

## Effects of Temperature and Heating Rate on the Characteristics of Molded Bio-char

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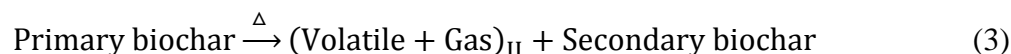
A slow pyrolysis of pinewood was investigated in this paper. Through the briquette process, the pinewood sawdust becomes molded biomass. The molded bio-char was produced from molded biomass with different pyrolysis factors, and the bio-char's heating value, char yield rates, and physicochemical and morphological properties were investigated. Molded bio-char's characteristics depended principally on pyrolysis factors. At low temperature (400 °C), the char yield rate was positively correlated to the heating rate. But at higher temperatures (500 to 700 °C), the char yield rates decreased as heating rates increased. As pyrolysis temperature increased from 400 to 700 °C, the following increased in molded bio-char: fixed-carbon content, percentage carbon, heating value, ash content, as well as surface areas. And its pore structure, graphite degree, and polymerization degree achieved a higher level. Compared with pulverized bio-char, the molded bio-char had a higher char yield rate, ash content, graphite degree, and structure ordering. The molded bio-char obtained from a low temperature (400 °C) and high heating rate (15 °C/min) can be used as a reducing agent, the molded bio-char from 600 °C is recommend as an activated carbon precursor, and the molded bio-chars from low temperature (400 °C) have a higher efficiency as fuel.

*Keywords:* Biomass; Bio-char; Physicochemical; Morphological

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### INTRODUCTION

Biomass, the precursor of fossil feedstock, is a renewable substitution for fossil fuels (Collard and Blin 2014). It can be converted into fuels and chemical materials by biological (fermentation and anaerobic digestion) or thermochemical (gasification, pyrolysis, and liquefaction) processes. Of these conversion processes, pyrolysis has the characteristics of higher energy recovery and lower resources consumption, thus making it a self-sufficient process (Dilek 2013). The mechanisms of biomass pyrolysis are complex; they are expressed by the three main steps below (Ayhan 2004):



In the initial period, only moisture and a small amount of volatiles are lost. As the temperature increases, the primary bio-char is generated, which is accompanied by the release of volatiles and gases. Finally, the primary bio-char decomposes to secondary bio-char, volatiles, and gases.

Bio-char is the solid product from pyrolysis, and it includes char, ash, and unreacted biomass. It is a carbon-rich product that has been used in many fields. As a fuel, bio-char has the characteristics of high heating value and low emissions, and it is an ideal substitute for solid fossil fuels. As a porous material, it can be used in water purification or as the precursor of activated carbon. As a reducing agent, it has been widely applied in metallurgy. Recently, bio-char has been attracting more interest for carbon sequestration and soil amendment.

Asia has the largest rural population and the largest quantity of biomass residues (Werther *et al.* 2000). China produces large amounts of the biomass residues every year, and residue disposal is a big problem in China and other Asian countries. With poor combustibility, low heating value, and high moisture content, most residues cannot be directly used as bio-fuel (Wang *et al.* 1993); thus, the improving of biomass utilization has become a top priority. Briquette technologies make bio-energy more efficient. In this process, biomass residues are molded with specific pressure and temperature, such that they have higher density and higher energy per unit.

The briquette process can be classified into cold briquetting and preheat briquetting. According to the literature (Wang *et al.* 1993), lignin would melt in the range 200 to 300 °C, and its viscosity would be greatly increased, making it a natural binder. Thus, in the briquette process, the preheated biomass would combine much more closely with the melting lignin. That is to say, the preheat briquetting would lead to production of molded biomass having higher density as well as better quality.

With improved combustibility, molded biomass can be used for household cooking or heating, and it can be transported and stored easily (Jiang and He 2007). Molded biomass has the potential to meet the additional energy demands of urban and industrial sectors, thereby relieving the biomass residue problem and contributing to economic development. (Grover *et al.* 1994)

Pinewood sawdust is a common residue produced in the forestry and furniture industry. After processing, sawdust is usually discarded, which is a waste of resources. Bio-char has been researched via sawdust pyrolysis (Ronsse *et al.* 2013; Huff *et al.* 2014), but sawdust briquetting has not been thoroughly investigated. The aim of this work is to reveal how the pyrolysis factors and briquette process would affect the characteristics of bio-char, and make discussions on the applications of molded bio-char.

## EXPERIMENTAL

### Materials

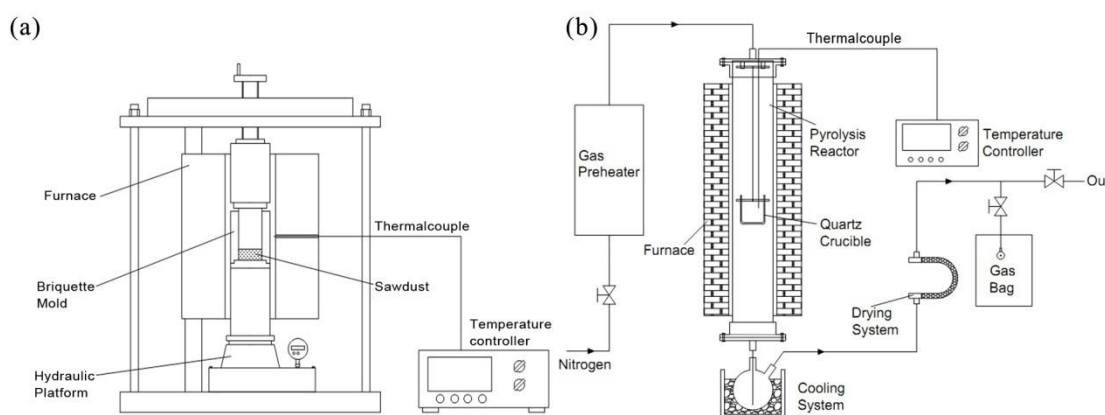
The pinewood sawdust was collected from the Gao Rong wood processing factory, Kunming, Yunnan, China. After air-drying, the sawdust was crushed into fine particles. The particles were screened to recover between 0.15 and 0.18 mm. All materials were then dried in an oven for 12 h at 105 °C.

