energy&fuels Article
pubs.acs.org/EF

Biomass Pyrolytic Polygeneration System: Adaptability for Different Feedstocks

Yingquan Chen, Haiping Yang, Xianhua Wang,* Wei Chen, and Hanping Chen

State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan, Hubei 430074, P. R. China

Supporting Information

ABSTRACT: Biomass pyrolytic polygeneration technology has attracted extensive attention, but to widen its applicability, the process must be adaptable for varying biomass resources. Here, the pyrolysis behavior of cotton stalks, rapeseed stalks, tobacco stems, rice husks, and bamboo were investigated. The lower heating values of all the biogas products exceeded 10 MJ/m^3. Although the feedstocks varied, the major component of the liquid oil was water (48−65%), and the ~50% organic components comprised acids, ketones, and phenols. Chars from the five feedstocks all exhibited good utilization potential. Subsequently, the target products of these five biomass via pyrolytic polygeneration technology were recommended as followed. Bamboo can simultaneously provide high quality gas fuel, phenols-enriched liquid oil, and carbon-based adsorbent. Rapeseed stalk and rice husk can provide high quality gas fuel and solid products, which is high quality solid fuel and silica/carbon-based adsorbent, respectively. Cotton stalk and tobacco stem provide liquid oil with high utilization potential on refining acids and N-containing compounds, and their chars may be used as good solid fuel and biochar, respectively. Meanwhile, the liquid products from rapeseed stalk and rice husk and the gas products from cotton stalk and tobacco stem were recommended to be burned as heating energy of the factory. These results suggested that this technology showed good feedstock adaptability.

1. INTRODUCTION

Bioenergy and biofuels, as replacements for fossil fuels, are being developed to reduce the risk of energy shortages and curb climate change. It is predicted that bioenergy will satisfy 30% of the world's energy demand by 2050.[1] In China, by 2020, the use of biomass will account for 4% of the primary energy consumption.[2] However, the limitations of biomass, such as its low energy density and scattered distribution that results in high collection costs, challenge the achievement of these objectives.[3] To address resource accessibility, different types of biomass are generally used as feedstocks in biomass conversion factories that generate biogas[4] or power by combustion[5] and gasification.[6] Hence, the adaptability of the feedstocks for the different biomass conversion technologies has attracted significant attention.

Pyrolysis provides an effective and beneficial conversion option for biomass utilization, as it produces biogas and bio-oils, which can be subsequently applied for energy recovery, or biochar, which can be used as a solid fuel or for carbon sequestration when stored in the soil.[7−9] However, the nature of the biomass can affect its pyrolysis behavior and the product properties. Mohan et al.[10] reviewed the properties of bio-oils obtained from various feedstocks and pointed out that the type of biomass can significantly influence the properties of each bio-oil. Jeguirim et al.[11] suggested that different biomass sources will exhibit different pyrolysis kinetics depending on their organic and inorganic mineral contents. Yang et al.[12] proved that cellulose, hemicellulose, and lignin can produce different products during pyrolysis, and the variation among the contents of these components in the biomass is the major influence on pyrolysis properties. Gomez-Monedero et al.[13] reported that different biomass materials can influence the distribution of products and their properties, because each biomass has a different chemical composition and structure.

The simultaneous and sustainable production of liquid, gaseous, and solid products from biomass pyrolysis is considered to have good potential for converting biomass into high value products;[14,15] this process is known as biomass pyrolytic polygeneration.[15] The influence of feedstocks has been investigated in bench- and pilot-scale biomass pyrolytic polygeneration systems. This research suggests that the individual properties of each biomass material, which possesses different organic components, ash contents, or structures, have an important influence on the distribution and properties of the pyrolytic products from the process.[9,13,14,16] However, these studies do not describe in any detail the adaptability of biomass pyrolytic polygeneration toward various feedstocks. Currently, a commercial biomass pyrolytic polygeneration plant based on a retort reactor is operated in China.[17] The design parameters were tailored to the pyrolysis properties of cotton stalks.[15] Previous work recommended that the optimum operating temperatures for biomass pyrolysis are 550−650 °C, which affords lower heating values (LHVs) for the biogas and charcoal of ~10 MJ/m^3 and 22 MJ/kg, respectively. Furthermore, the biogas and charcoal are easily sold, which contributes to the economic profitability of the plant.[15,17] As the commercialization of biomass pyrolytic polygeneration plants expands, different types of feedstocks will become available for use by this technology. However, it is unclear how changes in the feedstock will affect the performance of the biomass pyrolytic polygeneration system. Therefore, it is necessary to investigate

Received: October 5, 2015
Revised: November 27, 2015
Published: December 28, 2015

DOI: 10.1021/acs.energyfuels.5b02332
Energy Fuels 2016, 30, 414−422

the adaptability of the biomass pyrolytic polygeneration process for different feedstocks. This research will also further our understanding of the formation mechanisms for the liquid, gaseous, and solid products of biomass pyrolytic polygeneration. In this work, five biomass materials—cotton stalks, rapeseed stalks, tobacco stems, rice husks, and bamboo—were investigated to evaluate the adaptability of the process. It is believed that this work will further promote the development of biomass pyrolytic polygeneration as well as advance the utilization of biomass in China.

2. EXPERIMENTAL SECTION

2.1. Biomass Feedstock. The proximate and elemental compositions of the samples were measured using an SDTGA-2000 analyzer (Navas Instruments, Spain) and a Vario EL II elemental (CNHS/O) analyzer (Germany). The LHVs were measured using an oxygen bomb calorimeter (Parr 6300, Moline, IL, US). The fiber analysis was conducted using the Van Soest method; a detailed procedure is available in our previous work.[18]

A cutting mill (Chyun Tseh Industrial Co., Ltd., Taiwan) with an output of 0.75 kW and rotation speed of 2850 rpm, equipped with a D800 multifunction transducer (Zhongshan Harnwell Electrical Co., Ltd., China), was used to investigate the grindability and the grinding energy consumption of the feedstocks. In each experiment, a raw sample (∼1.5 kg, particle size 2−3 cm) was cut to the final sample size (particle size <0.152 mm), and the energy consumed was calculated by the time−power data collected by the multifunction transducer. The particle size distribution (PSD) was used to evaluate the grindability, which was measured using a particle size analyzer (Master Min, Malvern 2000, Malvern Instruments Ltd., Malvern, England).

A microroll-type briquetting machine (DZLP360, Jinan Hong Jing Machinery Co., Ltd., China), with an output of 30 kW and equipped with the D800 multifunction transducer, was used to investigate the energy consumption during compression. In each trial, finely ground particles (∼1 kg) were introduced into the machine, and afforded a briquette with an output diameter of 6 mm.

2.2. Polygeneration Process. The biomass samples were pyrolyzed in a fixed-bed apparatus consisting of a vertical tube (I.D. 38 mm; height 600 mm), an electric furnace, a gas-condensing system, and an uncondensed gas collection and analysis system. The pyrolysis temperature was 550 °C, which is the optimum temperature for obtaining high-quality pyrolytic products from the biomass polygeneration system.[15,19] In each trial, the sample (3 g) was moved rapidly in a sample carrier to the center of the reactor, which was preheated to the selected temperature, and the volatiles were purged from the reactor with a flow of high purity N_2 (1 L/min). From the products, liquid oil was trapped in an ice−water condenser whereas the noncondensed gaseous products were filtered through a glass wool filter and stored in a gasbag for further analysis. This process is described in detail in our previous reports.[15,19]

2.3. Analysis of Products. *2.3.1. Gases and Liquids.* The analysis procedure for the gas and liquid oil products is detailed in our previous report.[15] The compositions of the gas and liquid oil were analyzed by micro gas chromatography (micro-GC) and gas chromatography−mass spectroscopy (GC−MS; HP7890 series GC with an HP5975 MS detector), respectively. The water content of the liquid oil was measured by Karl Fischer titration (TitroLine KF-10, SCHOTT, Germany) according to the ASTM D 1744 protocol prescribed by the American Society for Testing and Materials (titrant: Hydranal Composite 2, Metrohm 787 KF Titrino). The gas and liquid products from 550 and 850 °C were tested three times to ensure repeatability, and the errors of these result were below 27%.

