Production of solid fuel biochar from waste biomass by low temperature pyrolysis

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HIGHLIGHTS

- The biochars were produced from woody and non-woody biomass by pyrolysis.
- Woody biomass showed higher biochar and energy yields than non-woody biomass.
- Woody biomass showed lower decomposition rate than non-woody biomass.
- The biochars exhibited significantly improved combustion behaviors.
- Slagging and fouling issues were similar for raw biomass and biochars combustion.

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ABSTRACT

Low temperature pyrolysis was employed to produce solid fuel biochars from woody (pine wood) and non-woody biomass (coconut fiber) in the present study. Chemical evolution of biomass under pyrolysis conditions was determined and fuel qualities of the biochars were evaluated including energy densities, ash-related problems and combustion behaviors. The results showed that dehydration reaction of the biomass had same preference with decarboxylation reaction under pyrolysis conditions. The hemicellulose and cellulose in non-woody biomass showed faster decomposition than those in woody biomass. The biochars derived from coconut fiber showed lower energy densities and energy yields than those from pine wood under identical conditions. All major ash forming metals originally contained in raw biomass were accumulated in the resultant biochars and more serious slagging and fouling problems were present during combustion of pyrolytic biochars compared to raw biomass. The reactivity of biomass decreased and the main mass loss shifted to elevated temperature zone with the increasing pyrolysis temperature, indicating increased thermal efficiency and environmental benefits were achievable during biochar combustion compared to raw biomass combustion. Taking into account combustion characteristics and energy yield, optimal pyrolysis temperatures for solid fuel production were around 300 °C for coconut fiber and 330 °C for pine wood.

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1. Introduction

The prospect of the exhaustion of fossil energy and climate change caused by the excessive use of fossil fuel necessitates shifting energy supply from fossil energy to renewable energy in the near future. Among all renewable energies, biomass energy is receiving increasing interests due to its wide availability worldwide [1]. Currently, biomass combustion alone or co-combustion with coal for heat and power generation in existing coal-fired systems is considered to be the lowest risk and least expensive

strategy of combining utilization of biomass energy with substantial CO₂ reduction in the atmosphere [2]. Unfortunately, raw biomass is not an ideal energy carrier and direct utilization of biomass faces great barriers originating from their inherent properties such as poor grindability, high moisture content and low energy density [3]. For example, poor grindability of biomass materials caused by its fibrous structure significantly increases energy consumption and creates a challenge during fuel preparation and feeding process. As for the high moisture content, it lowers the maximum combustion temperature and consequently could reduce the thermal efficiency and increase pollutant emissions [3]. To overcome these drawbacks, a pretreatment process is necessary to improve fuel quality of raw biomass prior to combustion.

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Pyrolysis has been employed to convert biomass feedstock into bio-fuels with high energy density, and biomass pyrolysis generates three product streams: liquid (bio-oil), gas, and solid product (biochar). The distributions and properties of these product streams are strongly dependent on pyrolysis conditions. Currently most attention is paid to the liquid and gaseous products, and many techniques and processes have been developed to increase the yield and improve the quality of these two target products [4–8]. However, due to the high instability and complex composition, bio-oil cannot be used directly, but requires further upgrading [4]. In the case of gaseous product, the low yield and complicated separation and purification processes limit its large-scale application in practice [8]. Under this situation, realizing high-value application of biochar can provide some advantages and a viable option to enhance biomass utilization efficiency.

Compared to liquid and gaseous products, only a few studies have been carried out with the aim of producing solid fuel biochars from waste biomass, and most of these studies focused on the improved physicochemical properties of woody biomass [9–16]. In contrast, limited studies are available for the biochars derived from most abundant agricultural wastes and there is a lack of information about the comparison of fuel qualities of the biochars from woody biomass and agricultural residue [10,13–16]. In addition, as we know, raw biomass combustion has low thermal efficiency and high pollutant emissions, and suffers from serious ash-related problems such as fouling and slagging problems [3]. However, combustion qualities and ash-related problems of pyrolytic biochars are scarcely studied in the literature although they are two key concerns for biomass used as solid fuel [17,18].

In the present study, the biomass was pyrolyzed with the specific intention of solid fuel biochars production. Fuel quality of the biochars derived from woody and non-woody biomass was investigated including energy yield and combustion properties. Moreover, chemical evolution of the biomass under pyrolysis conditions was examined by FT-IR technique.

2. Experimental

2.1. Materials

Pine wood (PW) and coconut fiber (CF) were selected as representative woody and non-woody biomass, and their properties

were presented in Table 1. PW and CF were dried at 60 °C for 24 h prior to biochar production.

