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The thermal performance of the polysaccharides extracted from hardwood: Cellulose and hemicellulose

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ABSTRACT

The pyrolytic behaviour of individual component in biomass needs to be understood to gain insight into the mechanism of biomass pyrolysis. A comparative study on the pyrolysis of cellulose (hexose-based polysaccharides) and hemicallulose (pentose-based polysaccharides) is performed by two sets of experiments including TG analysis and Py-GC–MS/FTIR. The samples of these two polysaccharide components are thermally decomposed in TGA at the heating rate of 5 and 60 K/min to demonstrate the different characteristics of mass loss stage(s) between them. The yield of pyrolytic products is examined by a fluidized-bed fast pyrolysis unit. The experiment confirms that cellulose mainly contributes to bio-oil production (reaching the maximum of 72% at 580 °C), while hemicellulose works as an important precursor for the char production (∼25%). The compounds in the gaseous mixture (CO and CO_2) and bio-oil (levoglucosan, furfural, aldehyde, acetone and acetic acid) are further characterized by GC–MS for cellulose and GC-FTIR for hemicellulose, and their formations are investigated thoroughly.

1. Introduction

Biomass energy has been given growing attentions globally as an important renewable energy (Garcia-bacaicoa, Mastral, Ceamanos, Berrueco, & Serrano, 2008; Kang, Park, Lee, & Kim, 2004; Kumar, Eskridge, Jones, & Hanna, 2009). The thermochemical conversion is regarded as one of the most promising processes for biomass utilization (Bridgwater, 2008). Cellulose forms the framework of biomass cell walls (40–90%) composed of the cohesive, interlaced cellulosic microfibrils matrix which is deposited by hemicellulose and lignin (Goodwin & Mercer, 1983; Keegstra, Talmadge, Bauer, & Albersheim, 1973). Hemicellulose constitutes 20–35% of the woody biomass and is the least stable composition among wood components, which is composed primarily of xylan and mannan (Blasi & Lanzetta, 1997; Spearpoint, 1999). The pyrolytic behaviour of these two types of polysaccharide is of great importance for the better understanding of biomass pyrolysis and design of efficient thermochemical plants.

The kinetics of pyrolyzing these two polysaccharides have been examined through a series of research works using DTA and DSC with or without TGA (Bilbao, Millera, & Arauzo, 1989; Blasi & Lanzetta, 1997; Colomba, 1998; Conesa, Cabollero, Marcillar, & Font, 1995; Mamleev, Bourbigot, & Yvon, 2007; Milosavljevic & Suuberg, 1995; Varhegyi, Jakab, & Antal, 1994; Varhegyi, Szabo, Mok, & Antal, 1993; Volker & Rieckmann, 2002). However there are certain limitations from those analytical techniques. As a result, the pyrolytic behaviour of the two polysaccharides is mainly reported on the analysis of the mass loss stage and the characteristics on the TG and DTG curves, while the changes of the molecular structure and the corresponding cracking reactions are rarely described. It will be particularly beneficial for understanding the nature of biomass thermal decomposition and its components, if a direct comparison of the pyrolytic behaviour between these two polysaccharides is made, considering their different chemical structure (hexose for cellulose; pentose for hemicellulose).

Another important aspect for pyrolysis of the two polysaccharides is the yield of the main products (gases, bio-oil and char) and the evolution/formation of the specified volatiles (Graham, Mok, Bergougnou, Lasa, & Freel, 1984; Hosoya, Kawamoto, & Saka, 2007a; Hosoya, Kawamoto, & Saka, 2007b; Li, Lyons-Hart, Banyasz, & Shafer, 2001; Liao, 2003; Ponder & Richards, 1991; Shafizadeh, Mcginnis, & Philpot, 1972). It is known that the yield and property of the products are dependent on feedstock, process, operating conditions and bio-oil collection system (Czenik & Bridgwater, 2004; Wang, Weller, Jones, & Hanna, 2008). In term of process, to date, most studies are based on the fixed bed systems such as plug-in furnaces (Hosoya et al., 2007a, 2007b; Li et al., 2001; Shafizadeh et al., 1972) and entrained draft gasifiers (Graham et al., 1984). Fluidized-bed systems which have the advantages of high heating

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rate, efficient heat transfer, low energy input and easy scale-up are less frequently used to pyrolyze the two polysaccharides (Piskorz, Radlein, & Scott, 1986). More knowledge from fluidized-bed pyrolysis system is needed. Analytical methods (such as FTIR, GC, HPLC, MS and NMR) are able to determine the compounds in bio-oil and gases (Bridgwater, 2008) and to examine the yield of the main products affected by the temperature, residence time, atmosphere and pressure (Li et al., 2001; Liao, 2003; Piskorz et al., 1986). However the chemical pathways for the formation of these products and their cracking reactions, involving the bond cleavage and molecular arrangement are difficult to specify systematically.