2.3.2. Char Product. The proximate and elemental compositions, as well as the LHV and PSD, of the char were determined in the same manner as for the raw samples. The pore characteristics were derived from the isothermal adsorption of nitrogen at 77 K using automatic adsorption equipment (Micrometrics, ASAP 2020, USA). These values included the Brunauer−Emmett−Teller (BET) surface area (S_{BET}), the pore volume and pore-size distribution determined by density functional theory (DFT) method, and the single-point-adsorption total pore volume.

The adsorption capacities of the char products for water, phenol, and CO_2 were also analyzed to evaluate their use as an adsorbent. The water adsorption was derived from the equilibrium moisture content (EMC) with a relative humidity (RH) of 90% at 30 °C, obtained using a controlled humidity chamber (HWS-150, Sengxin Corp., China).[20] The CO_2 adsorption study at 273 K was performed with the Micromeritics micropore analyzer, and the total cumulative adsorption at ambient pressure was measured. The adsorption of phenol was determined according to the GB/T 12496.12-1999 protocol. The char sample (200 mg) and phenol solution (50 mL, initial concentration (C_0) = 1 g/L) were mixed in an Erlenmeyer flask (250 mL), agitated in an orbital shaker for 2 h at room temperature, and then allowed to stand 22 h until filtration. The residual phenol concentration was analyzed at 269.5 nm using a Lambda 35 UV-spectrophotometer (PerkinElmer, USA). The adsorption capacity for phenol was calculated from the difference between the initial and residual phenol solution concentrations.

The combustion characteristics of the char product and a reference coal sample were measured by thermal gravimetric analysis (TGA) using a STA-409C thermal analyzer (NETZSCH, Selb, Germany). DTG_{max} (wt %/°C), T_{max}, T_i, and T_f were determined, denoting the maximum combustion rate, the corresponding temperature of the maximum combustion rate, and the ignition and burnout temperatures, respectively. Detailed procedures are available in our previous report.[21]

3. RESULTS AND DISCUSSION

3.1. Feedstock Characterization. Table 1 lists the different feedstocks. Cotton stalks and rapeseed stalks were directly collected from farms and were supplied between November and May and from June to September, respectively. In contrast, the tobacco stems, rice husks, and bamboo, obtained from factories that produce cigarettes or process rice or bamboo, respectively, were available year-round. The average collection cost of the feedstock from the farms is higher than from the factories, due to the variations in planting density and labor costs. In the area of high planting density and sufficient labor, the cost of per tons of cotton stalk could be controlled at 150−200 yuan RMB, which is an affordable price for the biomass pyrolytic polygeneration factory. However, to get more benefits, farmers would raise the price above 300 yuan RMB/t since a supply contract was difficult to obtain between a farmer and the factory. The collection of rapeseed stalk is similar to cotton stalk; however, in areas lacking fossil fuel, rapeseed stalk is generally used as a solid fuel by the farmer. For this reason, it has a high collection cost, 500 yuan RMB/t. If the supplier of biomass is the factory, a supply contract may be signed between the supplier and the biomass pyrolytic polygeneration factory; hence, the cost was relatively lower and more stable.

Table 1. Collection of Different Feedstocks

	supplier	supply duration	cost (yuan RMB/t)
cotton stalk	farmer	Nov to May	150−450
rapeseed stalk	farmer	Jun to Sep	200−500
tobacco stem	cigarette factory	all year	200−300
rice husk	rice processing factory	all year	200−300
bamboo	bamboo processing factory	all year	100−200

Table 2 presents the properties of the five feedstocks. As shown by the ultimate analysis, the carbon contents of the

DOI: 10.1021/acs.energyfuels.5b02332
Energy Fuels 2016, 30, 414−422

Table 2. Properties of Different Feedstocks[a]

	cotton stalk	rapeseed stalk	tobacco stem	rice husk	bamboo
			Ultimate Analysis (d, wt %)[c]		
C	45.22(4.42)	45.63(2.66)	34.14(3.04)	40.8(1.69)	49.29(3.87)
H	6.34(0.69)	5.73(0.55)	4.37(0.21)	5.22(0.27)	5.86(0.44)
N	1.15(0.04)	0.45(0.02)	2.42(0.19)	0.29(0.01)	0.20(0.02)
S	0.34(0.04)	0.21(0.01)	0.44(0.04)	0.08(0.01)	0.10(0.01)
O[b]	37.70(2.86)	39.50(2.34)	29.08(2.46)	35.46(1.38)	40.25(2.64)
			Proximate Analysis (ad, wt %)[c]		
moisture	4.66(0.55)	3.87(0.37)	5.23(0.20)	2.34(0.24)	3.58(0.15)
volatile	74.96(2.51)	81.99(9.44)	63.56(2.11)	66.12(3.89)	84.44(5.93)
ash	2.59(0.17)	4.60(0.36)	24.33(1.35)	15.84(0.85)	0.73(0.02)
fixed carbon[b]	17.80(2.05)	9.53(0.41)	6.88(0.80)	15.73(1.22)	11.25(1.01)
			Fiber Analysis (ad, wt %)[c]		
cellulose	21.98(2.54)	19.92(2.03)	11.78(1.16)	19.00(1.62)	26.10(0.80)
hemicellulose	35.50(2.45)	37.12(4.16)	26.43(2.20)	21.90(1.98)	40.10(2.43)
lignin	29.87(3.48)	22.10(1.80)	18.63(0.71)	27.80(0.92)	30.90(2.59)
LHV (MJ/kg)	17.18(1.97)	16.31(1.48)	12.34(1.41)	14.69(1.20)	17.58(1.88)
			Energy Consumption (kWh/t)[d]		
grinding	194 (8)	102 (6)	97 (9)	57 (11)	389 (64)
compressing	187(6)	57(4)	46(4)	346(21)	254(22)

[a]ad, air-dry basis; d, dry basis. [b]By difference. [c]Number enclosed in the parentheses were relative error of avergae value on two times of analysis. [d]Number enclosed in the parentheses were standard deviations with $n = 3$.

bamboo and rapeseed stalks are higher than that of the cotton stalks, whereas those of the rice husks and tobacco stems are lower. The nitrogen content of the tobacco stems is as high as 2.42 wt %, whereas it is negligible in the rapeseed stalks, rice husks, and bamboo. In the proximate analysis, bamboo produced 84.44 wt % volatiles and 0.73 wt % ash, whereas the tobacco stems had 24.44 wt % ash and 63.56 wt % volatiles. Hence, value gradients for the volatiles and ash contents were obtained, which may be beneficial in analyzing their influence on the products from the biomass pyrolytic polygeneration process.