2.2. Biochar preparation

The pyrolysis of biomass was conducted in a fixed-bed quartz reactor equipped with a temperature controller. In every run, biomass sample was charged into an alumina boat which was then placed in a quartz tube. The furnace was heated to desired temperature (200–330 °C) with a heating rate 15 °C/min and kept at final temperature 20 min under argon gas atmosphere. After cooled down to room temperature, the biochar in alumina boat was weighted and kept in a desiccator for the analysis. The biochars derived from CF and PW were designated as “CF-xxx” and “PW-xxx”, where “xxx” shows pyrolysis centigrade temperature. Fig. 1 shows the images of several typical biochars prepared in the present study.

2.3. Characterization

The carbon, hydrogen, nitrogen and sulfur contents were determined on an EA3000 Elemental Analyzer (Italy). The higher heating value (HHV) of the fuel was measured with a Kaiyuan 5E-KC5410 Express Calorimeter (China). The infrared spectrum (as KBr disk) was recorded in the wavenumber range of 4000–400 cm^{−1} with a Nicolet Nexus 670 Spectrophotometer (USA) at room temperature. The fuel ash was prepared at 575 °C according to standard test method for ash in biomass (ASTM D 1102). As for the major ash forming metal (K, Na, Ca, Mg, Ti, Si, Fe and Al) content determination, the fuel/ash was firstly digested in a mix of acids and hydrogen peroxide (HNO₃ + H₂SO₄ + HF + H₂O₂) at 180 °C for 30 min using a Hanon microwave digester (China). The digestion solutions were then evaporated to dryness to remove the fluorides and the resultant residues were dissolved in 1:1 HNO₃ solutions, followed by dilution by de-ionized water to desired volume. Subsequently the metal concentrations in the solution were quantified by ICP-OES Perkin Elmer Optima 3000 DV (USA). The metal oxide content was calculated according to corresponding metal content in ash.

Combustion analysis was conducted on a differential thermogravimetric analyzer TGA-7 (Perkin Elmer, USA). The fuel sample was heated from room temperature to final 700 °C at a linear heating rate of 20 °C/min under air flow rate of 30 ml/min. In order to eliminate mass and heat transfer effects, very small sample sizes (around 5 mg) were loaded into an alumina crucible. To ensure the reproducibility, three replicates of each TGA experiment were performed.

3. Results and discussion

3.1. Ultimate analysis, proximate analysis and major ash forming metal content analysis

As shown in Table 2, carbon contents increase and oxygen contents decrease in the biochars with increasing pyrolysis temperature, indicating increased energy densities of the biochars. In contrast, there is no obvious change for nitrogen and sulfur contents in the biochars with the increasing temperatures and their values are lower than those of lignite. The lower contents of nitrogen and sulfur in biochars imply that like raw biomass combustion, similar environmental benefits can be achieved from the combustion of the biochars. Fig. 2 shows the removal degrees of carbon and hydrogen at different temperatures and it is evident that woody biomass PW underwent lower remove rates of hydrogen and carbon than non-woody CF at identical pyrolysis conditions.

Table 1
Properties of coconut fiber and pine wood used in the present study.

Sample	Coconut fiber	Pine wood
<i>Ultimate analysis (daf, %)</i>		
C	47.75	48.15
H	5.61	6.70
N	0.90	1.35
S	0.23	0.20
O (by difference)	45.51	43.60
<i>Proximate analysis (db, %)</i>		
Volatile matter	80.85	85.45
Fixed carbon	11.10	13.15
Ash	8.05	1.40
<i>Major ash forming metals analysis (db, %)</i>		
K	1.600	0.105
Ca	0.329	0.198
Na	0.123	0.013
Mg	0.058	0.031
Fe	0.019	0.052
Al	0.005	0.018
Ti	0.007	–
Si	0.022	0.062
HHV (dry, MJ/kg)	19.23	19.83

– Not detected.

Fig. 1. Images of biochars prepared in the present study.

Table 2

Ultimate analysis, proximate analysis and energy analysis of the biochars derived from coconut fiber and pine wood.

