Fuel 113 (2013) 266–273

Contents lists available at SciVerse ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Assessment of pyrolysis polygeneration of biomass based on major components: Product characterization and elucidation of degradation pathways

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HIGHLIGHTS

- The cleavage of glycosidic bond was the first step for cellulose and xylan pyrolysis.
- Furans were produced accompanied by the formation of anhydro saccharides.
- The surface of cellulose formed a melted phase at low temperature.
- The depolymerization and dealkylation were the primary reactions during lignin pyrolysis.
- For the biomass polygeneration system, it is not suggested to pyrolyze over 750 °C.

ARTICLE INFO

Article history:
Received 20 November 2012
Received in revised form 17 May 2013
Accepted 18 May 2013
Available online 6 June 2013

Keywords:
Biomass major components
Polygeneration
Anhydro saccharides
Alkylated derivates
Polymerization

ABSTRACT

The pyrolysis behaviors of biomass components (cellulose, hemicellulose and lignin) were studied at various temperatures and the evolution mechanisms of the pyrolytic products were investigated with variant approaches. Anhydro-saccharides, light oxygenates and phenols were the main compounds in pyrolytic bio-oil from cellulose, xylan and lignin, respectively. The subsequent degradation of saccharides involved was the fragmentation to generate gaseous and light oxygenates, and these compounds formed competitively against the generation of phenols and aromatics. CO released from cellulose originated from the decomposition of saccharides while that from xylan was more likely to derive from the decarbonylation of ketones and decarboxylation of acids. H_2, CH_4 and light hydrocarbons formed during aromatization when exceeded 650 °C. Cellulose was the main contributor to the porosity of biomass chars and lignin was the main contributor for the mass of biomass chars. Furthermore, a new pathway for the pyrolysis of biomass and insights into how biomass materials used more efficiently and comprehensively, were provided.

1. Introduction

Biomass is a renewable substitute of petroleum that can be converted to fuel gas, solid char and liquid oil or other chemicals through thermochemical processes, such as pyrolysis, combustion and gasification. Among those technologies, pyrolysis is one of the most promising conversion routes and plays a crucial role in biomass thermochemical conversion [1,2]. Biomass contains three major components (cellulose, hemicellulose and lignin) along with minor amounts of extractives (proteins, fatty, acids, resins) and ash [3]. Different kinds of biomass have different compositions. The biomass constituents are found to pyrolyze at different rates and by different pathways [4,5]. It is suggested that the pyrolysis of any biomass can be considered as the superposition of the three major components [6]. So the elucidation of the pyrolytic behavior of individual components of biomass is essential to a better understanding of the intricate pyrolysis process of biomass.

Till now, numerous studies were carried out to investigate the degradation mechanism of biomass major components based on the properties of released products, such as gases [5,7–9], liquids [10–16] or solids [17,18]. Yang et al. [5] performed the pyrolysis of hemicellulose, cellulose and lignin in TGA and packed bed focusing on the gas releasing behaviors. The formation characteristics of gas compounds from cellulose pyrolysis were also investigated using entrained-flow reactor (EFR) [7] and FTIR at various conditions [8]. It was found that the formation of CO strongly depended on the temperature. CO_2 was mainly produced by the primary pyrolysis and barely affected by additional heating. Bassilakis et al. [9] studied the gas released from pyrolysis of D-glucose, chlorogenic acid and xylan using FTIR quantitatively. The liquids from pyrolysis are also an important indicator for the elucidation of

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http://dx.doi.org/10.1016/j.fuel.2013.05.061

decomposition pathways. The effects of temperature and residence time on the formation of main liquid products from cellulose and hemicellulose were performed by Lu [10] and Shen [11,12] using Py–GC/MS and Py–GC–FTIR. Lu found that levoglucosan exhibited good thermal stability and its formation was favored at elevated pyrolysis temperature and time. However, Shen indicated that the yield of levoglucosan is inhibited at the elevated temperature. Patwardhan [13,14] pyrolyzed corn stover lignin and hemicellulose using a micro-pyrolyzer coupled with a GC–MS/FID and the liquid products were characterized. Guo et al. [15] and Wang et al. [16] analyzed the bio-oil from the pyrolysis of milled wood lignin (MWL). The degradation of MWL was dominated by the demethylation reaction and the cleavage of aliphatic hydroxymethyl at the γ-position, followed by the cracking of C_α—C_β and C_4—C_α bonds. Hosoya et al. [17] investigated the pyrolysis of the model compounds of lignin in a closed ampoule reactor and found that the o-quinone methide was a key intermediate for lignin char formation during pyrolysis. Sharma et al. [18] analyzed the lignin char obtained under both pyrolytic and oxidative atmospheres and identified the surface area, presence of inorganics and aromaticity of char as potentially important factors in the formation of PAHs.

Other studies had focused on the pyrolysis parameters for maximizing the yields of individual products. Shen et al. found that the maximum bio-oil yield from cellulose was 72% at 580 °C, while that for hemicellulose was 45% at 475 °C [12,19]. The activated carbon was produced from wood components, cellulose, lignin, xylan and characterized by Khezami et al. [20]. It was found that only the char from cellulose had a significant BET-surface area of pores. Ferdous et al. [21] pyrolyzed Alcell and Kraft lignin in a fixed-bed microreactor to produce H_2 and medium Btu gas. The production of medium Btu gas was over 800 ml/g at 800 °C. As the total synthesis gas production was over 60 mol% of total gas, it could be an excellent candidate for liquid fuel production through Fischer–Tropsch synthesis. Piskorz et al. [22] performed the flash pyrolysis of cellulose to obtain levoglucosan and anhydro-oligosaccharides.