The fiber analysis results reveal that the cellulose of these five biomass sources is all lower than hemicellulose and lignin. Hemicellulose was the major fiber component for these biomass materials, except in the rice husks, which had a slightly higher lignin content than hemicellulose. The individual results for each biomass material are described as follows. Bamboo and tobacco stems have the highest and lowest cellulose contents, 26.1 and 11.78 wt %, respectively, whereas the cellulose content of the other three feedstocks is about 20 wt %. Hemicellulose contents above 35 wt % are observed in the cotton stalks, rapeseed stalks, and bamboo; however, only 26.43 and 21.9 wt % hemicellulose is contained in the tobacco stems and rice husks, respectively. The lignin content in the cotton stalks and bamboo is ~30 wt %, and the rice husks have 27.8%; however, the rapeseed stalks and tobacco stems have the lowest lignin content at only 20 wt %.

In the biomass pyrolytic polygeneration process, the major pretreatment method comprises grinding and compressing, because the block char from the biomass briquette is commercially attractive. Hence, the energy consumed during grinding and compressing is an important cost element for a biomass pyrolytic polygeneration factory. As shown in Table 2, the grinding and compressing energy consumption values for cotton stalks are 194 and 187 kWh/t, which accounts for over 60% of the costs of the factory. Compared with cotton stalks, the energy consumption for the pretreatment of rapeseed stalks and tobacco stems is significantly decreased. Although the grinding energy consumption of the rice husks is the lowest at 57 kWh/t, its compression energy consumption is the highest, 346 kWh/t, which raises the total energy consumption above that of cotton stalks. Bamboo is the hardest feedstock to pretreat, requiring an energy input as high as 643 kWh/t, which is higher than cotton stalks by about 68%. Although the grinding energy consumption of bamboo is the highest, the PSD results (Figure 1) show that it has a broader particle size distribution and finer particles, which results in the lowest volume average particle size, D[4,3], of 253 μm. This may be due to the dense, fibrous structure of the bamboo. Finally, the PSD values for rapeseed stalks, tobacco stems, and rice husks are similar. These materials contain a greater proportion of large particles than the cotton stalks and bamboo, and hence, their D[4,3] values are above 300 μm.

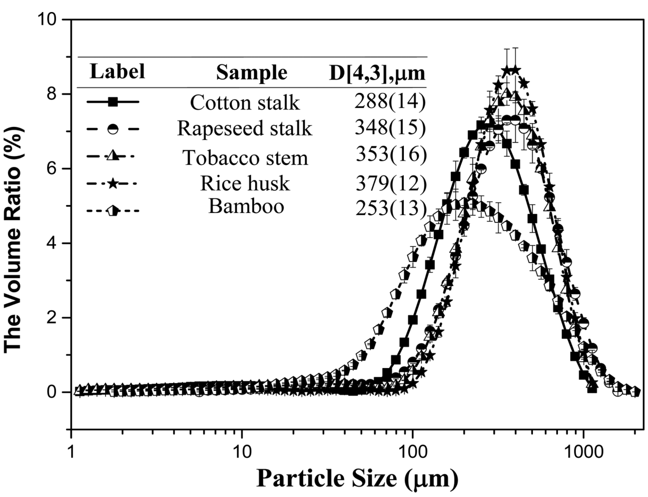

Figure 1. Particle size distribution of different feedstocks. Numbers enclosed in parentheses and the error bars are relative error of average value on two analyses.

DOI: 10.1021/acs.energyfuels.5b02332
Energy Fuels 2016, 30, 414−422

3.2. Product Distribution. Figure 2a shows the yield distribution of the biogas, liquid oil, and char products for the different feedstocks. Currently, the yields of biogas and char significantly influence the income for biomass pyrolytic polygeneration systems. The descending order of the char yield is tobacco stems > rice husks > cotton stalks ≈ rapeseed stalks > bamboo. The liquid oil yield from the rapeseed stalks is the highest, which may be caused by its lower biogas yield than that from cotton stalks. The biogas yields from the tobacco stems and rice husks are also lower than that from the cotton stalks. Thus, the feedstock inputs when using these three biomass sources should be increased. The char yield from bamboo is lower relative to the other biomass materials, and torrefaction, which tends to promote the cross-linking reactions of the holocellulose (cellulose + hemicellulose) rather than advance the char yield, should be considered as an pretreatment before pyrolysis.[19]

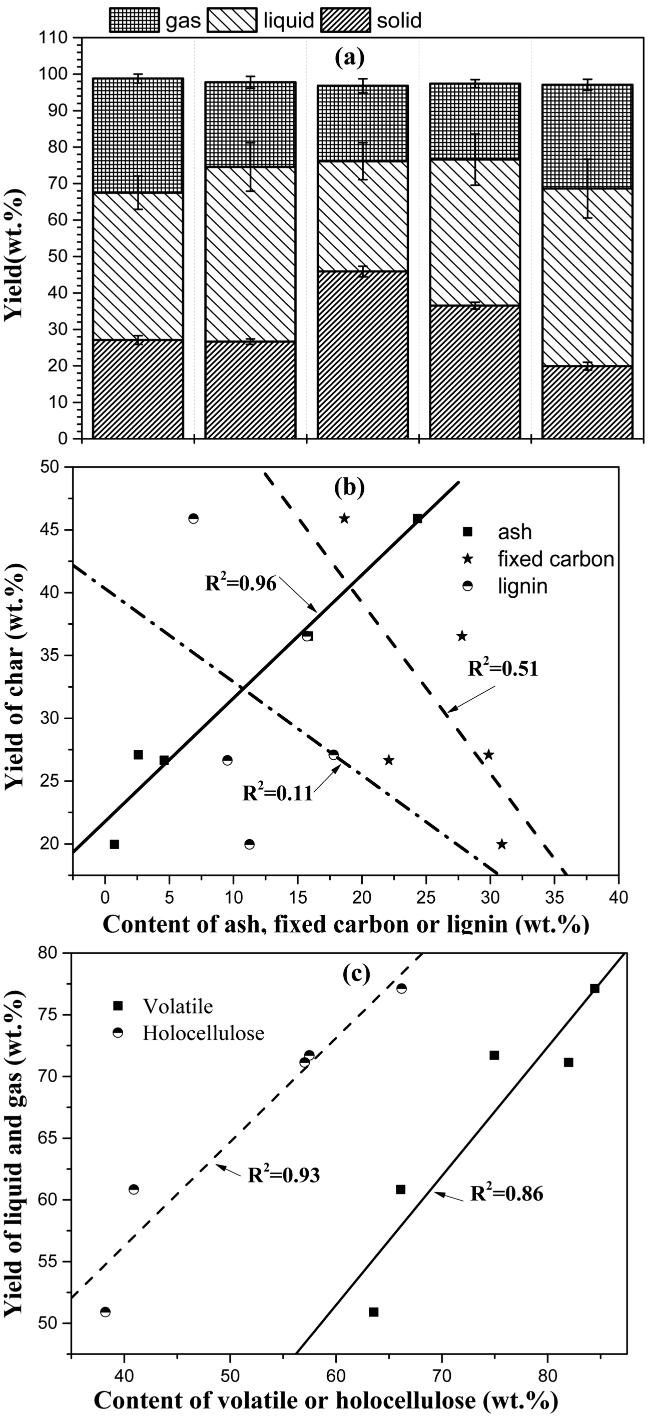

Figure 2. Yield distribution of char, liquid, and gas product for different feedstocks and the correlation between the yield of products and the properties of the feedstock: (a) yield distribution; (b) correlation on char yield vs the contend of ash, fixed carbon, and lignin of feedstock; (c) correlation on yield of liquid and gas vs content of volatile and holocellulose The error bars are relative error of average value on analyses.