Sample	Proximate analysis (db, %)			Ultimate analysis (daf, %)						Energy analysis	
	Volatile matter	Fixed carbon	Ash	N	C	H	S	O ^a	Biochar yield (%)	HHV (MJ/kg)	Energy yield (%)
CF-200	78.26	15.04	6.70	1.35	50.42	5.20	0.45	42.58	83.11	19.93	87.5
CF-225	76.98	15.90	7.12	1.02	51.83	4.99	0.30	41.86	80.13	20.36	81.9
CF-250	75.58	16.37	8.05	1.13	53.77	4.76	0.28	40.06	69.19	21.03	71.5
CF-275	70.20	21.04	8.76	1.12	58.08	4.55	0.28	35.97	63.87	22.63	68.7
CF-300	64.21	25.71	10.08	1.21	61.38	4.08	0.32	33.01	55.65	23.80	58.5
CF-330	60.64	28.38	10.98	1.18	65.36	4.12	0.29	29.05	50.21	25.36	53.5
PW-200	80.43	18.62	0.95	1.33	51.16	6.54	0.18	40.79	91.00	20.74	99.8
PW-225	78.25	20.77	0.98	1.34	51.74	6.50	0.17	40.25	89.17	20.00	90.3
PW-250	75.84	23.09	1.07	1.34	52.00	6.35	0.17	40.14	79.19	21.06	79.4
PW-275	70.33	28.51	1.16	1.65	53.37	6.20	0.18	38.60	72.00	21.66	74.1
PW-300	58.34	40.37	1.29	1.68	55.52	6.07	0.22	36.51	65.16	22.60	68.0
PW-330	50.71	47.90	1.39	1.60	59.86	5.81	0.20	32.53	61.42	24.49	63.3
Lignite	48.76	40.98	10.26	1.74	61.64	5.72	0.77	30.13	–	25.31	–

– Not available.

^a By difference.

Fig. 2. Removal degrees of carbon and hydrogen in coconut fiber and pine wood as a function of pyrolysis temperature.

Fig. 3. Atomic H/C and O/C ratios of coconut fiber, pine wood and their derived biochars (lignite for comparison).

Fig. 4. Retention rates of major ash forming metals during pyrolysis of coconut fiber and pine wood.

The removal degree of hydrogen is nearly two times higher than that of carbon in both CF and PW with the exception of PW pyrolysis at 200 and 250 °C. As we know, the hydrogen and carbon in biomass are removed mainly through dehydration and decarboxylation reactions, respectively. Considering co-occurrence of demethanation reaction, removal degrees of carbon and hydrogen

indicate that decarboxylation reaction has similar preference to de-hydration under low temperature pyrolysis. In addition, the variation in elemental composition of the biochars was also analyzed via a van Krevelen diagram as illustrated in Fig. 3. It can be seen that only the biochar obtained at 330 °C pyrolysis has similar atomic composition to that of the lignite. Besides low temperature

Fig. 5. DTG curves for the combustion of pyrolytic biochars derived from coconut fiber and pine wood.

pyrolysis, hydrothermal carbonization has also been employed to biomass upgrading and it was reported that the biochar produced from hydrothermal carbonization at 250 °C have similar compositions to that of lignite [9]. The difference between pyrolytic biochar and hydrothermal biochar reveals that the biomass underwent a less decomposition/carbonization degree under pyrolysis conditions compared to hydrothermal carbonization at same temperature [19].

Fuel ratio is a ratio of fixed carbon against volatile matter and is a characteristic value representing the property of a solid fuel and classifying coal rank according to ASTM 388. As shown in Table 2, the volatile matter contents in biochars decrease and fixed carbon

contents increase with the increasing pyrolysis temperature. Therefore, fuel ratios of the biochars increase with the increasing temperature, especially at the temperatures higher than 275 °C. The increased fuel ratios imply elevated combustion efficiencies and reduced pollutant emissions during biochars combustion compared to raw biomass combustion. Despite increased HHVs, the energy yields decrease with the increasing temperature due to the significantly decreased mass yields of the biochars. In comparison to non-woody biomass CF, woody PW has higher mass and energy yields under identical pyrolysis conditions. For CF, there is a significant decrease for energy yield when the temperature increases from 275 to 300 °C. While in the case of PW, the remarkable decrease is observed when the temperature increases from 300 to 330 °C.

To determine ash-related problems during biochar combustion, the fate of major ash forming metals in raw biomass were investigated during pyrolysis upgrading. The retention rate is defined as percentage of the mass content in the biochar relative to those contained in parent biomass and Fig. 4 presents the retention rates of major ash forming metals at different temperatures. Within tested temperatures, all major ash forming metals are totally remained in resultant biochars. As for the fate of metals during biomass pyrolysis, only several papers are available in the literature [20]. For example, it was reported that K and Na started to release around 400 °C, and Ca and Mg around 600 °C for pine sawdust pyrolysis in a wire-mesh reactor [20]. The results obtained in the present study are well consistent with previous reports and the 100% retention rates possibly are related to the low volatilization rate due to the low heating rate and low pyrolysis temperature. It is worthy to note that metal retention rates are different under pyrolysis and hydrothermal carbonization conditions, and most of alkali and alkaline earth metals (AAEMs) and high fraction of heavy metals are removed in hydrothermal biochars [19].