Although the pyrolysis of the biomass and its major components was investigated by many researchers, most of them focused on the possible mechanisms of the individual components and optimum conditions for producing single products. Generally, the yield and properties of gas, liquid and solid products from biomass pyrolysis were different and the optimum temperature for each product may vary. The by-products from biomass pyrolysis carry low economic value and are difficult to further process. Hence, the traditional processes may no longer meet the recent environmental and economic requirements.

The biomass-based polygeneration is one of the promising options to solve this problem as the production of solid char, liquid oil, and biogas can be synergistically optimized. Therefore, more efforts should be made to study the pyrolytic mechanisms of the three main components by taking into account the properties of products released comprehensively, i.e. products in gas, oil, solid forms. In this study, the pyrolysis characteristics of the major components of biomass were investigated to understand the mechanisms of their degradation thoroughly. Meanwhile, the relationship between biomass compositions and polygeneration was studied by examining the properties of the released products. Our findings may help better understand the mechanism of biomass pyrolysis and develop more efficient biomass utilization process.

2. Experimental

2.1. Materials

The three main components (cellulose, hemicellulose, and lignin) are provided by Sigma–Aldrich Co., Ltd. Cellulose, in the form of white and microcrystalline powders of 20 μm particle size. Alkaline lignin is in the form of dark brown powders. Customarily, xylan has been widely used as a model compound of hemicellulose in pyrolysis process. In this study, it is isolated from birchwood and in the form of yellow powder. The results of proximate and elemental analysis are listed in Table 1. It can be seen that the volatile content in cellulose is the highest (up to 95.5%) whereas that in lignin is the lowest (58.9%). Cellulose and xylan contains more oxygen and hydrogen than lignin due to the abundant hydroxyl group in carbohydrates.

2.2. Pyrolysis setup and procedures

Pyrolysis was conducted in a bench-scale tubular reactor (internal diameter 46 mm, length 400 mm). The experimental apparatus mainly consisted of a fixed-bed reactor, a controller system for temperature and purging gas and the systems for condensation, purification and analysis. Prior to each trial, the reactor was heated up to the designated temperature with nitrogen (99.999% 200 ml/min) as carrier gas and kept constant for 10 min. Afterwards, two porcelain arks with a thin layer of biomass particles (1 ± 0.001 g) were quickly pushed into the center of the reactor. The condensable volatiles were collected in the ice-water condenser while the non-condensable volatiles were filtered through a glass wool filter and dried using silica gel. After 15 min, the pyrolysis was finished and the sample holder was moved to the inlet and cooled down with nitrogen (1 L/min) to ambient temperature. The amounts of liquid bio-oil and char fractions were determined based on the weight differences of the glass tube and porcelain arks. The amount of gaseous products was calculated by combining all the gases collected during pyrolysis and converted from volume to weight percentage at ambient temperature and atmospheric pressure (the volume of 1 mol gas equals 24.45L at 1 atm and 25 °C) [23]. During the pyrolysis process, the mass balance during pyrolysis process was among 90–113%, which indicated that the process was feasible. Also, for each trial, it was repeated thrice with higher reproducibility with the relative error within 10% and all measured data presented were the average value.

2.3. Measurement of pyrolysis products

2.3.1. Determination of gaseous products

A dual-channel micro-GC system (Micro-GC 3000A, Agilent Technologies, USA), equipped with thermal conductivity detectors, was used to analyze quantitatively the gaseous products. Channel A was molecular sieve 5A for detecting H_2, CO, CH_4 at 110 °C and channel B was PLOT U for checking CO_2, C_2H_2, C_2H_4 and C_2H_6 at 105 °C. A standard gas composed of H_2(9.83 vol%), CO(20.7 vol%), CH_4(9.89 vol%), CO_2(20.1 vol%), C_2H_2(0.49 vol%), C_2H_4(0.5 vol%), C_2H_6(0.5 vol%) with N_2(37.99 vol%) was used as balance gas to calibrate gas species. Each gas sample was measured thrice to get the average value.

2.3.2. Specification of liquid oil

The composition of liquid oil was specified in detail using gas chromatography-mass spectroscopy (GC–MS, 7890A/5975C, Agilent) with a quartz capillary column (DB-WAX, length, 30 m; internal diameter, 250 μm; film thickness, 0.25 μm). The GC oven temperature program began with a 3 min hold at 50 °C followed by heating to 250 °C at 20 °C/min. The final temperature was held for 18 min. An injector temperature was set at 250 °C and a split ratio was 2:1. In each trial, 1 μL of the sample was injected. The flow rate of the carrier gas (Helium) for the column was 1.0 ml/min. After 4.5 min of solvent delay, the sample was directly introduced into the ion source of a DB-WAX series mass-selective detector operated in an electron-impact ionization mode and scanned

Table 1
Proximate and ultimate analyses of biomass three components.

Samples	Proximate analysis (wt%, db.)			Ultimate analysis (wt%, daf.)					Molar (H/C)	LHV (MJ/kg)
	V	FC	Ash	C	H	N	S	O^d		
Cellulose	95.5	4.5	0.0	42.7	6.2	0.03	0.05	51.0	1.74	15.47
Hemicellulose	76.8	21.4	1.8	41.6	5.7	0.02	0.03	52.6	1.65	15.31
Lignin	58.9	36.9	4.2	48.3	4.9	0.1	3.1	43.6	1.22	19.31

The O content was determined by difference.