Considering the needs to understand the pyrolytic mechanism of hemicellulose and cellolose, two sets of experiments are performed with the TG analysis and the Py-GC–MS/FTIR experiment. Their different pyrolytical behaviour is investigated at various heating rates in the TGA experiment, together with analyzing the characteristics of the mass loss stage(s). Furthermore a fluidized-bed fast pyrolysis unit is employed to examine the effect of temperature on the yield of the gas, bio-oil and char from the two polysaccharides in order to identify their performance variation. The formation of the main products in bio-oil and gases are characterized by GC–MS/FTIR and extensively discussed.

2. Experimental setup

2.1. Materials

The cellulose samples are made accordingly to the ISO-2000 National Standard, while the hemicellulose samples (O-acetyl-4-O-methylglucurono-xylan) are the commercial product (Sigma Chemical Co.) extracted from beech. The samples are in the form of white powders with average diameter of 200 μm. According to the elemental analysis, the content of C, H, S, N and O is estimated to be 44.97, 6.196, 0.096, 0.016 and 48.715% respectively in cellulose, compared to 40.8, 6.38, 0.26 and 41.01% in hemicellulose. The primary structure of cellulose can be interpreted as a linear homopolymer of glucopyranose residues linked by β-1,4-glycosidic bonds (Charlton, Haworth, & Peat, 1926; Chu & Jeffrey, 1968), where the glucopyranose is obtained from the hemiacetal of D-glucose between C-1 and C-5 positions (Fig. 1). The degree of polymerization of the native celluloses (n) depends on the source and is considered to be from 6000 to 8000 for those from woods (Severian, 2008). The hardwood hemicellulose is mainly composed of xylans, linearly constituted of 1,4-linked-β-xylopyranosyl units (Severian, 2008). The 4-O-methylglucurono-xylan from beech is determined to give a xylose-to-uronic ratio of 8:1, presenting every eighth xylopyranosyl unit substituted by the 4-O-methylglucuronic acid unit linked to xylan chain through (1,2)-linkage. It is also estimated that acetyl group content varies from 8 to 14% in every 8-xylose units, normally representing 3–7 acetyl groups which are linked to C-2 (sometimes C-3). The above findings give the speculative chemical structure of the hemicellulose sample (O-acetyl-4-O-methylglucurono-xylan) in Fig. 1, which also exhibits the detailed substituting positions of the acetyl groups and 4-O-methylglucuronic acid (4-O-MeGlcA) unit to the xlyan chain. Compared to cellulose, the degree of polymerization of the xylan units is very low less than 200.

2.2. TGA experiment

Thermogravimetric analyzer (Mettler Toledo TGA/SDTA 8951E) is used to investigate the mass loss stages of cellulose and hemicellulose. In the TGA experiment, the sample powders are heated from 30 to 900 °C at heating rate of 5 and 60 K/min under the inert atmosphere. The mass of the sample is less than 5 mg to avoid the possible temperature gradient inside the sample and ensure the kinetic control of the process (Blasi, Branca, Santoro, & Hernandez, 2001). During the experiment the cell of TGA is flushed with 40 ml/min nitrogen to maintain the inert atmosphere for thermal decomposition of the sample.