Figure 2b and c shows the correlation between the biomass properties and the product yields. Linear correlations between the ash content and char yield, and the holocellulose content and the yields of liquid and gas, are observed. It is reasonable that the char yield increases when the ash content increases, because the ash is always retained in the solid product. The holocellulose is the major component that is decomposed in the process;[12] hence, a higher holocellulose content results in higher yields of liquid oil and gas. Previous work has suggested that lignin is primarily converted to solid carbon in the char;[12,22] however, only a slight correlation between the lignin content and char yield is observed. Meanwhile, a significant correlation between the volatiles content and the yields of the liquid oil and gas is observed, although no strong correlation is noted between the fixed content and char yield. It is suggested that the ash and volatiles contents of the feedstocks, used to assess combustion characteristics, would be useful in predicting the product yields from the biomass pyrolytic polygeneration process.

3.3. Gas/Liquid Product Properties. Figure 3a shows the compositional distribution of the gas products for the different feedstocks. As part of the gaseous fuel, CH_4 plays a critical role in the heat value. For the rapeseed stalks, rice husks, and bamboo, the CH_4 content exceeds 20 vol %, which is higher than the levels obtained from fast pyrolysis[10] and gasification.[23] However, the cotton stalks and tobacco stems produce ∼12−13 vol % CH_4. This difference may be influenced by the biomass properties. CH_4 is formed primarily from the demethoxylation of lignin.[12] Hence, the amount of CH_4 released is correlated with the lignin content of the feedstock, as shown in Figure 3b. For the factory-produced biomass materials (tobacco stems, rice husks, and bamboo), the amounts of CH_4 show good linear relationships that increase with the lignin content. However, for the biomass obtained directly from farmland (the rapeseed and cotton stalks), a negative correlation is observed, which may be related to the preference for CH_4 formation during rapeseed stalk pyrolysis, and the preference for char formation for the cotton stalks.

Another desirable biogas quality should be lower CO_2 and CO contents, because CO_2 is incombustible and CO poses a safety risk for the user. In the biogas produced by cotton-stalk and tobacco-stem pyrolysis, CO_2 accounts for about 42 vol % of the total. The remaining biomass materials release less than 36 vol % CO_2. However, the difference in CO release is in contrast with CO_2. The rapeseed stalks, rice husks, and bamboo release more than 31 vol % CO, whereas the cotton stalks and tobacco stems release less than 22 vol % CO. CO_2 is formed during the cleavage reactions of glycoside bonds, whereas CO is formed during the decarbonylation of holocellulose.[12] Therefore, the holocellulose content of the feedstock is correlated with the amounts of CO_2 and CO released. Except for the rapeseed stalks, the other four biomass materials linearly release more

DOI: 10.1021/acs.energyfuels.5b02332
Energy Fuels 2016, 30, 414−422

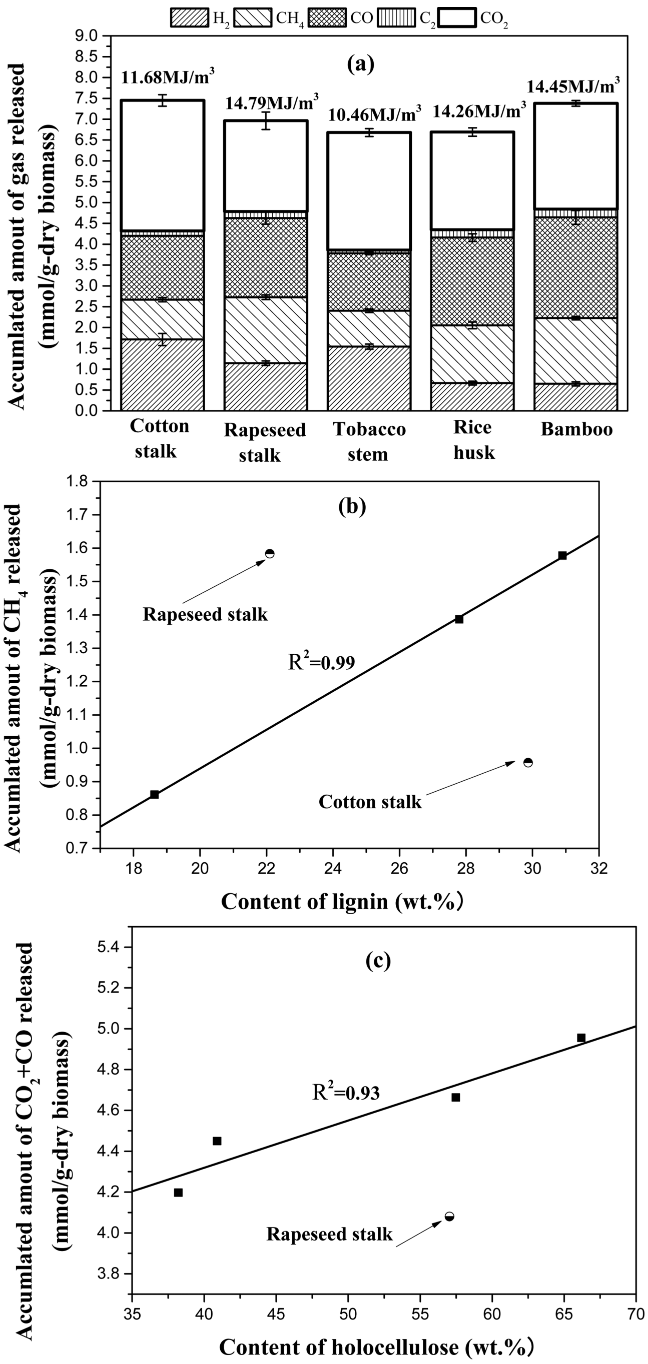

Figure 3. Composition distribution of gas product for different feedstock and the correlation between the yield of specific composition (CH_4 and CO_2 + CO) and the content of organic component (lignin and holocellulose). (a) Composition distribution; (b) CH_4 vs lignin; (c) CO_2 vs cellulose. In part a, the number in the top of the column is the lower heat value of gas. The error bars are relative error of average value on two analyses.

CO_2 and CO when the holocellulose contents increase. The rapeseed stalks release the lowest amounts of CO_2 and CO, even though their holocellulose content is not the lowest; this may be due to their ash content, which may have a special selective catalytic effect. As shown in Table 1S, Table 2S, and Figure 1S in the Supporting Information, a relatively higher content of K_2SO_4 was observed in the ash from rapeseed stalk, while K_2SO_4 inhibited the CO_2 and CO formation during the cellulose pyrolysis (shown in Figure 1S).

For use as a fuel, the generated gas should present a competitive LHV compared with that produced in biomass air gasification plants, which are popularly used in rural areas. Among these five biomass materials, the lowest LHV is 10.46 MJ/m^3, from the tobacco stems; this is higher than the gas product from a biomass air gasification plant, which has a best LHV of about 7−8 MJ/m^3.[24] Furthermore, the gas products from the rapeseed stalks, rice husks, and bamboo excelled in terms of their LHVs of 14 MJ/m^3. These results suggest that biomass pyrolytic polygeneration can be well adapted to the biomass to produce the desired gaseous fuel.