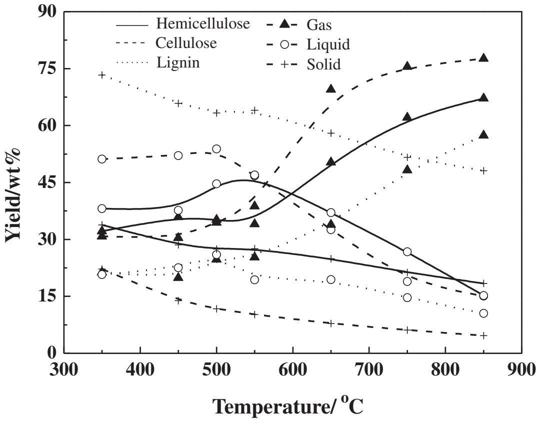

Fig. 1. Effect of temperature on product distribution.

from m/z 30 to 500. The GG1034C Chemstation, with a National Bureau of Standard library, was used to identify each compound based on the retention time and the matching mass spectrum of the standards in the spectral library.

2.3.3. Properties of solid char

The pore structure of the solid chars was characterized using automatic adsorption equipment (Micromeritics, ASAP 2020, USA). To obtain the information related to the micro-pore structure, a relatively low adsorption pressure of 10^{-6} were applied (P/P_0), and the N_2-adsorption isotherm was obtained at relative pressures (P/P_0) ranging from 10^{-6} to 0.995. The surface area (S_{BET}), micro-pore surface area (S_{mic}) and micro-pore volume (V_{mic}), total volume (V) of the solid products at varying temperatures were determined by Brunauer-Emmett-Teller (BET) method, t-plot method and single point adsorption analysis, respectively.

Proximate analysis of the three components was conducted by using ASTM standards. Ultimate analyses of the dried samples for carbon, hydrogen, nitrogen, and sulfur were carried out with a CHNS/O elementary analyzer (Vario Micro cube, Germany). The calorimetric values of the dried samples were measured by bomb calorimeter (Parr 6300, USA).

3. Results and discussion

3.1. Product distribution property

The product distribution of biomass major components is shown in Fig. 1. It can be seen that temperature exerts a great influence on the distributions of products. For cellulose, the mass loss of char was 14.4 wt% from 350 °C to 650 °C but only 3.2 wt% as the temperature increased from 650 °C to 850 °C. This suggested that the devolatilization of cellulose mainly occurred at low temperature. The increase in yield of gas was accompanied by decreases in the yields of liquid oil and bio-char. A maximum bio-oil yield of 53.8 wt% was obtained at 500 °C, which is consistent with the results of other studies [19]. As the temperature exceeded 550 °C, the yield of liquid oil decreased considerably. On the contrary, the amount of gas increased remarkably. It indicated that the gas was derived from the decomposition of primary volatiles. When the temperature rose up to 750–850 °C, the gas evolution rate was lowered.

With regard to xylan and lignin, different yields were found for the pyrolysis products. Among the three components, the bio-char yield of the lignin (75–50%) was the highest, followed by xylan (35–25%) and cellulose (23–5%). Therefore, lignin can be considered as the main contributor to the mass of biomass chars, which is consistent with previous study [24]. This may result from the fact that lignin is the most thermally resistant among the three main components [2,4] and contains the highest content of fixed carbon. Xylan and cellulose has higher liquid (40–50%) and gas yields (~30%), while that of lignin is quite low. It might be due to the fact that xylan and cellulose decompose more easily. Xylan generated less liquid oil and more gas than cellulose as the temperature was lower than 500 °C. When the temperature exceeded 550 °C, such observation was revised. It indicated that the liquid oil from xylan decomposed more easily than that of cellulose at low temperature (<550 °C) whereas that from cellulose was more prone to secondary cracking at elevated temperature.

Generally, the gas, liquid and solid products were always generated during pyrolysis, but the proportions could vary greatly over a wide range owing to various contents of three components in biomass [3]. Therefore, different operation parameters should be set for the biomass polygeneration of different biomass feedstocks.

3.2. Identification of gaseous products

The profiles of gas distribution at different temperature are plotted in Fig. 2. The gaseous products of the major components are mainly composed of H_2, CH_4, CO and CO_2 along with trace light hydrocarbons, such as C_2H_6 and C_2H_4. As shown in Fig. 2, CO_2 was the predominant component in gaseous pyrolytic products of cellulose at temperature below 450 °C. It was assumed that CO_2 was derived from the decarboxylation and dehydration reaction [11,12,25], which occured in primary reaction or early stage of cellulose pyrolysis [8]. On the contrary, the yield of CO was only 5.5 wt% at 350 °C and increased to a small extent at 450 °C. With the temperature increasing further, the amount of CO_2 changed slightly, which is consistent with other studies [19]. It showed that the releasing of CO_2 is predominated at low temperature. However, the formation of CO_2 might be inhibited at high temperature due to the exothermic property of decarboxylation [25].

The evolution rate of CO was enhanced significantly at 550–650 °C and gave rise to the notable increase in total gas yield. This demonstrated that severe secondary reaction had occurred. Moreover, decarbonylation was endothermic. Hence, the secondary reaction was further accelerated [25]. The evolution of CO at 750–850 °C was similar in trend with that of total gas yield, probably because the decomposition of volatile was weakened. On the contrary, condensation for solid char might be enhanced at high temperature as char yield in this study was significantly higher