The slagging and fouling inclination during biochar combustion are indicated as the values calculated by the follows equations [21]:

$$\text{Slagging index (SI)} = (B/A) \times S\% \quad (1)$$

$$\text{Fouling index (FI)} = (B/A) \times (\text{Na}_2\text{O} + \text{K}_2\text{O}) \quad (2)$$

where $B/A = (\text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O})/(\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2)$; S is the percent of the sulfur in dry fuel sample.

The 100% retention rates of major ash forming metals and comparable sulfur contents suggest that more serious slagging and fouling issues are expected during biochar combustion compared to raw biomass combustion. The calculated slagging and fouling indices according to Eqs. (1) and (2) also confirm that the slagging and fouling inclinations increase with increasing pyrolysis temperature and the biochars have increased SI and FI values than raw biomass generally (major metal oxides content in the ash and SI and FI values of raw biomass and the biochars are shown in

Table 3
Combustion parameters of the biochars derived from coconut fiber and pine wood.

	Temperature interval (°C)		Mass loss (%)		Peak temperature (°C)		DTG _{max} (%/°C)		Residue (%)
	Stage I	Stage II	Stage I	Stage II	Stage I	Stage II	Stage I	Stage II	
CF-200	264–412	412–500	53.31	25.28	309	454	0.54	0.42	8.64
CF-250	270–415	415–505	52.51	34.41	312	455	0.50	0.44	10.26
CF-300	282–416	416–500	44.44	39.81	370	459	0.37	0.56	12.29
CF-330	281–405	405–490	42.86	39.47	367	453	0.40	0.60	13.99
PW-200	301–385	385–480	51.47	22.00	331	464	1.71	0.32	2.56
PW-250	314–391	391–484	58.76	26.34	336	473	1.70	0.44	3.12
PW-300	328–402	402–486	47.82	35.96	346	480	1.58	1.38	3.80
PW-330	326–381	381–472	29.11	56.66	337	458	0.69	2.66	3.95

Supplementary Material). Considering lower ash content in PW derived biochars together with higher energy yields and lower slagging and fouling inclinations, woody biomass are more suitable for biochar production than agricultural biomass.

3.2. Combustion behavior of pyrolytic biochar

DTG profiles depicting the combustion process of the pyrolytic biochars derived from CF and PW are present in Fig. 5. The characteristic temperatures and peak points of the combustion process are summarized in Table 3.

The biochars derived from CF and PW exhibit different combustion patterns and in general, each biochar shows two main mass loss peaks in DTG curves.

Two overlap combustion peaks are present in all the biochars derived from CF. With the increasing pyrolysis temperatures, the maximum mass loss rate (DTG_{max}) and main mass loss of the biochars decrease within the low temperature range and shift to high combustion temperature range. For example, mass losses within low and high temperature range are 53.31% and 25.28% for CF-200, and 42.86% and 39.47% for CF-330, respectively. As for the DTG_{max} in low and high temperature ranges, their values of CF-200 are 0.54%/°C and 0.42%/°C and for CF-330, they are 0.40%/°C and 0.60%/°C, respectively. In comparison to CF derived biochars, two more separated sharp peaks were present in DTG curves of PW derived biochars. Like the biochars derived from CF, same trend was observed for PW derived biochars with increasing temperature: decreased DTG_{max} of low temperature range and increased mass loss within high temperature range. For PW-200, a sharp DTG peak was observed centered at 331 °C and a mass loss of 51.47% was measured within the temperature range of 385–480 °C. The second peak centered at 464 °C and the mass loss within the temperature range of 385–480 °C was around 22.00%. With the increasing pyrolysis temperature, DTG_{max} decreased in the low combustion range and increased in high temperature range. For example, DTG_{max} of low and high temperature ranges were 1.70%/°C and 0.44%/°C for PW-250, and 0.69%/°C and 2.66%/°C for PW-330, respectively. The decreased DTG_{max} and increased temperature range for main mass loss suggests the reactivities of the biochars decrease with increasing pyrolysis temperatures. In addition, the decreased volatiles content of the biochars is also consistent with the decreased reactivities (shown in Table 2). It is well known that low combustion temperature of raw biomass due to their high reactivity results in low thermal efficiency and high pollutant emissions [3]. Therefore, the decreased reactivity indicates that high energy recovery efficiency and environmental benefits can be achieved by biochar combustion. As a comparison, pyrolytic biochars have higher reactivities than hydrothermal biochars, and the higher reactivities are ascribed to the catalytic effect of AAEMs originally contained in raw biomass [22]. As aforementioned, AAEMs are accumulated in pyrolytic biochar while they are largely removed in hydrothermal biochars [23].