The compositional distributions of the liquid oil from the different feedstocks are shown in Table 3. The liquid oil from biomass pyrolytic polygeneration comprises 50−65 wt % water, which is higher than the bio-oil from fast pyrolysis, ∼30 wt %.[10,22] Hence, the use of the liquid oils from different biomass materials after pyrolytic polygeneration is challenged by their high water contents. Our previous work reported that the fractional condensation of the liquid oil may be able to handle this challenge by separating fractions with different compositions and allowing the relative enrichment of special compositions.[25]

On the other hand, the biomass pyrolytic polygeneration process tends to produce compositions comprising light molecules such as acids, ketones, furans, cyclopentanes, and phenols, with no sugars or pyrolytic lignins. Hence, the complexity of the liquid oil is less than that from a biomass fast pyrolysis process.[10] Furthermore, another similarity for these five biomass materials is that the contents of furan and cyclopentenes are lower than the other components. In the oil from the cotton stalks, the content of acids and ketones is higher than the other components, with a value as high as 44.76 area %. However, for the rice husks and bamboo, the phenolic content exceeds 45 area %, which suggests that the oils from these two biomass materials can be used for phenol refinement. The rapeseed stalk oil also exhibits a high phenolic content, as much as 37 area %; however, this is equivalent to the acids and ketones content. Hence, the fractional condensation technique may be useful for the utilization of rapeseed-stalk oil as well, to produce two classes of high value chemicals simultaneously.

In contrast to the other biomass materials, the tobacco stems yielded a lower phenols content, but a larger amount of *N*-containing compounds in the liquid oil. As much as 44.18 area % nitrogenated compounds and derivatives were obtained, which reflects the higher *N*-content in the tobacco stem particles. These *N*-compounds and derivatives include pyridines, pyrroles, pyrimidines, and piperidines, which are high value chemicals. Recently, a number of studies have focused on producing these high-value *N*-containing chemicals from biomass.[26] Here, we have shown the possibility of obtaining such compounds from tobacco-stem oil. However, we should emphasize that the *N*-containing compounds must be used properly to avoid secondary environmental pollution from the tobacco stems as a feedstock. Hence, further research on the utilization of the liquid oil from tobacco stems is needed. In summary, when fractional condensation is used in biomass pyrolytic polygeneration, the income from the liquid oil could be increased by using bamboo, rice husks, and rapeseed stalks as feedstocks.

3.4. Char Product Properties. The PSD values of the char products are shown in Figure 4. Compared with the raw

DOI: 10.1021/acs.energyfuels.5b02332
Energy Fuels 2016, 30, 414−422

Table 3. Composition of Liquid-Oil under the Optimal Condition of Biomass Polygeneration for Different Feedstocks[a]

samples	water[b] (wt % of oil)	(area % of result from GCMS) acid and ketones[c]	furan and cyclopentens[b]	phenols[b]	N-containing compound[b]
cotton stalk	64.16(7.39)	44.76(6.77)	15.76(0.99)	27.01(1.71)	8.49(0.44)
rapeseed stalk	63.59(4.18)	31.58(1.45)	11.85(2.06)	37.72(5.64)	ND
tobacco stem	56.25(2.61)	32.94(4.83)	4.08(0.18)	15.52(1.63)	44.18(5.99)
rice husk	48.52(2.87)	30.39(1.33)	14.01(1.55)	45.48(4.50)	ND
bamboo	53.46(1.65)	27.20(4.55)	7.18(0.61)	47.86(7.90)	1.09(0.11)

[a]Numbers enclosed in parentheses are relative error of average value on two analyses. [b]The percentage value is calculated based on the total mass of liquid oil. [c]The percentage value is calculated based on the analysis of organic components in liquid oil by GCMS.

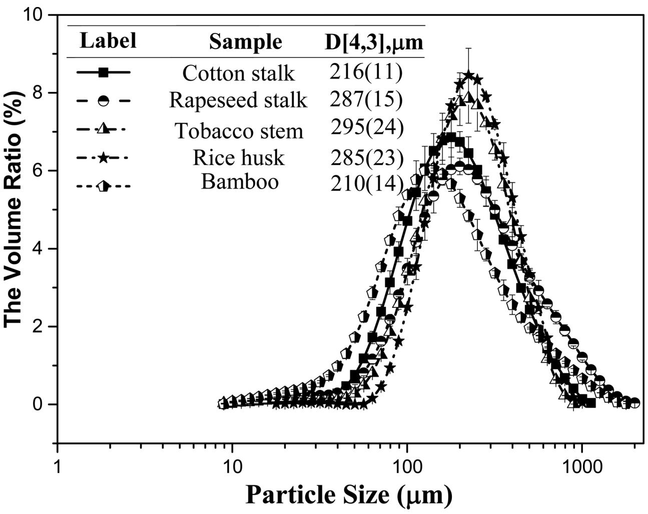

Figure 4. Particle size distribution of chars from different feedstock at 550 °C. Numbers enclosed in parentheses and the error bars are relative error of average value on two analyses.

feedstocks, the centers of the PSDs of the char products shift to finer particles, and the D[4,3] values of all feedstocks are reduced. However, the degree of shrinkage is different for the various feedstocks. Calculating from the D[4,3] values of the chars and raw materials, the shrinkage of the particle volume during pyrolysis is as high as 58% for the cotton stalks and rice husks. This means that the desired volume of the reactor in the pyrolysis zone may be half of that of the nonpyrolysis zone, and the reactor cross-section may be contracted for a continuously operated pyrolytic reactor. The rapeseed stalks, tobacco stems, and bamboo exhibit about 40−44% volume shrinkage, slightly lower than those of the cotton stalks and rice husks, but when the feedstock is changed, the material continuity in the same reactor would not be affected. This suggests that the reactor in a biomass pyrolytic polygeneration system would have good feedstock adaptability.

To evaluate the potential use of the char as an absorbent or as a soil improvement, the pore characteristics and adsorption properties of the chars were analyzed; the results are shown in Table 4 and Figure 5. The chars from cotton stalks, rice husks, and bamboo present good pore properties and have S_{BET} values from 142 to 277 m^2/g. They all have abundant micropores, which account for more than 97% of the pores, as shown in Figure 5. The major difference between these three chars is observed in the mesopore and macropore contents. Rice-husk char has a broad distribution of mesopores, from 2 to 10 nm, whereas narrow mesopore distributions (2−4 nm) are observed in the cotton-stalk and bamboo chars. In terms of macropores, the amount in the rice-husk char is also larger than that from the cotton stalks and bamboo. Generally, abundant micropores are preferred for good adsorption capacity when a material is used as an adsorbent,[27] which is proven by the results for the adsorption of phenol and CO_2. The order of the adsorption capacity for phenol is similar to the order of the micropore content: bamboo > rice husks > cotton stalks > rapeseed stalks ≈ tobacco stems. However, the order for the CO_2 adsorption capacity changes: the cotton-stalk char adsorbs more CO_2 than the rice-husk char, although its number of pores is lower. This may be related to a difference in the basic functional group content.[15,27]

The poor performance in the adsorption of CO_2 and phenol for the rapeseed-stalk and tobacco-stem chars may be due to their poor pore properties. The S_{BET} values of the rapeseed-stalk and tobacco-stem chars are 1.1 and 2.9 m^2/g, respectively, and almost no micropores are observed. However, these two chars possess a good number of large pores, especially those in the range from 10 to 400 nm, and macropores in the tobacco-stem char are the most abundant. Generally, the water adsorption capacity is influenced by these large pores.[28] Hence, the chars from the rapeseed stalks and tobacco stems

Table 4. Pore Structure and Adsorption Properties of Chars for Different Feedstocks

	cotton stalk	rapeseed stalk	tobacco stem	rice husk	bamboo
		Pore Structure[a]			
S_{BET} (m^2/g)	142.0	1.1	2.9	198.5	277.3
pore volume (cm^3/g)	0.068	0.024	0.046	0.043	0.173
		Adsorption Capacity (mg/g)[b]			
water	96.2(0.7)	180.6(14.1)	437.6(24.9)	79.5(2.7)	89.1(2.8)
phenol	7.26(0.39)	3.83(0.36)	3.42(0.16)	9.24(0.57)	9.47(0.50)
CO_2	80.36(4.27)	7.49(0.22)	6.20(0.45)	67.65(5.37)	98.86(6.49)

[a]Analysis was only carried out one trial since the experiment duration was rather long up to 72 h, and the cost also was very high. Furthermore, in this analysis, almost half of obtained sample was used and the sample uniformity was good. [b]Numbers enclosed in parentheses are relative error of average value on two analyses.