## Briquette Formation

Each experiment was performed with 3 g of sawdust. The briquette mold (Fig. 1(a)) was operated at 200 °C with a heating rate of 10 °C/min. At the final temperature, the hydraulic platform exerted a 5 MPa pressure, which was sustained for 10 min.

## Pyrolysis

The pyrolysis experimental set-up was composed of a vertical furnace with a pyrolysis reactor (quartz, 1300 mm length × 60 mm width, Jincheng Quartz Products Co. Ltd., Lianyungang, China), carrier gas feeding system (N<sub>2</sub>, 99.5%), hanging system, cooling system, and gas collecting system (Fig. 1(b)). The raw material was separated into molded and pulverized biomass, which was loaded in the quartz crucible (40 mm length × 40 mm width). The pyrolysis temperature for molded biomass was set at 400, 500, 600, and 700 °C, with a heating rate of 5, 10, and 15 °C/min. For pulverized biomass, the temperature was set at 400, 500, 600, and 700 °C with a heating rate of 10 °C/min. Each experiment consumed 3 pieces (approximately 9 g) of molded biomass or 5 g of pulverized sawdust. Prior to each experiment, the reactor was purged with N<sub>2</sub> (160 mL/min) for 30 min to provide an inert atmosphere. The bio-char product was named M10-600 for molded bio-char produced at 600 °C with the heating rate of 10 °C/min; the pulverized product made in the same conditions (600 °C and 10 °C/min) was named P10-600.



**Fig. 1.** The experimental set up for (a) briquette and (b) pyrolysis

The term “char” represents the effective components in a bio-char product. The char yield rate was calculated by,

$$\text{Char yield rate(\%)} = \frac{M_{\text{dry,c}} - M_{\text{ash,c}}}{M_{\text{dry,b}} - M_{\text{ash,b}}} \quad (4)$$

where  $M_{\text{dry,c}}$  is the mass of dry bio-char,  $M_{\text{ash,c}}$  is the mass of ash in bio-char,  $M_{\text{dry,b}}$  is the mass of dry raw biomass, and  $M_{\text{ash,b}}$  is the mass of ash in raw biomass. (Ronsse *et al.* 2013)

## Characterizations

The proximate analysis, higher heating value determination, and ultimate analysis of raw material were investigated.

The ash and volatile content were determined according to the ASTM 3174 (2004) and ASTM 3175 (2011) standards, respectively. The fixed carbon content was determined by difference.

The higher heating values (HHV) of raw material were determined by a Parr 6200 calorimeter (Moline, USA).

The ultimate analysis was performed on an EA-2400 elemental analyzer (Perkin Elmer, Waltham, USA), CHNS mode, with the furnace temperature at 975 °C. The oxygen content was determined by difference.

The bio-char characterization was performed by various analyses; these included proximate analysis, higher heating value determination, ultimate analyses, Fourier transform infrared spectroscopy (FT-IR), x-ray diffraction (XRD), BET surface areas, and scanning electron microscopy (SEM).

The proximate, higher heating value, and ultimate analyses were determined as shown above.

FT-IR analysis was performed on a Bruker VERTEX-70 spectrometer (Karlsruhe, Germany) in the near IR region (wavenumber: 4000 to 600  $\text{cm}^{-1}$ ) and a spectral resolution of 4  $\text{cm}^{-1}$ . The sample was held in a KBr salt plate in a micro compression cell. The software OPUS 6.5 (Bruker, Karlsruhe, Germany) was used for baseline corrections. The bands due to the atmospheric contributions of  $\text{CO}_2$  have been subtracted.

XRD analyses were performed on a D/max-TTRIII diffractometer (Rigaku, Tokyo, Japan) with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ), an operating voltage of 40 kV, and a current of 40 mA. The diffraction angle ( $2\theta$ ) was scanned from 10 ° to 90 °.

The BET surface areas were determined by a nitrogen adsorption method using a CHEM BET-3000 instrument (Quantachrome, Boynton Beach, USA).

For SEM, bio-char was ground into fine particles for better viewing. All samples were observed on a Vega3 scanning electron microscope (Tescan, Brno, Czech Republic), with high voltage at 30 kV and magnification at 2500 x and 1000 x.

## ANALYSES AND RESULTS

### Briquette Analysis

The proximate and ultimate analyses results of raw materials are shown in Table 1. It can be seen that the pinewood sawdust is a kind of biomass residue with high volatile content, low ash content, and relatively low heating value. There were just few differences between molded and untreated sawdust, suggesting that the briquette process only conferred physical changes. Considering the conditions of briquette process, these differences could be caused by the loss of a minor portion of hemicelluloses and the melting of lignin.

**Table 1.** Proximate and Ultimate Analyses Results of Raw Materials

	Proximate Analysis (wt.%, Dry)			HHV (MJ/kg)	Ultimate Analysis (wt.%, Dry)				
	A	V	FC <sup>a</sup>		C	H	N	S	O <sup>a</sup>
Molded	0.45	83.22	16.33	18.02	48.44	6.28	0.14	0.60	44.09
Sawdust	0.35	84.01	15.64	17.75	47.73	6.52	0.36	0.64	44.42

<sup>a</sup>By difference (O (%) = 100% - A (%) - C (%) - H (%) - N (%) - S (%))  
A: Ash; V: Volatile matter; FC: Fixed carbon; HHV: Higher heating value;  
C: Carbon; H: Hydrogen; N: Nitrogen; S: Sulfur; O: Oxygen

At 200 to 300 °C, lignin melts and becomes viscous, which makes it a natural binder. With the pressure from hydraulic platform, the biomass became tight and compact, and it had a much higher energy per unit. Due to the deformation of lignin, the briquette process would change the structure of molded biomass.