In addition, it can be seen that there is significant improvement for the combustion property of the biochar when pyrolysis temperature increase from 300 to 330 °C for PW and from 250 to 300 °C for CF, respectively. Previous studies showed that the temperature played significant role in biomass upgrading and in general the temperature range of 200–300 °C was suggested to produce solid fuel biochar from biomass [10,12,15]. In the present study, it was shown that woody biomass PW should be pyrolyzed at higher temperature than agricultural waste CF to obtain better combustion efficiency. Taking into account of energy yield, the suitable pyrolysis temperatures for the production of solid fuel are around 330 °C for PW and around 300 °C for CF, respectively. This conclusion is well supported by a previous report that the pyrolysis performed at 200–300 °C cannot improve the combustion property of biomass

Fig. 6. FT-IR spectra of coconut fiber, pine wood and their derived biochars.

feedstocks due to the high decomposition temperature of cellulose, especially for woody biomass [13].

Compared to raw biomass, improved combustion behaviors of the biochars suggest that increased thermal conversion efficiency and reduced pollutant emissions are expected during biochars combustion.

3.3. FT-IR analysis

FT-IR technique was employed to determine the structural evolution of biomass under pyrolysis conditions. Fig. 6 shows FT-IR spectra of raw biomass and corresponding biochars, with the assignment of the peaks based on IR mentor Pro 2.0 and related publications [19,24]. The broad adsorption peak from 3200 to 3600 cm^{-1} is ascribed to the intra- and inter molecular hydrogen and characteristic peak of crystalline cellulose [25,26]. It can be seen that the intensity of this peak had a significant decrease in both CF and PW after 250 °C pyrolysis, especially for CF. The peaks around 1734 cm^{-1} in PW and 1735 cm^{-1} in CF are attributed to the C=O vibration of the carboxylic acids in hemicellulose. This peak disappears in CF-200 and a corresponding new peak appear at 1700 cm^{-1} is caused by the degradation product of hemicellulose [27]. Different with CF, hemicellulose is still present in the biochar PW-300 and the peak of the corresponding degradation product is around 1698 cm^{-1} . The aromatic C–O stretching of methoxyl and phenyl propane structure and aromatic ring vibration in lignin correspond to the peaks at 1231 and 1561 cm^{-1} in CF, and 1271 and 1517 cm^{-1} in PW [28,29]. There is less change for the intensities of these peaks within the temperature range 200–330 °C for both CF and PW, indicating high degradation temperature of the lignin. The peaks caused by the antisymmetric stretching of glycosidic bond of cellulose are around 1162 cm^{-1} and 1169 cm^{-1} in CF and PW, respectively. It can be seen that the degradation of cellulose in CF is more sensitive to pyrolysis temperature than that in PW. The cellulose in CF is almost totally degraded at temperature higher than 275 °C. While in the case of PW, considerable amount of cellulose is still present at pyrolysis temperature at 330 °C. The higher degradation rate of CF than PW under identical conditions is possibly associated with the catalysis effect of high contents of AAEMs in CF, especially K [22]. Based on above analysis, it is obvious that same constituent (hemicellulose, cellulose and lignin) of biomass in non-woody and woody biomass shows different decomposition/carbonization temperatures, indicating woody and non-woody biomass have different optimal pyrolysis conditions for solid fuel production.

4. Conclusions

Non-woody (Coconut fiber) and woody biomass (pine wood) were upgraded to produce solid fuel biochar by low temperature pyrolysis. The dehydration and decarboxylation reactions of biomass had same preference for the biomass under pyrolysis conditions. All the major ash forming metals were retained in the biochars during biomass pyrolysis. The combustion of the biochars occurred in two temperature zones and the main mass loss shifted to high temperature zone with increasing pyrolysis temperature. Hemicellulose and cellulose in coconut fiber and pine wood showed different decomposition behaviors and consequently significant improvement of combustion performances was observed after 300 °C pyrolysis for coconut fiber and 330 °C for pine wood, respectively. The present study shows that low temperature pyrolysis have promising potential to produce solid fuel biochar from waste biomass.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.fuel.2015.05.032>.

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