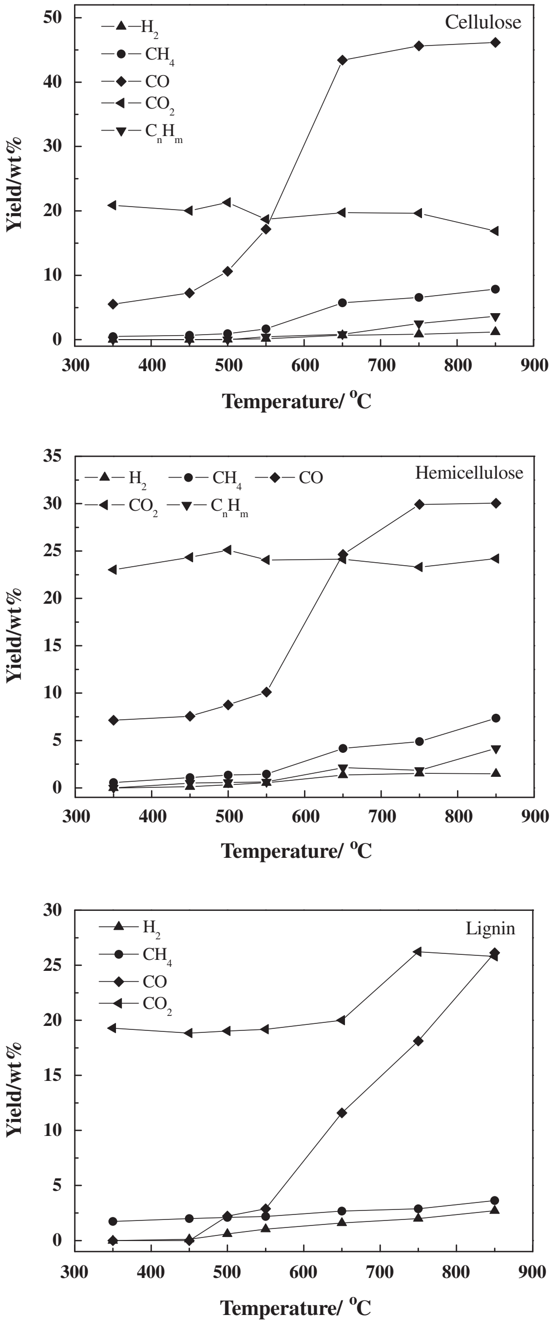

Fig. 2. Gas yield of biomass three components at different temperature.

(7 wt%) than the result reported by other studies [12]. The yield of CH_4 and light hydrocarbons exhibited an evident increase only when the temperature exceeded 550 °C. It suggested that these hydrocarbons presumably originated from the secondary reactions. Fig. 2 showed that the general trend of the gas releasing characteristic of xylan pyrolysis was similar to that of cellulose, probably because both cellulose and xylan are polysaccharides. However, there are also dissimilarities in the amount of gas released. The yield of CO_2 from xylan was slightly higher than cellulose due to its higher carboxyl content. Nevertheless, xylan generated less CO but more light hydrocarbons. This indicated that the formation of CO from xylan may be different from that of cellulose.

In the case of lignin, small amount of CO was generated at 350–450 °C. However, the yield of CO increased substantially as the temperature increased further. It might be due to the decarboxylation process in the aromatic condensation of lignin [26]. The yield of CH_4 from lignin was significantly higher than that of cellulose and xylan at 350–450 °C. Methoxyl was considered to be the precursor of CH_4[5]. Therefore, it seemed that methoxyl was sensitive to temperature. Although lignin had the highest content of methoxyl group, the yield of CH_4 was not as high as expected at elevated temperature (>650 °C). One plausible explanation was that a large proportion of CH_4 might be derived from the secondary cracking of volatiles at higher temperature. In addition, the trend of the yield of H_2 was similar to that of CH_4 suggesting that the formation of H_2 might be accompanied by the generation of CH_4.

Pyrolytic gas of high quality, such as higher calorific value and consistent compositions is important for biomass utilization. With the calorific value over 13 MJ/m^3 at 650 °C, the gas from cellulose and xylan can be used for household cooking and industrial heating. In addition, gaseous products from cellulose and xylan can be used to obtain H_2, CO, etc. H_2 and CH_4 released from lignin pyrolysis were high in content, which was favorable for reforming to obtain H_2. Furthermore, the ratio of CO/H_2 was about 1, which was suitable for methanol synthesis.

3.3. Properties of the liquid products

The composition of bio-oil from cellulose, xylan and lignin pyrolysis is complex with over 100 hydrocarbons, and the present study focuses on 27 main components as shown in Table 2. Furthermore, since it is difficult to calibrate and analyze the oil species quantitatively, only the relative chromatographic peak area of bio-oil species is used to represent the releasing property of bio-oil during biomass pyrolysis [10].

Levoglucosan (LG) was the predominated component in cellulose bio-oil accompanied by a small amount of 1,4:3,6-dianhydro-α-D-glucopyranose, 1,6-anhydro-D-glucofuranose produced. The yield of light oxygenates, such as acetic acid increased slightly whereas 1,4:3,6-dianhydro-a-D-glucopyranose decreased remarkably as the temperature increased from 350 °C to 550 °C. This suggested that these light oxygenates might be originated from the decomposition of the anhydro saccharides. The plausible decomposition pathway for anhydro saccharides might be the ring-opening. A high yield of LG was obtained even at 550 °C, demonstrating its high thermal stability, which is consistent with other studies [10,27]. As the temperature increased further to 650 °C, the yield of LG decreased remarkably. Meanwhile, the yield of acetic acid and phenol showed an abrupt increase. The yield of gaseous products was also enhanced significantly. Hence, it can be concluded that the decomposition of LG gave rise to the formation of these products. The bicyclic structure of LG could be opened with light oxygenates or radicals formed through the breaking of the C—O bond between C_1 and C_2[7]. As shown in Table 2, the yield of phenols increased remarkably and naphthalene was also detected at 650 °C. However, no aromatic rings were found in cellulose structure. Therefore, the phenols and aromatics were formed by the polymerization of fragments or radicals, such as propargyl or cyclopentadienyl radicals [28]. The above results also suggested a competitive relationship between the generation of light oxygenates and phenols and aromatics. Meanwhile, the formation of the former is predominated at low temperature. As the temperature rose up to 750–850 °C, no LG and low molecular compounds were detected and aromatics were massively generated, suggesting that the polymerization and aromatization might be predominated.