### Proximate Analysis

The proximate analysis results of the bio-char produced at different pyrolysis temperatures and heating rates are shown in Table 2. The volatile matter of molded bio-char decreased with increasing pyrolysis temperature from 400 to 700 °C. It decreased from 33.08% to 10.11%, 34.47% to 9.11%, and 35.04% to 8.78%, with the heating rates of 5, 10, and 15 °C/min respectively. Volatiles are released by the breaking of chemical bonds. Increased temperature supplies more energy to the system, resulting in more broken bonds. Compared with the molded bio-char produced at the same temperature, the volatile content decreased while the heating rate increased, except for 400 °C. The high volatile content of bio-char suggests that the biomass had not undergone complete transition to char, and the biomass was only partially pyrolysed (Gozde *et al.* 2011). In that condition, a lower heating rate would require the biomass to spend a much longer time to achieve 400 °C, which means that it would stay in the higher temperature atmosphere for a longer time. Thus the biomass would have a more complete transition to char and release more volatiles. Thus, M5-400 bio-char has a lower volatile content than M10-400 and M15-400 (Huang *et al.* 2014). The pulverized and molded bio-char showed similar properties.

**Table 2.** Proximate Analysis (Dry Basis), Char Yield Rate, and Higher Heating Value of Bio-char

Species	Volatile Matter (wt.%)	Fixed Carbon <sup>a</sup> (wt.%)	Ash Content (wt.%)	Char Yield Rate (wt.%)	Higher Heating Value (MJ/kg)
M5-400	33.08	65.10	1.82	30.47	30.75
M5-500	20.49	76.83	2.68	27.46	31.94
M5-600	13.80	83.01	3.19	26.33	32.24
M5-700	10.11	86.37	3.52	25.01	33.29
M10-400	34.47	63.09	2.44	30.71	30.33
M10-500	20.31	76.80	2.89	26.59	31.79
M10-600	12.48	84.07	3.45	24.38	32.59
M10-700	9.11	87.06	3.83	23.21	33.19
M15-400	35.04	61.78	3.18	31.09	30.14
M15-500	18.96	77.42	3.62	24.80	32.11
M15-600	11.56	84.51	3.93	22.62	32.76
M15-700	8.78	87.09	4.13	21.74	33.67
P10-400	33.97	64.40	1.63	30.46	30.36
P10-500	20.09	78.21	1.70	25.02	32.24
P10-600	12.16	86.08	1.76	23.85	34.30
P10-700	9.19	88.89	1.92	22.79	34.97

<sup>a</sup> By difference (Fixed Carbon (%) = 100% – Ash (%) – Volatile (%))

The ash content measures the non-volatile and non-combustible components. As the temperature increased from 400 to 700 °C, the ash content of molded bio-char increased

separately from 1.82%, 2.44%, and 3.18% to 3.52%, 3.83% and 4.13%, respectively, for heating rate at 5, 10, and 15 °C/min. Other species of bio-char show the same trend (Ronsse *et al.* 2013; Guo and Bi 2015), but different kinds of biomass are quite different in ash content. The ash content of pulverized bio-char was much lower than that in the molded form, which is similar to pulverized sawdust bio-char (DeSisto *et al.* 2010; Amutio *et al.* 2012; Ronsse *et al.* 2013). In briquette process, the volatiles in lignin and hemicelluloses would become slightly reduced. Also, the structural changes in briquette would probably bring molded bio-char some materials after pyrolysis, such as graphite, which cannot be fully burnt at 950 °C. Thus, it was inferred that the ash content of molded bio-char increased due to the changes in composition ratio and structure of the molded biomass.

As the pyrolysis temperature increased from 400 to 700 °C, the fixed carbon content of molded bio-char increased; at 700 °C, the fixed carbon content ranged from 86.37% to 87.09%. The pulverized bio-char had higher fixed carbon content (88.89% at 700 °C). The fine particle size let the heat transfer much easily, thus making the pyrolysis of pulverized bio-char more complete. In other studies (DeSisto *et al.* 2010; Amutio *et al.* 2012; Ronsse *et al.* 2013), the fixed carbon content showed the same trend with slightly different values. These analyses showed that pyrolysis is an impurity removal process. It breaks weak bonds to release volatiles and gases, and subsequent rearrangement reactions strengthen the carbon matrix, resulting in a bio-char with high fixed carbon content and low volatile content.

### Char Yield Rate

The char yield rates decreased with increasing temperatures, whether in molded or pulverized bio-char (Table 2). For molded bio-char, the char yield rate decreased from 30.47% to 25.01%, 30.71% to 23.21%, and 31.09% to 21.74% for heating at 5, 10, and 15 °C/min, respectively. Higher temperature releases more volatiles, thus making char yield lower. The heating rates had a noticeable effect on the char yield. At a lower temperature (400 °C), the char yield rate was positively correlated to heating rate. From the proximate analysis, the biomass was only partially pyrolysed at 400 °C. A longer reaction time in low heating rate would result in the bio-char more complete. Thus, M5-400 bio-char had a lower char yield rate than M10-400 and M15-400. At higher temperatures (500 to 700 °C), the bio-char were carbonaceous, and the heating rate was negatively correlated to char yield rate. With a low heating rate, weak bonds break, but many others remain stable. The polymer's structure is slightly affected, which favors the rearrangement reactions and the stable carbon matrix would inhibit the release of volatiles, thus resulting in a higher yield of bio-char (Collard and Blin 2014). At a higher heating rate, more bonds break before the rearrangement reactions happen. These results are similar to the research on pinewood pyrolysis (Williams and Besler 1996). The compact structure of molded biomass delays the heat transfer, such that the heating rates are lower than the set values. Hence, the char yield rate of molded bio-char is higher.