DOI: 10.1021/acs.energyfuels.5b02332
Energy Fuels 2016, 30, 414−422

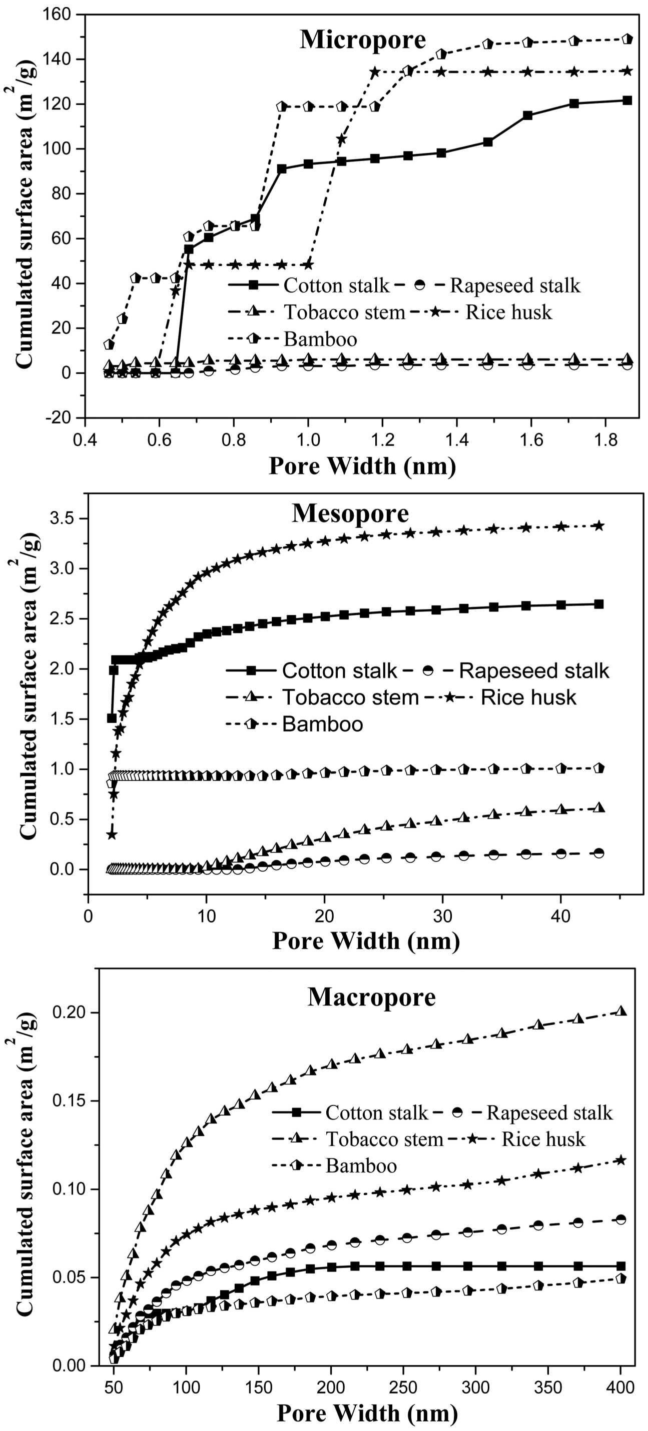

Figure 5. Pore size distribution of chars by DFT.

demonstrate higher water adsorption capacities, especially the latter at 437.6 mg/g, which might be attributed to the synergy between the surface nitrogen functional groups and the good distribution of macropores. These results suggest that these two chars can be used as biochars for soil improvement.[28]

The basic properties as a solid fuel for these chars and the reference coal are shown in Table 5. The lower sulfur content in the chars as compared with the coal means that SO_x pollution would be negligible. Meanwhile, the H content for these chars is also lower than the reference coal. The chars from cotton stalks, rapeseed stalks, and bamboo have higher C and fixed carbon contents, and hence, they have higher LHVs than the coal, particularly the bamboo char which has an LHV of 31.24 MJ/kg. This suggests that, although the rapeseed-stalk char demonstrates poor adsorption properties, it would be suitable for use as a solid fuel. Meanwhile, the chars from the cotton stalks and bamboo would be useful as both adsorbents and solid fuels, and hence, the char products from these two biomass feedstocks may be more in demand and easily saleable. The other two chars, from the rice husks and tobacco stems, have lower LHVs relative to coal, with values below 17 MJ/kg. However, the rice-husk char has a good pore structure that makes it attractive as an adsorbent. Furthermore, the amorphous silica in the rice-husk char is also attractive as a high-value product.[29] Tobacco-stem char has not only the lowest LHV, but also the highest N content (4.14 wt %), which limits it use as a solid fuel. However, the high N content would translate into good nutrient properties when introduced into the soil. Therefore, the best water adsorption capacity and potentially high nitrogen nutrient content increases the attractiveness of tobacco-stem char as a biochar for soil improvement. A higher content of $CaCO_3$ was observed in tobacco stem ash, which was obtained at 600 °C (shown in Table 2S), while the ash content of char was determined at 800 °C, then $CaCO_3$ may be degraded subsequently; the ash content of tobacco char was lower than that of rice-husk char.

Figure 6 shows the combustion properties of the chars based on TGA, and Table 6 shows their ignition and burnout characteristics. The major weight loss for the five chars and reference coal occurs between 300 and 600 °C, which suggests that the chars can well replace the coal in a corresponding combustion system.[30] Chars from tobacco stems and rapeseed stalks have a second peak at the range of 600−800 °C, which may be due to the combustion of residual carbon coated by ash and may decrease the combustion efficiency. The results in Table 6 show that these chars are easily ignited compared with coal, although the chars from the cotton stalks, rice husks, and bamboo can easily burn out. Furthermore, exact for the bamboo char, the DTG_{max} values of the chars from the biomass are far lower than that of coal, due to the annealing effects for these chars.[31] The DTG_{max} value for the bamboo char is similar to that of the reference coal; this may be due to its good pore structure, which can expand the effective surface area during combustion, and its relatively lower ash content, which can promote the possibility of relatively higher contact between the oxygen and carbon material in the char.[32]