Furans were typical compounds from cellulose and biomass pyrolysis. It is evident from Table 2 that the yield of furans in bio-oil decreased continuously, suggesting that furans and anhydro saccharides might be generated simultaneously. Studies indicated that the furfural was derived from the secondary reaction of

Table 2
Main composition of pyrolysis bio-oil of biomass three components.

No.	Species	Cellulose						Hemicellulose						Lignin					
		350	450	550	650	750	850	350	450	550	650	750	850	350	450	550	650	750	850
1	2-Propanone, 1-hydroxy-	0.9	1.0	3.5	7.8	–	–	16.3	13.2	14.8	3.6	–	–	–	–	–	–	–	–
2	2-Cyclopenten-1-one	0.9	1.0	1.1	0.8	–	–	2.1	2.1	2.2	–	–	–	–	–	–	–	–	–
3	1-Hydroxy-2-butanone	0.4	0.5	0.8	1.2	–	–	16.4	10.7	11.3	2.1	–	–	–	–	–	–	–	–
4	Acetic acid	3.5	2.2	4.3	9.2	1.0	–	15.6	14.5	15.4	13.3	0.5	–	–	–	–	–	–	–
5	Furfural	9.8	4.6	2.4	1.8	–	–	3.6	2.6	1.8	0.7	–	–	–	–	–	–	–	–
6	5-methyl furfural	2.0	1.2	1.0	0.6	–	–	–	–	–	–	–	–	–	–	–	-	–	–
7	5-hydroxymethylfurfural	3.6	1.8	1.1	1.2	–	–	–	–	–	–	–	–	–	–	–	–	–	–
8	Propanoic acid	–	1.2	2.3	4.3	–	–	6.9	5.2	3.9	5.1	–	–	–	–	–	–	–	-
9	Naphthalene	–	–	–	0.9	4.6	27.2	–	0.2	0.8	2.3	6.1	16.9	2.3	1.3	1.9	2.3	4.4	6.9
10	Naphthalene,-methyl	–	–	–	1.6	5.9	3.1	–	–	–	2.9	7.9	5.4	–	–	–	2.0	3.8	4.5
11	Naphthalene,-ethyl	–	–	–	1.7	0.4	–	–	–	–	0.6	0.2	0.4	–	–	–	–	–	–
12	Naphthalene, 2-ethenyl-	–	–	–	0.6	2.6	1.7	–	–	–	1.5	3.1	3.0	–	–	–	–	–	–
13	Naphthalene, 2,6-dimethyl-	–	-	–	0.5	1.5	0.5	–	–	–	3.3	1.6	3.1	–	–	–	–	1.2	4.6
14	1,2-Cyclopentanedione, 3-methyl-	1.8	1.2	0.9	–	–	–	2.1	2.3	3.3	0.5	–	–	–	–	-	–	–	–
15	Phenol	–	1.8	2.2	10.5	20.4	4.5	–	–	–	13.0	14.6	0.6	14.1	23.3	41.6	30.2	16.9	1.4
16	Phenol, 3-methyl-	–	0.3	0.4	4.7	6.3	0.4	2.0	3.0	9.7	14.4	6.7	–	5.2	12.9	21.5	14.0	9.4	–
17	Phenol, 2-ethyl-	–	–	0.9	2.2	0.5	–	–	–	–	–	–	–	0.9	–	1.5	1.3	–	–
18	Phenol, 3,4-dimethyl-	–	0.2	1.0	1.0	0.4	–	0.9	2.9	9.5	3.3	–	–	–	1.8	4.0	1.7	1.1	–
19	Biphenylene	–	–	–	0.9	9.1	7.9	–	–	–	2.6	11.7	13.1	–	–	–	–	–	–
20	Dibenzofuran	–	–	–	0.7	2.8	1.3	–	–	–	0.8	1.3	0.9	–	–	–	–	–	–
21	Fluorene	–	–	–	1.2	8.5	6.9	–	–	–	3.0	13.5	7.6	–	–	–	–	1.1	1.2
22	1,4:3,6-Dianhydro-α-d-glucopyranose	13.4	7.2	2.5	2.3	–	–	–	–	–	–	–	–	–	–	–	–	–	–
23	Phenanthrene	–	–	–	0.5	–	12.9	–	–	–	–	-	–	–	–	–	3.5	6.7	2.4
24	Fluoranthene	–	–	–	–	1.2	15.2	–	–	–	–	4.6	11.0	–	–	–	1.6	3.7	5.6
25	1,6-anhydro-β-D-Glucopyranose	43.2	56.5	55.1	14.4	–	–	–	–	–	–	–	–	–	–	–	–	–	–
26	Anthracene	–	–	–	–	–	–	–	–	–	1.5	8.8	13.6	–	–	–	5.5	10.0	16.1
27	Guaiacol	–	–	–	–	–	–	–	–	–	–	–	–	43.1	23.2	1.0	–	–	–

"–" Not detected.