### Higher Heating Value

The higher heating value (HHV) measures the potential use of bio-char as fuel (Table 2). From 400 to 700 °C, the HHV of molded bio-char increased from 30.75 to 33.29 MJ/kg with a heating rate of 5 °C/min. With heating at 10 °C/min and 15 °C/min, HHV increased from 30.33 to 33.19 and 30.14 to 33.67 MJ/kg, respectively. The HHV of bio-char increased with pyrolysis temperature but was almost independent of the heating rate. Pulverized bio-char had a somewhat higher HHV, and this could be due to its higher fixed

carbon content, lower ash content and fine particle size. The trends were similar to those in bio-char produced from walnut shells and olive stones (Gonzalez *et al.* 2009; Ronsse *et al.* 2013).

### Ultimate Analysis

Ultimate analysis was performed on bio-char obtained from various pyrolysis temperatures and heating rates (Table 3). As the pyrolysis temperature rose from 400 to 700 °C, the carbon content of the molded bio-char increased from 75.39% to 88.35%, 75.15% to 88.28%, and 77.13% to 89.70% at the heating rates of 5, 10, and 15 °C/min, respectively. The pulverized bio-char carbon content was slightly higher, increasing from 76.89% to 92.06% as the temperature increased from 400 to 700 °C. This result confirmed that the smaller particle size leads to more complete pyrolysis process. For all groups, the hydrogen content, sulfur content, and oxygen content decreased as the temperature rose.

Combined with the proximate analysis, the results showed that the chemical composition of bio-char depends on the temperature. The bio-char at higher temperatures would break more weak chemical bonds and release more volatiles, thus the H, O, and S content decreased. The stable carbon matrix fixes the carbon content, making bio-char a carbon-rich product. From the results, it can be concluded that the heating rates have no obvious effect on bio-char's chemical composition.

The H/C and O/C molar ratios of bio-char gradually decreased with increasing pyrolysis temperatures, which indicated that the bio-char became more aromatic and carbonaceous (Table 3).

**Table 3.** Ultimate Analysis (Dry Basis) results of Bio-char

Species	C (wt.%)	H (wt.%)	N (wt.%)	S (wt.%)	O <sup>a</sup> (wt.%)	O/C Molar Ratio	H/C Molar Ratio
M5-400	75.39	3.78	0.48	0.32	18.22	0.18	0.60
M5-500	81.85	2.99	0.56	0.22	9.71	0.11	0.44
M5-600	86.75	2.16	0.61	0.13	4.41	0.06	0.30
M5-700	88.35	1.46	0.61	0.06	3.57	0.05	0.20
M10-400	75.15	3.96	0.46	0.46	17.54	0.18	0.63
M10-500	84.00	3.22	0.41	0.29	9.21	0.08	0.46
M10-600	84.90	2.18	0.52	0.19	8.78	0.08	0.31
M10-700	88.28	1.36	0.43	0.04	6.08	0.05	0.18
M15-400	77.13	3.64	0.43	0.38	15.26	0.15	0.57
M15-500	82.88	3.03	0.53	0.29	9.65	0.09	0.44
M15-600	87.88	2.12	0.44	0.18	5.45	0.05	0.29
M15-700	89.70	1.31	0.37	0.10	4.40	0.04	0.17
P10-400	76.98	3.76	0.65	0.30	16.69	0.16	0.59
P10-500	84.03	2.99	0.80	0.22	10.28	0.09	0.43
P10-600	90.87	2.29	1.08	0.14	3.87	0.03	0.30
P10-700	92.06	1.89	1.24	0.09	2.81	0.02	0.25

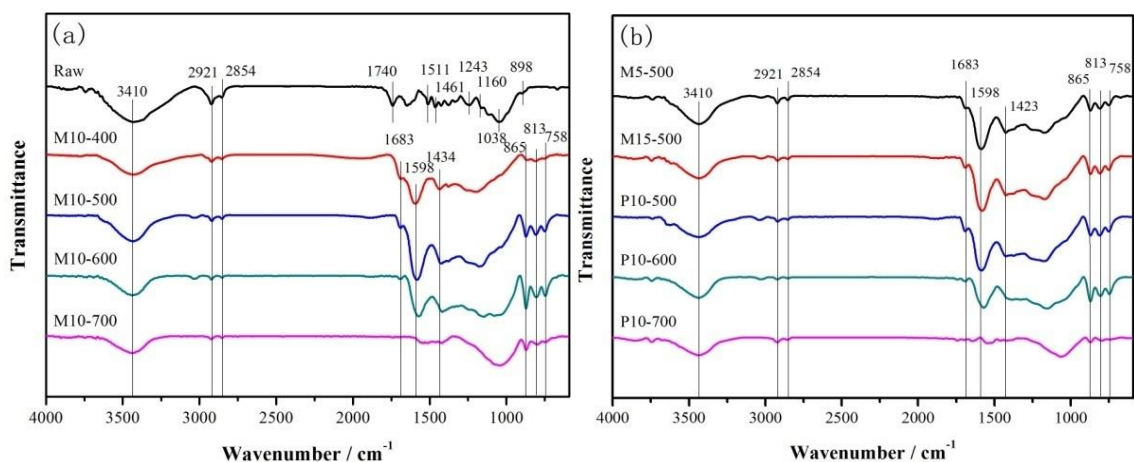
<sup>a</sup> By difference (O (%))=100%-Ash (%)-C (%)-H (%)-N (%)-S (%)

C: Carbon; H: Hydrogen; N: Nitrogen; S: Sulfur; O: Oxygen

Bio-char has a lower N and S contents and higher HHV than most solid fuels (Amutio *et al.* 2012). Considering the CO<sub>2</sub> emission and air pollution problems (SO<sub>x</sub>, NO<sub>x</sub>) of traditional solid fuels, bio-char has the potential to change the present energy structure. With the advancement of bio-char technologies, perhaps it will be regularly used as solid fuel in the future.

