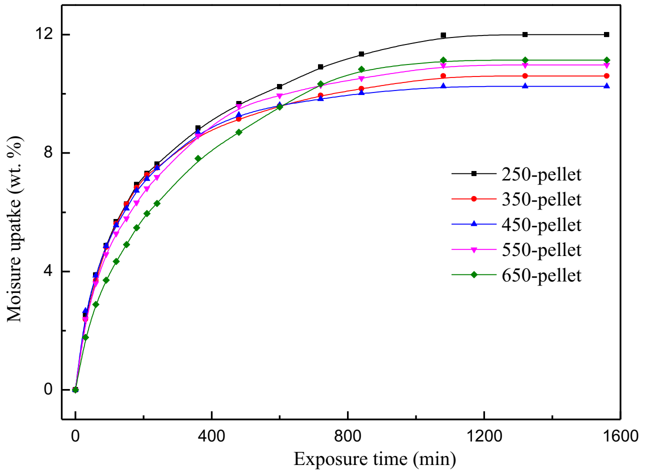

Fig. 4. Moisture uptake rate of the bio-char pellets formed with the conditions of 128 MPa, 10% lignin and 35% water addition content, at a relative humidity of 70% and a temperature of 30 °C.

the saturated moisture adsorption content of raw woody shavings was 15.43 wt.%, and bio-char and its derived pellets obviously showed superior hydrophobicity than the raw biomass as pointed out by former studies (Gray et al., 2014). Additionally, more moisture adsorption content was absorbed by bio-char pellets in comparison with the corresponding bio-char particles at 30 °C and 70% relative humidity, indicating that densification improved the moisture adsorption ability of bio-char, which maybe due to the rigid structure of pellets and the hydrophilic oxygen-containing functional groups introduced by lignin (Hu et al., 2015).

The superior quality of bio-char pellets was available at appropriate thermal treatment temperature under the stated densification conditions. The physicochemical characteristics of the densification raw char materials, produced at different pyrolysis temperatures, were the main contribution factors in the compacting results as explained in detail below. In this study, higher temperature brought about lower solid char yield but of superior quality. Moreover, bio-char with a lower sulfur content, higher carbon content and higher calorific value was obtained at the higher temperature, as shown in Table 1. As seen in Fig. 3, the char yield was 21.21% at pyrolysis temperature of 550 °C, while the 550-pellet had the density of 965.07–992.94 kg/m^3 and compressive strength of 8.75–9.11 MPa with the energy consumption being 17.92–21.20 J/g during the compacting process. The char yield of 650-char was 19.17%, while the corresponding qualities of volume density, compressive strength and energy consumption were 1050.73–1105.28 kg/m^3, 12.98–14.89 MPa and 19.90–21.02 J/g, respectively. Additionally, the saturated moisture adsorption content was largely reduced compared with the raw biomass, which is advantageous for long distance transportation and storage treatment. Accordingly, in terms of quality upgrading, the enhanced volume and energy density, elevated compressive strength, considerable saving on energy consumption, improved moisture adsorption properties and the lower sulfur release of the bio-char pellets obtained at the thermal treatment temperature of 550–650 °C, which would obviously be of benefit for subsequent applications. Further study on the thermal treatment methods and high value-added use of the upgraded pellets are needed to develop technology suitable for the industrial conversion of woody biomass.

3.3. Bonding mechanism

The bonding mechanism of the bio-char pellets is illustrated by the SEM images of the surfaces of the pellets since they provided a insight into the magnified appearance to understand the failure mechanisms, inter-particle adhesion and the strength of pellets (Kaliyan and Morey, 2010; Reza et al., 2014; Stelte et al., 2011b). Fig. S2 in the Supplementary data shows the SEM images (magnification of 600×) of pellets prepared with bio-chars derived from different pyrolysis temperatures, at the pressure of 128 MPa, lignin content of 10% and water addition content of 35%. Significant differences can be seen in the particle sizes of the pellets formed at temperatures from 250 to 650 °C. The gradual reduction in particle size with increasing temperature was consistent with the results shown in Table 1. The 250-pellet, with large particles, apparently maintained the fiber structure of the plants (Fig. S2a), which formed by bio-char with slight thermal cracking (torrefaction) at relative low temperature. The cross and intertwined structure and the elasticoplastic softness of such an immature char component enhanced the mechanical interlock of 250-pellet. Since solid lignin bridge is a network polymer and went through softening and coalescing during densification process as a function of bonding, which was different from the connected bio-char particles. The soft and transition of lignin into solid bridges at the surface of 350-pellet and 450-pellet, which obviously promoted their aggregation and formation during the densification process. However, the inter-particle gaps and voids showed in Fig. S2b and c indicated the poor adhesive quality of both 350-pellet and 450-pellet, which destroyed the strength and reduced their qualities as measured before. The homogeneousness, orderliness and smooth surfaces with the solid bridges of softened lignin embedded in the fine particles of 550-pellet and 650-pellet, showed in Fig. S2d and e, indicate the dense and rigid properties. And a closer comparison found that 650-pellet has a finer and denser surface than 550-pellet, which speculated higher volume density, better mechanical strength and lower energy consumption of 650-pellet as shown in Fig. 3.

It is believed that the fiber structure, lipid extractive and lignin promote the adhesion of bio-char particles as a rigidifying and bulking agent (Tumuluru et al., 2011), which was maintained at a lower thermal temperature. On the other hand, the hydrophilic functional groups existing in 250-char (mainly hydroxyl vibration at 3200–3700 cm^{-1}, shown in Fig. S3 in the Supplementary data) provided the medium for forming hydrogen bond when 250-char was compacted with water. This could be the reason for the relative good quality of 250-pellet. Whereas, the finer granularity of bio-chars produced through pyrolysis at higher temperatures (550-char and 650-char), speculated to form dense pellets due to the lack of empty spaces and interspaces at the pressure of 128 MPa. The carbonized, brittle and fine bio-char particles derived from pyrolysis in high temperature may promote the formation of the pellets with the densification of water and lignin. Lignin, a random network polymer with the linkages based on phenyl propane units, was studied to have a glass transition behavior in the temperature range of 137–157 °C (Reza et al., 2012). The presence of water during the compacting process decreased the glass transition temperature of lignin. And the lignin binder played a significant role in the bio-char densification process. It is speculated that during the densification of bio-char with 35% water content and 128 MPa pressure, lignin transformed and formed into solid bridges between particles, which enhanced the compressive strength of bio-char pellets. The irregularity rigid particles, moderate mean particle size and less hydrophilic functional groups of 450-char could be the explanation for the low volume density, inferior compressive strength and high energy consumption when densification it into pellets. Consequently, in this study, it concluded that hydrophilic functional groups, particle size and binder are the main factors that contribute to the quality of bio-char pellets because of their relation to hydrogen bond, gaps and voids, and adherence force during densification, respectively.

4. Conclusions

In this study, the quality of pellets made from woody shavings char was investigated. Both the volume density and compressive strength of pellets decreased initially and subsequently increased, while energy consumption during compacting process increased first and then reduced, with the increase of pyrolysis temperature. The main factors contributing to the cohesion of bio-chars at the different temperatures were hydrophilic functional groups, particle size and binder. Bio-char pellets formed at the compressive pressure of 128 MPa, water content of 35% and pyrolysis temperature of 550–650 °C, exhibited superior properties to be handled and used in the following application process.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2015.10.077.

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