5-hydroxymethylfurfural along with the formation of formaldehyde. Besides, the acetal reaction of the hydroxyl groups on C_{-2} and C_{-5} was considered as the essential step to form 5-hydroxymethylfurfural [12]. Other studies suggested that furfural was generated from the positions of either C_1–C_5 or the C_2–C_6 of D-glucose [29]. However, in the present study, the yields of furfural, 5-hydroxymethylfurfural and 5-methyl furfural all decreased with the increase of temperature. Meanwhile, the yield of furfural is much higher than 5-hydroxymethylfurfural at 350 °C. It seemed that the 5-hydroxymethylfurfural was mainly produced by the competitive reactions with the formation of furfural. Moreover, negligible amount of 2,5-furandicarboxaldehyde was generated. It suggested that the decomposition of 5-hydroxymethylfurfural was more likely to lead to the formation of 5-methyl furfural through the breaking of the C—OH bind [30].

In the case of xylan, anhydro saccharides were not found in bio-oil, suggesting that saccharides from xylan were prone to decomposition. Furfural was regarded as a typical ring-containing product in hemicellulose bio-oil [31] and its yield was lower than that of cellulose. The formation of furfural from xylan differed from that of cellulose as it might be derived from the ring-opening reaction of the depolymerized xylan unit or rearrangement of the 4-O-methylglucuronic acid [11]. However, light oxygenates have a significant higher yield (shown in Table 2). The depolymerized xylan followed by the fragmentation will produce molecular fragments with two or four carbons and these fragments might be the precursor of propanoic acid, 1-hydroxyl-2-propanone, etc. For example, 1-hydroxyl-2-propanone might be derived from the fragments of C_4–C_6 and C_1–C_3 of D-glucose [32]. From Table 2, it is observed that the yield of ketones decreased remarkably from 550 to 650 °C, while the amount of acids only decreased slightly. In addition, the yield of phenols and aromatics plus CO showed a notable increase. Therefore, it seemed that CO was derived from the decarbonylation of ketones, and the subsequent propargyl radicals might generate aromatics. The yield of CO increased continuously from 650 °C to 750 °C. This increment of CO might be mainly attributed to the decarboxylation of acids since the yield of acids decreased remarkably at this temperature.

Table 2 clearly presents the opposite changes in the yield of light oxygenates from xylan and cellulose at 350–650 °C. The yield of light oxygenates from xylan decreased monotonically while that from cellulose exhibited opposite trends. It seems that the decomposition of cellulose anhydro saccharides mainly generated gas and light oxygenates. For example, CO originated from the decomposition of saccharides directly. However, parts of the xylan saccharides were more likely to produce phenols and aromatics through polymerization or aromatization since phenols and aromatics have a higher yield in xylan bio-oil. On the other hand, the yield of CH_4 and light hydrocarbons exhibited an evident increase at 650–850 °C, implying that CH_4 and light hydrocarbons were formed accompanied by aromatics.

The building blocks of lignin are believed to be a three carbon chain attached to rings of six carbon atoms, called phenyl-propanes [3]. Hence, the bio-oil from lignin pyrolysis was mainly composed of phenols and aromatics. The typical product, guaiacol, was abundantly generated at 350 °C, suggesting that the primary reactions of lignin pyrolysis were depolymerization and dealkylation. Small amount of acids and ketones were detected at 350 °C. Therefore, the branch aliphatic chains on lignin structure might decompose to light gases (CO, H_2, CH_4, etc.). With the temperature increasing to 450–550 °C, the yield of guaiacol decreased remarkably whereas large amount of phenols were generated. The decomposition of guaiacol would lead to the formation of phenol and CH_4(Fig. 2). Studies indicated that the O—CH_3 bond homolysis and the radical induced methoxyl ($-OCH_3$) rearrangement were regarded as two important secondary reaction pathways for guaiacol and aromatic compounds with methoxyl group [17,33]. As shown in Table 2, large amount of alkylated phenols such as cresols and xylenols were produced, suggesting that the formation of alkylated derivates was competitive with the formation of CH_4 during lignin pyrolysis. Guaiacol was absent in bio-oil but polycyclic aromatic hydrocarbons such as phenanthrene and anthracene emerged at 650 °C. The formation of polycyclic aromatic hydrocarbons (PAHs) might be attributed to the polymerization of ring-containing monomers which were generated by the rearrangement of radicals or the dehydroxylation of phenolic compounds. With the temperature increasing further to 750–850 °C, the aromatics were prevalently generated while the amount of phenols decreased continually. The condensation of polycyclic aromatic hydrocarbons with 3–6 benzene rings might generate secondary char. This could also contribute to the char yield of lignin pyrolysis.

Liquid oil is a storable and transportable product from biomass pyrolysis with the potential to supply a number of valuable chemicals [34]. However, the utilization of bio-oil depends upon its chemical compositions which in turn depend on the biomass composition and operation parameters. Generally, although high quality of gas can be obtained at high temperature, it was not advisable to pyrolyze biomass over 750 °C. Otherwise, the bio-oil would be difficult to further process. The liquid from cellulose is rich in anhydro saccharides at low temperature which can be hydrolyzed to produce bio-ethanol, etc. Xylan can be pyrolyzed at 500–600 °C since the liquid oil is composed of large amount of acids and ketones which can be purified to obtain chemicals. The bio-oil from lignin pyrolysis at around 550–600 °C contains large amounts of phenols and may be further purified to obtain monomer phenol.