### Fourier Transform Infrared Spectrometry

The FT-IR results are shown in Fig. 2. It can be seen that the raw biomass (Fig. 2(a)) show a typically polysaccharide characteristics, for the bands at 1038 and 1115 cm<sup>-1</sup> representing the  $\nu(\text{C-O})$  of ethanol group in pyranose ring. The bands at 1160 and 1243 cm<sup>-1</sup> meant the Alkylaryl ether bonds vibration. The  $\nu(\text{C=C})$  at 1511 cm<sup>-1</sup> suggested the existence of aromatic ring. These illustrated that the existence of cellulose, hemicelluloses and lignin in biomass. The bands at 2921 and 2854 cm<sup>-1</sup> corresponded to the aliphatic  $\nu_{\text{as}}(\text{CH}_2)$  and  $\nu_{\text{s}}(\text{CH}_2)$  stretching vibrations. The band at 3410 cm<sup>-1</sup> corresponded to the  $\nu(\text{O-H})$  in hydroxyl groups; the broader range indicated the existence of OH-ether hydrogen bonds (Fu *et al.* 2009).



**Fig. 2.** FT-IR of (a) raw sawdust and M10 bio-chars and (b) M5-500, M15-500, P10-500, P10-600, and P10-700 bio-chars

Compared with raw sawdust, the  $\nu(\text{C-O})$  absorbance bands at 1115, 1038, and 898 cm<sup>-1</sup>, which were representing the cellulose and hemicelluloses, disappeared in M10-400 bio-char. The  $\nu(\text{C=O})$  at 1740 cm<sup>-1</sup> disappeared, which means that the non-conjugated carbonyl in lignin was decomposed. The 1683 cm<sup>-1</sup> band was located in bio-char, suggesting the existence of conjugated carbonyl groups. The aliphatic  $\nu_{\text{as}}(\text{CH}_2)$  and  $\nu_{\text{s}}(\text{CH}_2)$  stretching vibrations still could be found, but much weaker. A high intensity band at 1598 in bio-char was attributed to the  $\nu(\text{C=C})$  vibration, indicating that the aromatic structures were predominant. The bands 1434 cm<sup>-1</sup> were also caused by  $\nu(\text{C=C})$ . The broad band between 1300 and 1050 cm<sup>-1</sup> in bio-char was caused by the combination and overlapping of various types of  $\nu(\text{C-O})$ , *e.g.*, alcohols, ethers, and esters (Sharma *et al.* 2004). In the bio-char fingerprint region, there were bands at 865, 813, and 758 cm<sup>-1</sup>, which corresponded to aromatic C-H stretching vibrations and adjacent aromatic hydrogen; these bands were not seen in sawdust. The bands at 813 and 758 cm<sup>-1</sup> represented the lower-substitution aromatic structures, which were stronger than the band at 865 cm<sup>-1</sup>. These



results indicated that the bio-char at 400 °C was mainly composed of lower-substitution aromatic structures, and the polymerization was in its initial period (Jiang *et al.* 2005).

At 500 °C, the vibrations at 1598  $\text{cm}^{-1}$  and the fingerprint region were enhanced, corresponding to the increase in aromatic structures. When the pyrolysis temperature rose to 600 °C, the vibration at 1598  $\text{cm}^{-1}$  became weaker than at 400 and 500 °C. Because FT-IR adsorption depends on changes in dipole-moment vibrations, the higher polymerization degree resulted in lower changes in dipole-moment through aromatic ring vibrations, indicating that the decrease in the band at 1598  $\text{cm}^{-1}$  was caused by the increase in polymerization. The vibration at 865  $\text{cm}^{-1}$  was stronger than at 400 °C and 500 °C, which confirmed that the bio-char became more aromatic. Other bands in the fingerprint region were visible, suggesting that there were still many Ar-H and that the polymerization degree was still relatively low.

At 700 °C, the vibration at 865  $\text{cm}^{-1}$  still existed, but other bands in the fingerprint region almost disappeared. The band at 1598  $\text{cm}^{-1}$  declined noticeably. Thus, 700 °C can be seen as a transition temperature for molded bio-char. At this temperature, Ar-H was reduced, the higher-substitution aromatic structures dominated, and the carbon-net structure had a rapid development. As shown in Fig. 2(a), the red-shift happened at 1598 and 1434  $\text{cm}^{-1}$ ; it was inferred that the conjugation effect happened between  $\nu(\text{C}=\text{O})$  and the aromatic structure ( $\text{C}=\text{C}$ ). With increasingly poly-aromatics in bio-char, the conjugation effect was enhanced, resulting in the continuously decreasing in wave numbers and bond energy, which made the chemical groups more stable.

Different heating rates did not produce different functional groups (Fig. 2(b)). Pulverized bio-char showed the same trend, which confirmed that the briquette process did not change the chemical properties of biomass.