4. CONCLUSIONS

Although the feedstocks varied, the products from the biomass pyrolytic polygeneration technology all demonstrated good potential for use as high-value materials. The LHVs of the biogas ranged from 10 to 15 MJ/m^3, and the liquid oils' enrichment in acids, phenols, and *N*-compounds suggests their use as feedstocks for further refinement. The chars from the cotton stalks and bamboo are recommended for use as both solid fuels and adsorbents together, while the silica enrichment in the rapeseed-stalk and rice-husk chars and high N-content in the tobacco-stem char recommend their use as a solid fuel, adsorbent, and biochar, respectively. Overall, the biomass pyrolytic polygeneration process has been shown to exhibit good feedstock adaptability. On the other hand, the correlation between product properties and feedstock characteristics was performed. The ash and volatile contents of feedstock would be useful in predicting the product yields from the biomass pyrolytic polygeneration. When lignin increases in biomass, the

DOI: 10.1021/acs.energyfuels.5b02332
Energy Fuels 2016, 30, 414−422

Table 5. Proximate and Ultimate Analysis of Chars for Different Feedstocks Obtained at 550 °C[a]

	cotton stalk	rapeseed stalk	tobacco stem	rice husk	bamboo	bituminous coal
			Ultimate Analysis (daf, wt %)[b]			
C	90.26(6.52)	86.84(8.61)	63.79(6.65)	85.88(3.72)	91.26(8.32)	81.30(4.77)
H	2.14(0.07)	2.11(0.14)	1.35(0.14)	2.61(0.27)	2.50(0.07)	4.87(0.20)
N	1.26(0.10)	0.20(0.02)	4.14(0.20)	0.76(0.05)	0.60(0.02)	0.95(0.10)
S	0.22(0.02)	0.31(0.03)	0.70(0.02)	0.14(0.01)	0.13(0.01)	2.70(0.12)
O[c]	6.12(0.55)	10.54(0.56)	30.01(2.88)	10.61(0.57)	5.50(0.16)	10.17(0.92)
			Proximate Analysis (ad, wt %)[b]			
moisture	6.22(0.34)	4.86(0.39)	5.03(0.26)	3.12(0.32)	3.46(0.17)	2.79(0.26)
volatile	12.29(1.24)	32.31(3.73)	37.40(4.09)	26.10(1.95)	29.69(1.77)	32.32(1.51)
ash	7.89(0.22)	13.38(0.74)	38.86(3.82)	41.84(1.76)	2.20(0.24)	24.91(0.72)
fixed carbon[c]	73.60(8.07)	49.44(4.60)	20.56(0.65)	28.92(1.78)	65.07(7.38)	39.98(1.94)
LHV (MJ/kg)[b]	27.97(1.76)	24.68(2.42)	14.67(0.80)	16.76(0.81)	31.24(1.84)	22.29(1.73)

[a]ad, air-dry basis; d, dry basis. [b]Numbers enclosed in parentheses are relative error of average value on two analyses. [c]By difference.

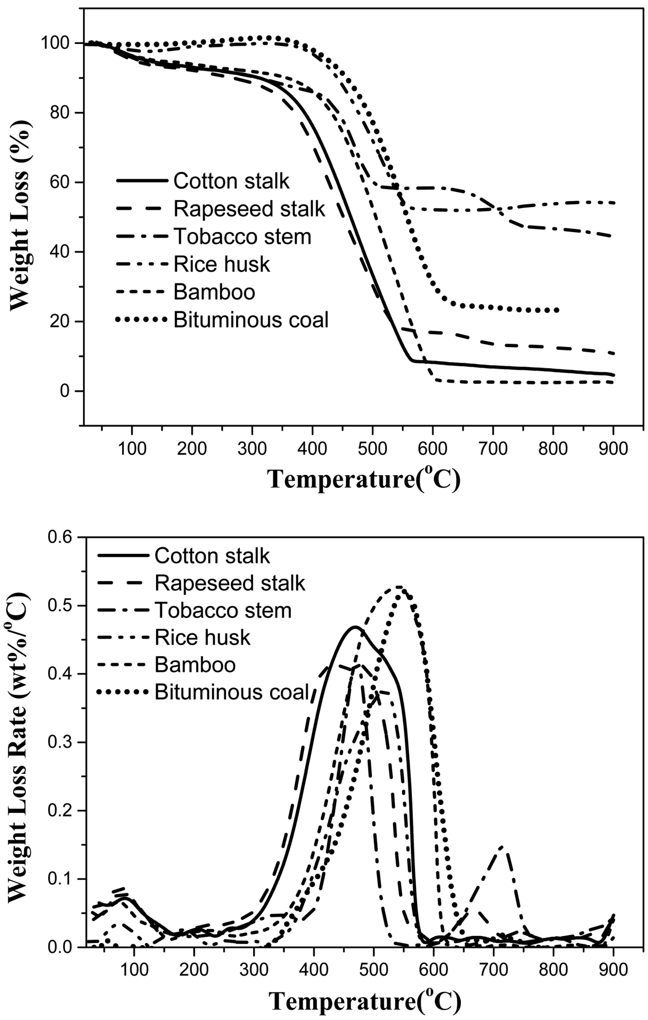

Figure 6. Combustion property of chars based on TG analysis.

CH_4 yield increases; while when the holocellulose increases, the CO_2 and CO yield increase. It was also interesting that K_2SO_4 in rapeseed stalk could inhibit the formation of CO_2 and CO.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.energyfuels.5b02332.

Table 1 composition of the ash content analyzed by XRF; Table 2 phase analysis of the ash by XRD; Figure 1 CO_2 and CO yield of the mixture of cellulose with different potassium salts (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*Mailing address: 1037 Luoyu Road, Wuhan, Hubei 430074, P. R. China. E-mail: wxhwhhy@sina.com. Tel.: 086 + 027-87542417-8211. Fax: 086 + 027-87545526 (X.W.).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors wish to express great appreciation for the financial support from National Natural Science Foundation of China (51406061), Special Fund for Agro-scientific Research in the Public Interest (201303095), Key Projects of National Fundamental Research Planning (2013CB228102), China Postdoctoral Science Foundation Grant (2014M552037), Science and technology support program of Hubei Province (2014BBB009). The study also benefits from the technical support from the Analytical and Testing Center at Huazhong University of Science & Technology (http://atc.hust.edu.cn).

Table 6. Ignition and Burnout Characteristic of Chars and Coal[a]

	cotton stalk	rapeseed stalk	tobacco stem	rice husk	bamboo	bituminous coal
T_i (°C)	361(5)	345(21)	406(6)	423(31)	414(12)	453(8)
T_f (°C)	572(54)	642(15)	680(3)	550(36)	597(44)	610(22)
T_{max}(°C)	469(45)	437(15)	471(8)	517(23)	542(10)	546(34)
DTG_{max} (wt %/°C)	0.457(0.026)	0.412(0.034)	0.420(0.027)	0.376(0.021)	0.527(0.036)	0.523(0.041)

[a]Numbers enclosed in parentheses are relative error of average value on two analyses.

DOI: 10.1021/acs.energyfuels.5b02332
Energy Fuels 2016, 30, 414−422

REFERENCES

(1) Guo, M. X.; Song, W. P.; Buhain, J. Bioenergy and biofuels: History, status, and perspective. *Renewable Sustainable Energy Rev.* **2015**, *42*, 712−725.

(2) Zhao, X. G.; Feng, T. T.; Ma, Y.; Yang, Y. S.; Pan, X. F. Analysis on investment strategies in China: the case of biomass direct combustion power generation sector. *Renewable Sustainable Energy Rev.* **2015**, *42*, 760−772.