3.4. Evolution properties of solid char

The surface area of the chars obtained at various temperatures is presented in Table 3. The cleavage of glycosidic bond and the subsequent dehydration might occur since the absorbance of C—O—C or C—O group exhibited a striking decrease in the chars obtained at 350 °C. Consequently, a rapid decrease in molar H/C and oxygen content of the cellulose char at 350–450 °C was observed. Compared with the raw cellulose sample, the S_{BET} and S_{mic} are smaller at 350–450 °C. The S_{BET} was less than 1.3m^2/g and S_{mic} was around 0.5m^2/g. Furthermore, the average pore size (adsorption average pore diameter, 4 V/A by BET) was undeterminable at this temperature. This indicated that the measured S_{BET} was only the outer surface of resultant char. Studies suggested that cellulose forms a transient liquid phase in the process of thermal depolymerization [22] and the ‘‘active cellulose’’ was a condensed phase, which was solid at room temperature [35]. Therefore, it seemed that the decrease in the surface area might be caused by the coverage of the liquefied volatiles which is rich in C=O groups. This might explain why the absorbance of C=O increased at 350 °C and the oxygen content of resultant char was high (Table 4).

With the temperature increasing to 550 °C, the S_{BET} increased significantly from 1.08 m^2/g to 274.44 m^2/g. A high total pore volume (0.123 ml/g) and low pore volume of micropore (0.006 ml/g) were obtained. Therefore, the S_{BET} might be attributed to the mesopores or macropores resulting from the rapid release and decomposition of volatile at this temperature. Meanwhile, the liquefied volatiles were no longer found on the surface of the char since the absorbance of C=O decreased remarkably and the oxygen content of resultant char decreased evidently. Nevertheless, the micropores might be blocked by the carbonized volatile. At 650 °C, the S_{mic} increased significantly from 22.66 m^2/g to 324.42 m^2/g while the increment of S_{BET} was only about 100 m^2/g. Besides, the V_{mic} accounted for 86% of total pore volume. This indicated that large number of micropores was generated. As a result, a remarkable increase in the yield of gaseous products, especially CO was observed. In addition, the pore structure became more uniform as the average pore size remained nearly constant. The S_{BET} and S_{mic} increased coincidently as the temperature increased further to 750–850 °C. Some studies found that the S_{BET} decreased at high temperature (>750 °C), as a result of the plasticity of solid charcoal and the release of tar [23,36]. However, in the present study, the condensation of volatile at this temperature was predominated with more char generated. Therefore, the increase of S_{BET} and S_{mic} might be attributed to the secondary char.

With regard to xylan, the absorbance of C—O—C also decreased remarkably at 350 °C while the C=O stretching vibration increased notably. The C—O—C linkage in xylan was attributed to the glycosidic bond. Hence, the cleavage of glycosidic bond occurred at initial stage of the depolymerization process. At 350–550 °C, the S_{BET} of xylan char was also lower than that of its raw sample. The thermal stability of xylan and the anhydro saccharides is lower than that of cellulose [2,5]. Hence, the saccharides were unlikely to condense on the surface of char. However, the decrease in the S_{BET} might be due to the blockade of saccharides within the pores. Xylan char has a higher average pore size compared to that of cellulose char at this temperature. This is probably because hemicellulose was heterogeneously branched while cellulose has a linear structure [3]. As the temperature increased to 650 °C, the S_{BET} reached the maximum value (111m^2/g). Meanwhile, an evident decrease in the average pore size was observed (from 6.95 to 2.13 nm). The rapid release and decomposition of volatile led to the generation of large amount of gases (CO and CH_4). At the same time, the skeleton structure of xylan char might collapse and merge, which resulted in the formation of numerous fine pores. At 750–850 °C, the S_{BET} decreased whereas the average pore size increase slightly. This might be due to the blocking or remerging of some surface pores described in the previous literature [23].

To sum up, the surface of cellulose formed a melted phase at 350–450 °C, and the anhydro saccharides decomposed to generate gaseous and light oxygenates in bio-oil, As the temperature increases (550–650 °C), the release of volatile accelerated and the char was porous with large amount of micropores emerged. Meanwhile, the decomposition of levoglucosan generated CO, acetic acid, propanone and phenol. The light oxygenates were formed competitively against the generation of phenols and aromatics. In addition, the formation of the former is predominated below 650 °C. At 750–850 °C, the polymerization and aromatization was predominated and the formation of aromatics gave rise to the increase of BET surface area of char.

The vibration of aryl–alkyl ether linkage was not observed at 350 °C, suggesting that lignin was depolymerized. This is in agreement with results of the bio-oil. In addition, the absorbance of methoxyl (—O—CH_3) decreased remarkably at initial temperature. It also demonstrated that the methoxyl is sensitive to temperature and generated CH_4. Besides, the absorbance of hydroxyl group and aliphatic C—H was absent as well. It might be due to the loss of phenolic and branch aliphatic chain. The S_{BET} of lignin char was as low as ~0.3 m^2/g at 350–550 °C, which was lower than that of cellulose and xylan at the same temperature. However, it is still much higher than the raw sample. This is probably because small amount of volatile was released at low temperature and minor pores were generated. The char became aromatic at 450 °C since the vibration of aromatic skeletal appeared and its absorbance increased with the rise of temperature. Studies found that the fused ring systems were formed at around 400–500 °C [18]. As the temperature increased further, the releasing rate of volatile increased. The S_{BET} and S_{mic} of lignin char increased significantly at 650 °C, which resulted in the massive release of volatile and gases (CO, CH_4 and H_2). The S_{BET} increased steadily at 750–850 °C, since more

Table 3
Surface property of chars of three components at different temperature.