### X-Ray Diffraction

The M10 bio-char XRD results are given in Fig. 3(a). The high intensity diffraction peak at  $2\theta=26^\circ$  corresponded to the (002) band of crystalline graphite. With increased temperature, the diffraction peak became more intense, indicating that the graphite structure increased in size and that defects were removed. In addition, its structure ordering improved (Zuo *et al.* 2015).

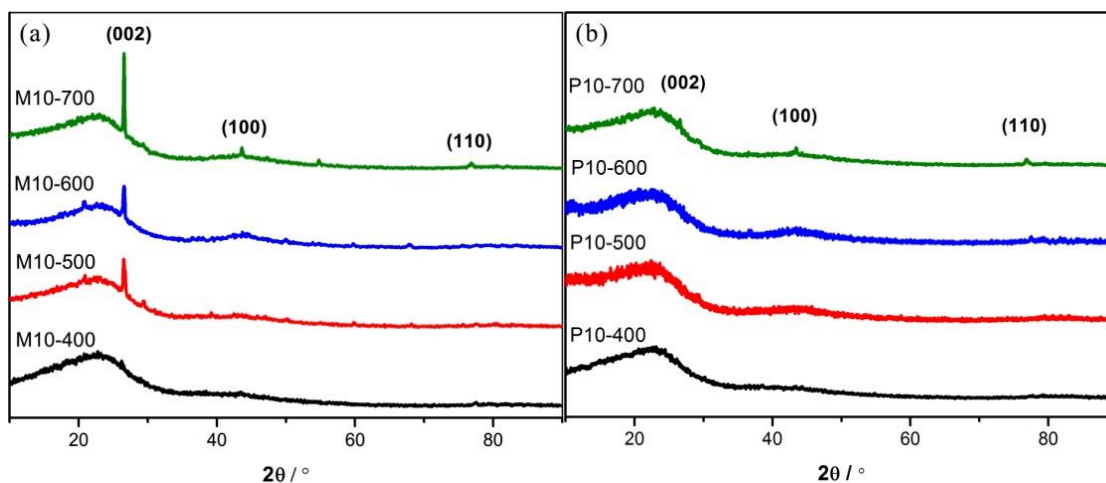


Fig. 3. XRD of (a) M10 bio-char (b) P10 bio-char

At 700 °C, there were weak diffraction peaks at around  $2\theta=43^\circ$  and  $2\theta=78^\circ$ , which corresponded to the (100) and (110) bands. These peaks could represent the growth of graphite crystallite and the increasing three-dimensional crystallite structure, which means that the degree of structure ordering was higher (Zhang *et al.* 2006).

The diffraction peaks of pulverized bio-char were hard to identify compared with the M10 bio-char in the same conditions (Fig. 3(b)). From 400 °C to 600 °C, the diffraction of bio-chars were almost broad peaks with a typically turbostratic structure. At 700 °C, there was very weak peak at around  $2\theta=26^\circ$ ; thus, the bio-char produced at 700 °C had a better graphite crystallite structure than the other pulverized bio-chars. The (100) and (110) bands were present, which means that the structure-ordering became higher. Taken together with the FT-IR results, it can be concluded that the higher temperature leads to a higher degree of polymerization and structure ordering, thus making the bio-char more stable and organized.

In the briquette process, the structural changes of biomass were promoted by the temperature and pressure, resulting in a more organized structure. The molded biomass would develop graphite crystallites more easily during pyrolysis. Compared with the proximate analysis, the higher ash content of molded bio-chars could be caused by the existence of graphite crystallite. The impacts of graphite crystallite structures in bio-char need a further study.

### BET Surface Areas

The BET results of M10 bio-char are given in Table 4. There was an explosive growth in molded bio-char (from 3.1 to 359.1 m<sup>2</sup>/g), suggesting that the bio-char at 400 °C was not porous. As described above, the biomass was only partially pyrolysed at low temperature. The ash, sticky tars, and other macro-molecular substances could block M10-400 bio-char's weak pore structure. At 500 °C, the increasing temperature caused more volatile release, and tars changed from liquid oil to the gaseous phase. In this stage, the bio-char surface areas increased dramatically, indicating that the bio-char became porous. At 600 °C, the bio-char was highly pyrolysed, and the residual volatiles were released, which gave bio-char a highly developed pore structure. When the temperature rose to 700 °C, the surface area of bio-char slightly decreased, suggesting the occurrence of bio-char shrinkage, pore widening, coalescence of neighboring pores, or the melting of ash. Hence, high temperatures were detrimental to the pore structure of molded bio-char.

Compared with other bio-chars (DeSisto *et al.* 2010; Amutio *et al.* 2012), the surface area of molded bio-char was higher, which could be due to molded biomass' high volatile content, low ash content (Table 1), and organized structure.

**Table 4.** BET Surface Areas of M10 Bio-Char

	M10-400	M10-500	M10-600	M10-700
$S_{BET}$ (m <sup>2</sup> /g)	3.1	191.8	359.1	327.2

### Scanning Electron Microscopy

The SEM photomicrographs of M10-400, M10-500, M10-600, M10-700, and P10-700 are shown in Fig. 4. An absence of detectable pores indicated that amounts of volatiles remained in the bio-char at 400 °C (Fig. 4(a)). There were many orderly arranged open

pores over the bio-char surface in Fig. 4(b), (c), and (d). The pores were formed by the release of volatiles. Combined with the  $S_{BET}$  analysis, the porous material with open pores was expected to have a high surface area (Sharma *et al.* 2004). At 500 and 600 °C, bio-char had a relatively flat surface. In the M10-700 photograph (Fig. 4(d)), grooves, widened pores, and ruptures can be found. This observation confirmed the  $S_{BET}$  results, as increased temperature was detrimental to the pore structure. Considering the fragility of bio-char, grooves were formed, and they gave surface a rough appearance. The pulverized bio-char produced at 700 °C (Fig. 4(e)) had a much complex appearance, with more cracks, deeper grooves, and messy distributed pores compared with M10-700 (Fig. 4(f)). Thus, it was inferred that the organized structure of molded biomass caused the pores to be distributed in an orderly manner after pyrolysis. And the complex appearance of surface may have resulted from the fragility and fine particle size of the bio-char.