2.3. The fast pyrolysis unit

2.3.1. The apparatus

The pyrolysis unit is composed of feeding system, pyrolysis reactor, carbon filter, vapour-condensing and gas storage, as shown in Fig. 2. The reactor is a quartz tube (diameter of 15 mm, length of 1200 mm and thickness of 2 mm) heated by the carborundum heater with a power of 8 kW, while there is a 4 mm gap to ensure the same temperature in the tube and heater. The feeding system and carbon filter can be disassembled from the quartz tube reactor at the conjunction 1 and 2 in Fig. 2. The carbon filter is disassembled after the experiment to obtain the mass of char residue by checking the mass difference of the carbon filter. The bio-oil is collected by the two-step condensing system. Most of the high molecular weight compounds (heavy tars) are condensed and collected in the U tube, while the light tars are coagulated by the mixture of dry ice and acetone (about −30 °C) and collected in the spiral tube. The non-condensable vapour is then stored by the gas-bag. The yield of gaseous products is calculated from the density and volume of the collected gaseous mixture. The density is found from the composition analysis of the mixture by GC (Voyager, Finnigan) while the volume is read from the integral flowmeter. The final yield of the gaseous products is found by excluding the carrier gas (N_2) in the mixture.

2.3.2. The process

While the experimental temperature reaches the fixed value, the feeding system is connected to the reactor via the closed valve 2 in Fig. 2. The flushing flow initially runs for about 1 min to purge all oxygen out of the system to ensure the inert atmosphere in the reactor tube. Then, the valve 1 is closed and the valve 2 is opened to carry feedstock up to the heated reactor by the feeding flow. The sample is pyrolyzed rapidly inside the reactor, and the stream mixed of produced volatiles and char residues moves upward passing through carbon filter where the char residue is separated. The purified volatile stream then flows through the two-step condensing system where tars are condensed and collected, the non-condensable volatiles together with the carrier gas (nitrogen) are collected by gas sample bags. The temperature is varied from 400 to 790 °C in this experiment while the feeding flow rate is constant as 600 l/h (corresponding to residence time of about 0.5 s) in order to investigate the effect of temperature on the process. The mass balance closure for the different experiments, described as (the yield of char, tar and gases)/(the mass of feedstock) is estimated between 98.9 and 101.2%. The experimental results are considered to be reasonable while the error is less than 5% as an acceptable deviation. Two runs are operated for each experiment, and the repetition is made when the deviation exceeds the limitation (5%).

2.3.3. The compounds in the bio-oil

The oxygenated composition in bio-oil is very complicated, so the GC–MS technique is employed to characterize the typical compounds in the bio-oil from cellulose. The column of the GC should be applicable for the oxygenated and polar compounds containing hydroxyl, carbonyl and carboxyl groups. The conditions for GC–MS are presented as: capillary column: Wax-10 (length: 30 m, diameter: 0.25 mm), injector temperature: 250 °C, column temperature: 60 °C (5 min), 60–250 °C (heating rate of 10 K/min), 250 °C (25 min),

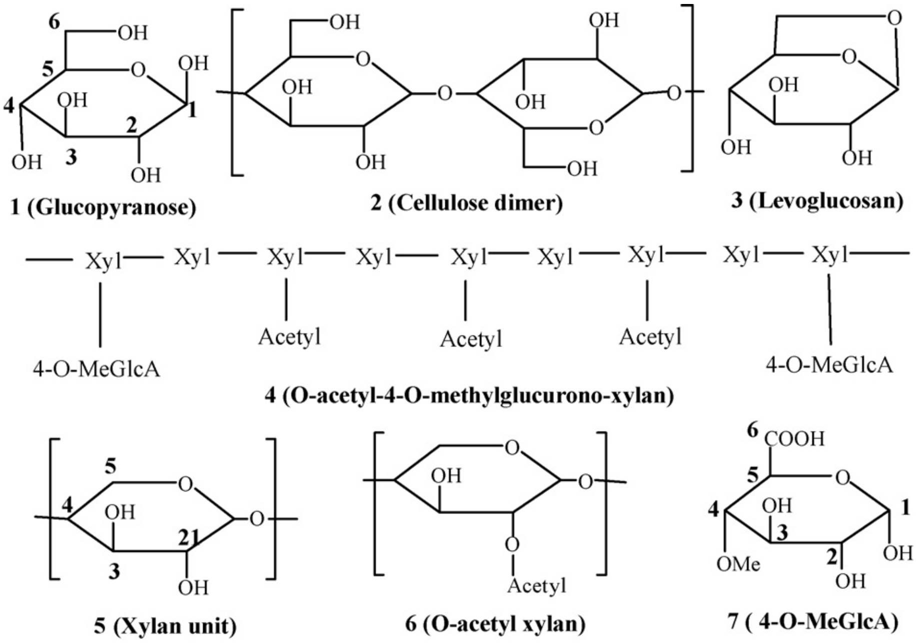

Fig. 1. The chemical structures of the cellulose and hemicellulose.

carrier gas: helium, flow rate: 2 ml/min, ionization mode: electronic ionization, electronic bombardment energy: 70 eV, scanning time: 0.5 s, scanning range: 30–500 μm.