(3) Ji, L. Q. An assessment of agricultural residue resources for liquid biofuel production in China. *Renewable Sustainable Energy Rev.* **2015**, *44*, 561−575.

(4) Chen, Y.; Hu, W.; Sweeney, S. Resource availability for household biogas production in rural China. *Renewable Sustainable Energy Rev.* **2013**, *25*, 655−659.

(5) Zhao, X. G.; Tan, Z. F.; Liu, P. K. Development goal of 30 GW for China's biomass power generation: Will it be achieved? *Renewable Sustainable Energy Rev.* **2013**, *25*, 310−317.

(6) Roy, P. C.; Datta, A.; Chakraborty, N. An assessment of different biomass feedstocks in a downdraft gasifier for engine application. *Fuel* **2013**, *106*, 864−868.

(7) Strezov, V.; Popovic, E.; Filkoski, R. V.; Shah, P.; Evans, T. Assessment of the Thermal Processing Behavior of Tobacco Waste. *Energy Fuels* **2012**, *26* (9), 5930−5935.

(8) Kim, K. H.; Kim, T. S.; Lee, S. M.; Choi, D.; Yeo, H.; Choi, I. G.; Choi, J. W. *Renewable Energy* **2013**, *50*, 188−195.

(9) Aysu, T.; Kucuk, M. M. Biomass pyrolysis in a fixed-bed reactor: Effects of pyrolysis parameters on product yields and characterization of products. *Energy* **2014**, *64*, 1002−1025.

(10) Mohan, D.; Pittman, C. U.; Steele, P. H. Pyrolysis of wood/biomass for bio-oil: A critical review. *Energy Fuels* **2006**, *20* (3), 848−889.

(11) Jeguirim, M.; Bikai, J.; Elmay, Y.; Limousy, L.; Njeugna, E. Thermal characterization and pyrolysis kinetics of tropical biomass feedstocks for energy recovery. *Energy Sustainable Dev.* **2014**, *23*, 188−193.

(12) Yang, H. P.; Yan, R.; Chen, H. P.; Zheng, C. G.; Lee, D. H.; Liang, D. T. In-depth investigation of biomass pyrolysis based on three major components: Hemicellulose, cellulose and lignin. *Energy Fuels* **2006**, *20* (1), 388−393.

(13) Gomez-Monedero, B.; Bimbela, F.; Arauzo, J.; Faria, J.; Ruiz, M. P. Pyrolysis of Red Eucalyptus, Camelina Straw, and Wheat Straw in an Ablative Reactor. *Energy Fuels* **2015**, *29* (3), 1766−1775.

(14) Yang, Y.; Brammer, J. G.; Mahmood, A. S. N.; Hornung, A. Intermediate pyrolysis of biomass energy pellets for producing sustainable liquid, gaseous and solid fuels. *Bioresour. Technol.* **2014**, *169*, 794−799.

(15) Chen, Y. Q.; Yang, H. P.; Wang, X. H.; Zhang, S. H.; Chen, H. P. Biomass-based pyrolytic polygeneration system on cotton stalk pyrolysis: Influence of temperature. *Bioresour. Technol.* **2012**, *107*, 411−418.

(16) Shi, X. H.; Wang, J. A comparative investigation into the formation behaviors of char, liquids and gases during pyrolysis of pinewood and lignocellulosic components. *Bioresour. Technol.* **2014**, *170*, 262−269.

(17) Yang, H.; Liu, B.; Chen, Y.; Chen, W.; Yang, Q.; Chen, H. Application of biomass pyrolytic polygeneration technology based on retort reactor in China. *Bioresour. Technol.* **2016**, *200*, 64.

(18) Chen, L.; Wang, X. H.; Yang, H. P.; Lu, Q.; Li, D.; Yang, Q.; Chen, H. P. Study on pyrolysis behaviors of non-woody lignins with TG-FTIR and Py-GC/MS. *J. Anal. Appl. Pyrolysis* **2015**, *113*, 499−507.

(19) Chen, Y.; Yang, H.; Yang, Q.; Hao, H.; Zhu, B.; Chen, H. *Bioresour. Technol.* **2014**, *156*, 70−77.

(20) Chen, Y. Q.; Liu, B.; Yang, H. P.; Yang, Q.; Chen, H. P. Evolution of functional groups and pore structure during cotton and corn stalks torrefaction and its correlation with hydrophobicity. *Fuel* **2014**, *137*, 41−49.

(21) Yang, Z. X.; Zhang, S. H.; Liu, L.; Li, X. P.; Chen, H. P.; Yang, H. P.; Wang, X. H. Combustion behaviours of tobacco stem in a thermogravimetric analyser and a pilot-scale fluidized bed reactor. *Bioresour. Technol.* **2012**, *110*, 595−602.

(22) Oasmaa, A.; Solantausta, Y.; Arpiainen, V.; Kuoppala, E.; Sipila, K. Fast Pyrolysis Bio-Oils from Wood and Agricultural Residues. *Energy Fuels* **2010**, *24*, 1380−1388.

(23) Begum, S.; Rasul, M. G.; Akbar, D.; Ramzan, N. Performance Analysis of an Integrated Fixed Bed Gasifier Model for Different Biomass Feedstocks. *Energies* **2013**, *6* (12), 6508−6524.

(24) Han, J. Y.; Mol, A. P. J.; Lu, Y. L.; Zhang, L. Small-scale bioenergy projects in rural China: Lessons to be learnt. *Energy Policy* **2008**, *36* (6), 2154−2162.

(25) Sui, H. Q.; Yang, H. P.; Shao, J. G.; Wang, X. H.; Li, Y. C.; Chen, H. P. Fractional Condensation of Multicomponent Vapors from Pyrolysis of Cotton Stalk. *Energy Fuels* **2014**, *28* (8), 5095−5102.

(26) Xu, L. J.; Han, Z.; Yao, Q.; Deng, J.; Zhang, Y.; Fu, Y.; Guo, Q. X. Towards the sustainable production of pyridines via thermo-catalytic conversion of glycerol with ammonia over zeolite catalysts. *Green Chem.* **2015**, *17* (4), 2426−2435.

(27) Zhang, X.; Zhang, S. H.; Yang, H. P.; Feng, Y.; Chen, Y. Q.; Wang, X. H.; Chen, H. P. Nitrogen enriched biochar modified by high temperature CO2-ammonia treatment: Characterization and adsorption of CO2. *Chem. Eng. J.* **2014**, *257*, 20−27.

(28) Sun, F. F.; Lu, S. G. Biochars improve aggregate stability, water retention, and pore- space properties of clayey soil. *J. Plant Nutr. Soil Sci.* **2014**, *177* (1), 26−33.

(29) Carmona, V. B.; Oliveira, R. M.; Silva, W. T. L.; Mattoso, L. H. C.; Marconcini, J. M. Nanosilica from rice husk: Extraction and characterization. *Ind. Crops Prod.* **2013**, *43*, 291−296.

(30) Chen, Y.; Zhi, G.; Feng, Y.; Liu, D.; Zhang, G.; Li, J.; Sheng, G.; Fu, J. *Environ. Sci. Technol.* **2009**, *43* (24), 9495−9500.

(31) Shim, H.-S.; Hurt, R. H. *Energy Fuels* **2000**, *14* (2), 340−348.

(32) Koppejan, J.; Van Loo, S. *The handbook of biomass combustion and co-firing*; Routledge, 2012.

DOI: 10.1021/acs.energyfuels.5b02332
Energy Fuels 2016, 30, 414−422