## SUMMARY AND DISCUSSIONS

Pyrolysis proceeded in three steps (Eq. 1-Eq. 3) as temperature was increased. In the initial period (ambient temperature-240 °C), only moisture and very little volatiles were lost. As the temperature was increased from 240 to 400 °C, the weak bands in hemicelluloses, cellulose, and lignin began to break, such as O-H and C-O, and large amounts of volatiles were released. At the same time, the benzene rings formed. These rings combined together in a polycyclic structure, which favor the rearrangement reactions, and result in a higher stability of the residue (Collard and Blin 2014). Such generated solid residue is bio-char. In this period, the bio-char is called the primary bio-char, which is only partially pyrolysed, and has a higher char yield rate. The bio-char from low temperature pyrolysis, such as M10-400, can be seen as the primary bio-char. In comparison with other M10 bio-chars, the M10-400 bio-char had higher volatile content, higher char yield rate, and higher O/C molar ratio, but lower heating value, lower surface areas and graphite degree, as well as lower polymerization degree. As the temperature increased from 400 to 700 °C, the primary bio-char would decompose to secondary bio-char and volatiles at a very slow rate. The bio-char became more carbonaceous, aromatic, and porous, and its heating value increased. The graphite degree and polymerization degree of bio-char highly improved. But the char yield rate was in a downward trend, for the residual volatile released. 700 °C is the transition temperature for molded bio-char, which had a much higher degree of aromatic condensation as well as higher graphite degree. But the surface areas slightly decrease due to the pore widening or the cracking of pore structure, *etc.*

The heating rates had an essential effect on the char yield rate. At a lower temperature (400 °C), the biomass was only partially pyrolysed, and the char yield rate was positively correlated to heating rate. At higher temperatures (500 to 700 °C), the bio-char was carbonaceous. Thinking of the high cellulose content in biomass (Gani and Naruse 2007), the heating rate has an enormous effect on the pyrolysis of cellulose. The rapid heating of the biomass favors the polymerization of cellulose and the formation of volatiles and suppresses the dehydration to anhydrocellulose and char formation (Ayhan 2004). And considering the rearrangement, reactions are likely to happen at a lower heating rate. Thus, at higher temperatures, the higher heating rate resulted in the lower char yield rate. Seeing the experimental results, the heating rates had very little effect on other characteristics of bio-char.

The molded bio-char was produced from briquette and pyrolysis processes. It had a higher char yield rate, higher graphite degree and much organized pore structure compared with pulverized bio-char. In a briquette forming process, the melting of lignin in fine biomass particles and the high pressure from hydraulic platform would make the structure of molded biomass not only compact but also organized. The molded biomass would be regular shaped after briquette formation, which means that it would have a bigger particle size as well as a higher density and mechanical strength. With compact structure and increased particle size, the heat transfer in molded biomass would be delayed, such that the actual heating rate would be lower than the set heating rate. Thus, the molded bio-char would have a higher char yield rate. With a much organized structure, the molded biomass would result in molded bio-char with organized pore distribution after pyrolysis. And the improvement of graphite degree could also be caused by the organized structure after pyrolysis. As the experimental results showed, the briquette forming process had no obvious effect on the chemical compositions of molded biomass as well as molded bio-char, which means that the briquette process only conferred physical changes. Considering the daily uses, the molded bio-char is more convenient in storage and transportation.

The bio-char produced from different pyrolysis factors would have different characteristics, thus it can be used in different fields.