The GC-FTIR method is used to characterize the compounds in the bio-oil from hemicellulose. The column of the GC is the same as the above one, while the FTIR spectrometer is set to collect 32 interferograms at a resolution of 4 wavenumbers with a scanning rate of 0.6329 cm/s and the spectral range is set to be 4000–400 cm^{-1}. The yield and the structure of the compounds are determined by the computer software from the specified GC-FTIR graphs.

3. Results and discussion

3.1. The TG analysis

Fig. 3 shows the TG and DTG curves of cellulose and hemicellulose under nitrogen at the low heating rate of 5 K/min. An "abrupt mass loss stage" for cellulose is observed within the narrow temperature gap from 300 to 380 °C, where the cellulose decomposes rapidly and the products are intensively released. On the other hand, hemicellulose has a steady decline of the mass loss from 190

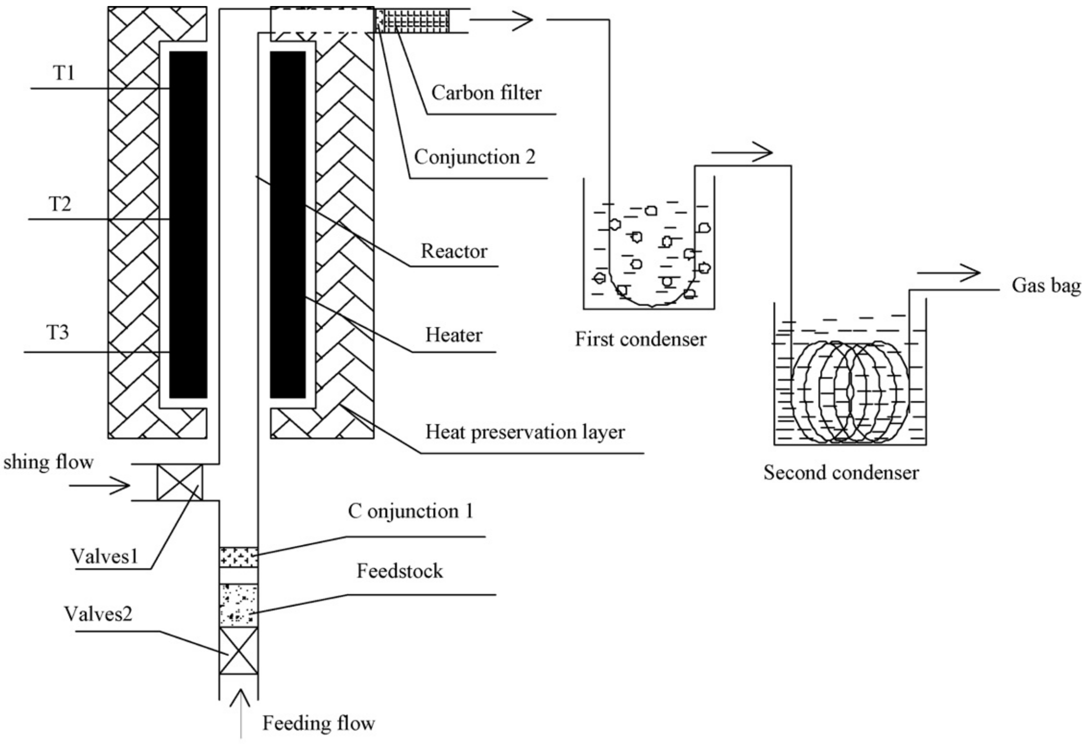

Fig. 2. The apparatus schematics for the biomass gasification and volatiles condensation system.