Samples	Temperature (°C)	S_{BET} (m^2/g)	Surface area of micropore S_{mic} (m^2/g)	Total pore volume V (10^3 ml/g)	Pore volume of micropore V_{mic} (10^3 ml/g)	Average diameter 4 V/A by BET (nm)
Cellulose	Raw	1.9	0.5	5.3	0.2	10.3
	350	1.3	0.3	1.8	1.5	–
	450	1.1	0.6	3.8	2.1	–
	550	274	23	123	6.7	1.8
	650	368	324	174	150	1.9
	750	393	356	184	165	1.9
	850	478	438	223	204	1.0
Xylan	Raw	5.1	–	16.8	–	13.2
	350	1.4	0.6	3.0	0.5	7.6
	450	2.8	1.3	5.7	1.3	8.5
	550	3.7	1.6	5.6	2.4	7.0
	650	111	83	59	38	2.1
	750	42	24	55	11	5.3
	850	65	41	61	19	3.8
Lignin	Raw	0.03	0.01	0.2	–	–
	350	0.2	0.03	0.1	0.1	4.5
	450	0.3	0.1	0.6	0.3	15.7
	550	0.1	0.02	0.3	0.2	1.6
	650	20	18	10	8	2.0
	750	29	22	17	10	2.3
	850	57	41	31	19	2.2

volatile was released and more pores were generated. Large amount of aromatics were generated at this temperature (Table 2); hence, the condensation and deposition of polycyclic aromatic hydrocarbons on char surface might occur. Studies suggested that micropore was constructed by amorphous structures possessing 3–6 fused benzene rings [36]. That is probably why the average pore size decreased at high temperature. The above results suggested that the lignin char was not porosity material. The depolymerization and dealkylation were the primary reactions during lignin pyrolysis. Guaiacol and methoxyl were sensitive to temperature and the secondary reaction involved was the demethoxylation of guaiacol and the radical rearrangement caused by the homolysis of the O—CH_3, which yielded CH_4 and alkylated phenols. As the temperature increased up to 650 °C, the quick volatile decomposition and the release of gas (CO) were accompanied by the significant increase in the surface area of char. Besides, the formation of CH_4 was less competitive and more alkylated phenols were generated. At 750–850 °C, the dehydroxylation of phenols and the coupling of monomer aromatic were accelerated and resulted in the formation of PAHs.

Charcoal is an important product from biomass pyrolysis that is widely used as solid fuel, adsorbent, soil amendments. Porous chars can be obtained from cellulose pyrolysis above 550 °C, which may be used as adsorbents or nano-carbons. Hemicellulose is combined with cellulose in plant species, which may be utilized in the same way as cellulose. Since lignin char was not porous, it may be used to produce high value-added carbon based materials above 650 °C, such as graphitic structures.

4. Conclusions

The pyrolysis behaviors of the major components of biomass and the relationship between biomass composition and polygeneration was investigated. The glycosidic bond is sensitive to the temperature and the cleavage of glycosidic bond was the first step for the decomposition of cellulose and xylan. The saccharides from depolymerized xylan were more likely to produce phenols and aromatics while cellulose saccharides mainly generated gaseous and light oxygenates. The depolymerization and dealkylation were the primary reactions during lignin pyrolysis. The demethoxylation of guaiacol and the radical rearrangement caused by the homolysis of the O—CH_3 resulted in the formation of CH_4 and alkylated phenols.

Table 4
Elemental composition of chars of three components at different temperature.

		Temperature (°C)						
		350	450	500	550	650	750	850
Cellulose	C	75.0	81.6	84.8	85.8	86.0	87.3	88.1
	H	4.3	3.2	3.2	2.8	2.3	2.0	1.7
	O	20.6	15.1	12.0	11.4	10.8	10.6	10.1
	Molar H/C	0.7	0.5	0.4	0.4	0.3	0.3	0.2
	LHV (MJ/kg)	25.5	27.1	28.6	28.3	28.8	28.2	29.2
Hemicellulose	C	56.1	57.4	57.6	57.5	54.2	53.6	52.2
	H	2.9	2.3	2.1	1.9	2.0	1.6	1.6
	O	41.0	40.3	40.3	40.5	43.8	44.8	46.2
	Molar H/C	0.6	0.5	0.4	0.4	0.4	0.4	0.4
	LHV (MJ/kg)	15.6	15.4	15.3	15.0	13.5	14.2	14.0
Lignin	C	52.5	56.5	58.3	58.7	58.9	60.1	64.1
	H	2.8	2.3	2.3	2.3	2.1	2.0	1.6
	O	42.6	39.2	37.9	37.6	37.4	35.8	31.8
	S	2.0	2.0	1.4	1.4	1.5	2.1	2.4
	Molar H/C	0.6	0.5	0.5	0.5	0.4	0.4	0.3
	LHV (MJ/kg)	16.2	17.4	17.7	18.3	18.2	18.7	19.2

For biomass-based polygeneration system, it is not advisable to pyrolyze over 750 °C. The feedstock that contains more holocellulose (cellulose and hemicellulose) can be pyrolyzed at 550–600 °C. The calorific value of gas was over 10 MJ/m^3 and the liquid was rich in light oxygenates and can be upgraded to produce liquid fuels. The resultant char was porous and can be used as adsorbents, soil amendments, etc. Residues with high content of lignin can be pyrolyzed around 600–650 °C. The gas consists of H_2 and CH_4 with high content, the liquids contains large amounts of phenols and may be further purified to obtain monomer phenol. The char has the potential to be carbon based materials.

Acknowledgements

The authors wish to express the great appreciation of the financial support from National Basic Research Program of China (973 Program) (2013CB228102), the National Key Technology R&D Program (2012AA051803) and National Nature Science Foundation of China (51021065), Open funding from Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences (y207k81001). The technical support from Analytical and Testing Center in Huazhong University of Science & Technology is greatly appreciated. Mr. Ho Simon Wang at HUST Academic Writing Center has provided tutorial assistance to improve the manuscript.

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.2013.05.061.

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