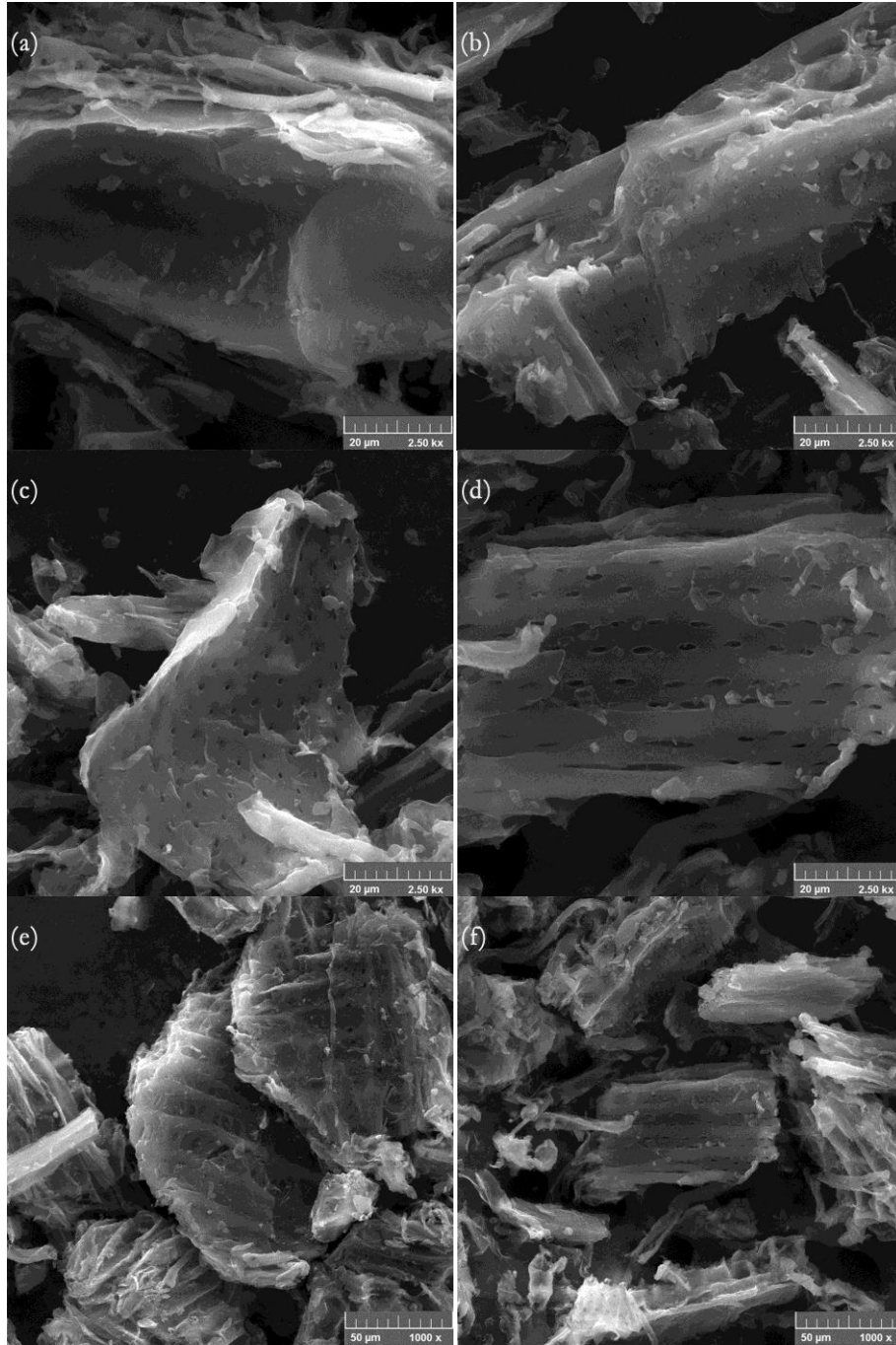
As a reducing agent, it is expected to have a relatively higher mechanical strength and higher reactivity. The quick devolatilization of biomass in rapid pyrolysis favors the formation of char with higher reactivity. Also, the reaction of secondary charring makes the bio-char less reactive (Ayhan 2004). Thus, the molded bio-char with higher heating rate and lower temperature was recommended, such as M15-400.

The bio-char can be used as the precursor of activated carbon when its pore structure and surface areas are appropriate (Ayhan *et al.* 2006). Considering the high temperature is detrimental to the pore structure of bio-char, the molded bio-char produced at 600 °C is more suitable. With orderly distributed open pores and higher surface areas, the molded bio-char from 600 °C is expected to have a highly developed internal pore structure and surface areas after activation. The activated carbon can be used in many applications, such as water purification and harmful substances absorption.

As for fuel, the bio-char can be seen as an ideal substitution for solid fossil fuels. The bio-char has a good combustibility and relatively high heating value. Thinking of the emission problems of SO<sub>x</sub> and NO<sub>x</sub>, the bio-char seems much more environmentally friendly than traditional fuels. Making the comprehensive consideration of char yield rate and heating value, the bio-char from low temperature seems to have the higher performance-price ratio. The molded bio-char from 400 °C has a higher char yield rate and a relatively good heating value. It can produce 9.3 to 9.4 MJ heat from 1 kg biomass per reaction, which is higher than other bio-chars. For the industrialized production of bio-char, the low temperature and higher heating rate seems more efficient, such as M15-400.

Recent years, the bio-char used as a soil amendment has attracted lots of attention. The bio-char produced from higher temperature (>300 °C) presents alkaline, and its alkaline degree increased with the temperature (Dilek 2013; Huff *et al.* 2014). Thus, the bio-char can be used in acidic soil to regulate the acidity of soil. Also, some of the characteristics of bio-char, such as O/C molar ratio would affect the cation exchange capacity in soil (Mullen *et al.* 2010; Lee *et al.* 2010). From the experimental results, the pinewood bio-char seems not suitable to be used as an efficient material to improve the cation exchange capacity in soil, for its low O/C molar ratio.

The briquette technologies still have lots of unexploited potentials. Considering the operability of briquette process, the additives with high carbon content, such as plastic, coal and rubber, could be added in different ratios, which would produce the bio-char with better quality. Even the catalysts could be added, thus making the bio-char a multifunctional material.



**Fig. 4.** SEM microphotographs of bio-char (a) M10-400, (b) M10-500, (c) M10-600, (d) M10-700, (e) P10-700, [1000 x], and (f) M10-700, [1000 x]

## CONCLUSIONS

1. The characteristics of bio-char principally depended on the pyrolysis factors, whether molded or pulverized. With increased pyrolysis temperature, bio-char would have increased HHV, fixed carbon content, ash content, percentage carbon, pore structure development, polymerization degree, and graphite degree. But it would be decreased in char yield rate, volatile content, hydrogen content, and oxygen content.
2. The heating rates have an essential effect on the char yield rate. At a lower temperature (400 °C), the char yield rate is positively correlated to heating rate. At higher temperatures (500-700 °C), the char yield rates are negatively correlated to heating rate.
3. The briquette forming process tends to arrange the molded biomass as well as molded bio-char into a compact and organized structure. Compared with pulverized bio-char, the molded bio-char has higher char yield, ash content, graphite degree and pore-structure ordering, but a lower HHV.
4. Molded bio-char produced from pinewood at appropriate pyrolysis factors would be suitable for being a reducing agent (M15-400), activated carbon precursor (M10-600), or fuel (M15-400).

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