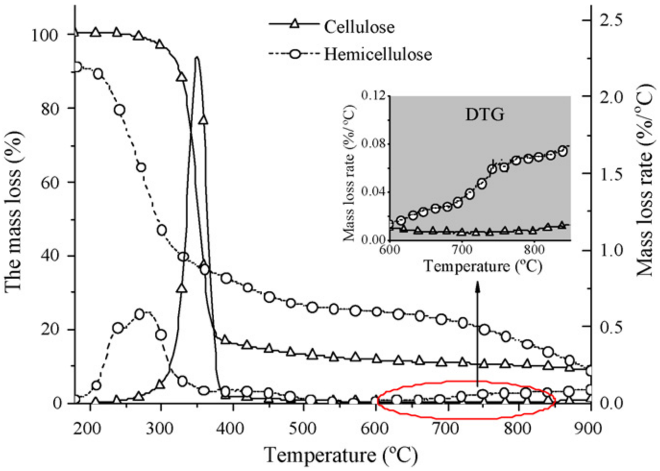

Fig. 3. The TG and DTG curves of cellulose and hemicellulose at 5 K/min.

to 360 °C. Comparatively the main mass loss stage for cellulose is later than that for hemicellulose, as more energy is required for the depolymerisation of the cellulose chain and the cracking of its monomer (Liao, 2003). Two visible peaks are identifiable on the DTG curve of hemicellulose, where the first one is ascribed to the decomposition of the side units (4-O-methylglucuronic acid and acetyl groups) and the other one is corresponding to the cracking of the main xylan chain (Severian, 2008).

The TG and DTG curves of cellulose and hemicellulose at the high heating rate of 60 K/min are shown in Fig. 4. The mass loss stages for cellulose and hemicellulose shift towards high temperature from 330 to 430 °C and from 225 to 400 °C, respectively. The second peak of the DTG curve of hemicellulose is more visible than that under the low heating rate in Fig. 3, due to the fact that thermal decompositions of the side units and main xylan chain are highly overlapped under the high heating rate.

Compared to cellulose, a mass loss stage for hemicellulose is visible after 600 °C at the low heating rate (Fig. 3). This indicates that the char residue from hemicellulose is more reactive than that from cellulose under the high temperature. However, the "visible mass loss stage" for hemicellulose after 600 °C disappears at the high heating rate (Fig. 4), due to the short exposure duration for the solid residue under the high temperature at the high heating rate. Another plausible explanation is that the structure of the char residue obtained at the higher heating rate is more stable and inhibits the cracking of the cross-linked molecules (Liao, 2003).

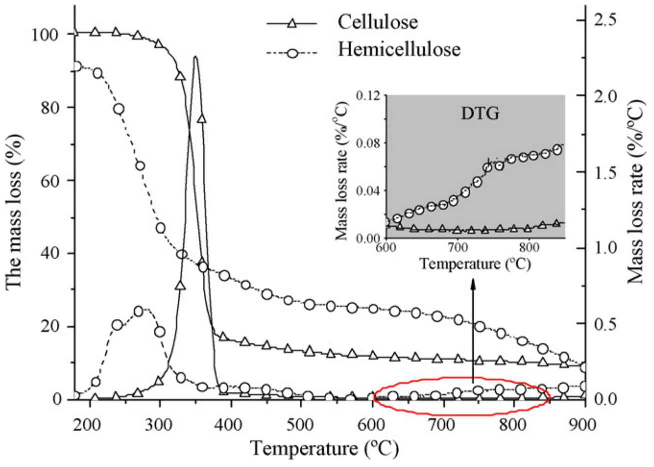

Fig. 4. The TG and DTG curves of cellulose and hemicellulose at 60 K/min.

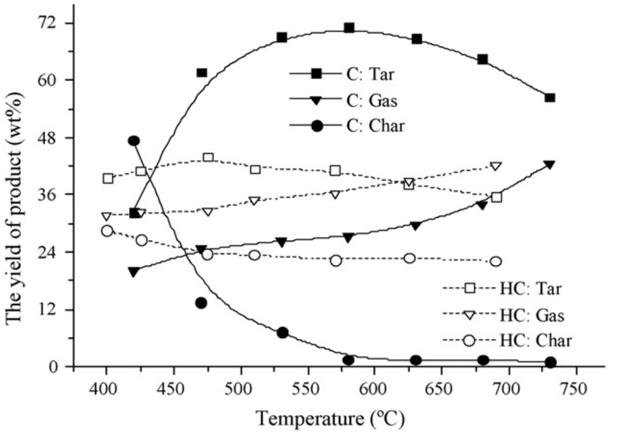

Fig. 5. The yield of the products under different temperatures (C: cellulose and HC: hemicellulose).

Further examination shows that the final char residue from cellulose at the heating rate from 5 to 60 K/min is decreased from 10.11 to 7.49%, while that from hemicellulose is increased from 10.21 to 24.46%. Such phenomenon can be explained as follows. It is known (Arseneau, 1971) that the cellulose polymer tends to be carbonized through the dehydration and cross-linking reactions under the low temperature (from 250 to 300 °C). The structure of cellulose is chemically and physically rearranged after the "preheating process", enhancing the final production of char residue (Maschio, Koufopanos, & Lucchesi, 1992). It translates that the char residue from the cellulose pyrolysis would increase with the longer preheating process at the low heating rate (Broido & Nolson, 1975). For hemicellulose, the structure of the char residue formed at the low heating rate is less stable than that at the high heating rate, leading to the second cracking reactions under the high temperature.

3.2. *The fast pyrolysis experiment*

The cellulose and hemicellulose is tested in the fast pyrolysis unit to investigate the effect of temperature on product yield. Fig. 5 shows the yields of gas, tar and char from the pyrolysis of cellulose (C) and hemicellulose (HC) under the temperatures from 400 to 750 °C. The yield of gas from the two components increases at the elevated temperature, while the yield of char behaves differently. The yield of tar (bio-oil) at the elevated temperature initially increases and reaches the maximum 72% at about 580 °C for cellulose, whereas 45% at about 475 °C for hemicellulose. This temperature is defined as the "critical temperature".

The production of tar for the two polysaccarides is remarkably increased at the expense of the char residue before the critical temperature, while the yield of the gaseous products is not visibly changed, owing to the fact that more energy is required to promote the secondary reactions of the primary products which favour the formation of the gases. The yield of the char residue is stable when the temperature is higher than the critical temperature. Consequently, it is found that the yield of gas at higher temperature increases in proportion to the decreased production of tar, which clearly demonstrates the competitive formation of tar over the condensable products.

It should be noted that the formation of char residue from hemicellulose (22%) is much higher than that from cellulose (5%) at the high temperature (around 700 °C). The cleavage of the β-1,4-glycosidic bond of cellulose and the sequential cracking reactions are more convenient over the cross-linking reaction under the high temperature (Liao, 2003), while the formation of the char residue from hemicellulose is more stable and slightly varied under the

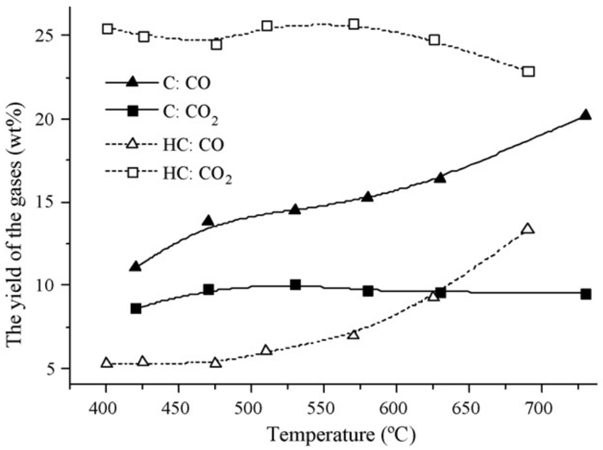

Fig. 6. The yield of the gases under different temperatures (C: cellulose and HC: hemicellulose).

high temperature. It is thus concluded that cellulose is the main contributor for the tar (bio-oil) production during fast pyrolysis, while the contribution for the char residue should be attributed to hemicellulose.

Although the overall yield of gaseous products only varies slightly between the two polysaccharides, the gaseous compounds vary distinctively at different temperatures. Fig. 6 shows the evolution of CO and CO_2 from cellulose and hemicellulose at the different temperatures. The yield of CO from cellulose is enhanced at the elevated temperature and increased residence time, while the yield of CO_2 changes slightly. It is reported (Li et al., 2001) that the formation of CO is highly affected by the secondary reactions of the low molecular weight products (especially the aldehyde-type compounds), while the CO_2 is presumably produced in primary reaction or early stage of cellulose pyrolysis under the high temperatures. Comparatively, the evolution of CO_2 from hemicellulose is mainly ascribed to the decarboxylation reaction of the large content of O-acetyl groups linked to the xylan chain normally on C-2 position (Fig. 1). Furthermore, more CO is produced at the elevated temperature while the yield of CO_2 only changes slightly. It is explained that the formation of CO is highly affected by the decomposition of the ring-opened intermediate and the secondary reactions of the low molecular weight products (especially decarbonylation of the aldehyde-type compounds) (Hosoya et al., 2007a, 2007b), while the CO_2 is presumably produced in the primary reactions.

3.3. *The formation of condensable products*

The composition of bio-oil from the thermal decomposition of biomass is very complicated and difficult to be thoroughly characterized by a single analytical technique (Piskorz et al., 1986). A number of polar organic compounds in the bio-oil are detected by GC–MS for cellulose and GC-FTIR for hemicellulose in this work. The molar fraction of some typical products in the bio-oil, influenced by temperature, is shown in Table 1 for cellulose and Table 2 for hemicellulose. The chemical pathways for the primary products and the secondary decomposition of the fragments are extensively investigated, underpinning the formation mechanisms of the main products. It should be noted that the chemical pathways for the product formation will be validated in our future research to specifically pyrolyze the model compounds under the same conditions.

3.3.1. *The anhydro-sugars (levoglucosan)*

Table 1
The molar fraction of the main compounds in the tar from the pyrolysis of cellulose under different temperatures (feeding flow rate: 600 l/h).

Compounds		530 °C	630 °C
Name (abbreviation)	Formula		
Acetone	C_3H_6O	2.13	3.94
Hydroxyacetone	$C_3H_6O_2$	2.22	4.69
Hydroxyacetaldehyde	$C_2H_4O_2$	4.72	7.53
Furfural	$C_5H_4O_2$	0.75	0.97
Anhydro-D-mannose	$C_6H_{10}O_5$	2.32	1.61
5-Hydroxymethl-furfural	$C_6H_6O_3$	1.62	3.54
Levoglucosan	$C_6H_{10}O_5$	62.22	51.07

Levoglucosan (1,6-anhydro-β-D-glucopyranose) is the main component in the bio-oil from cellulose (Table 1). This has been confirmed in (Piskorz et al., 1986) which shows the initial thermal decomposition of cellulose proceeds by disruption of the cellulose polymer chain to form various anhydrosugar derivatives. In addition, it is found that the yield of levoglucosan is suppressed at increased temperature while almost all of the other products increase, indicating the competitive mechanism between the levoglucosan and other products. The formation of levoglucosan is facilitated by the cleavage of the 1,4-glycosidic linkage in the cellulose polymer, followed by intramolecular rearrangement of the monomer units (Li et al., 2001). The 1,4-glucosidic bond is possibly broken accompanying with the acetal reaction between C-1 and C-6, evolving hydroxyl radical from C-6. Then, the free hydroxyl radical coalesces with the disrupted glucosidic bond on C-4 to form levoglucosan (1,6-anhydro-β-D-glucopyranose).

The 1,4-anhydro-D-xylopyranose is one of the main condensable products from the hemicellulose pyrolysis, and the production decreases at the elevated temperature (Table 2). This implies that high temperature inhibits the formation of this product. The formation of 1,4-anhydro-D-xylopyranose is mainly attributed to the cleavage of the glycosidic linkage of the xylan chain, followed by the rearrangement of the depolymerized molecules. Comparatively the content of the 1,4-anhydro-D-xylopyranose in the bio-oil from hemicellylose is less than that of levoglucosan from cellylose, due to the nature that the 1,4-intramolecular-glycosidic bond on the xylopyranose is less stable than the 1,6-acetal bond on the glucopyranose (levoglucose) (Ponder & Richards, 1991). Most of the produced 1,4-anhydro-D-xylopyranose, acting as an intermediate product, is probably consumed instantly to produce the two-carbon, three-carbon fragments and gases through the cracking reactions.

3.3.2. *The ring-contained products (furfural and 5-hydroxymethyl furfural)*

The yields of 5-hydroxymethyl furfural (5-HMF) and furfural (FF) from cellulose are clearly enhanced at the elevated temperature (Table 1). The formation for 5-HMF is possibly initiated by the cleavage of the ring glucosidic bond on cellulose unit to form an aldehyde-structure on C-1, followed by the formation of double-bond between C-4 and C-5 through the chain structure rearrangement. Another double-bond between C-2 and C-3 is formed through the dehydration of the corresponding hydroxyl groups. Then, the acetal reaction of the hydroxyl groups on C-2 and C-5 is considered to be the essential step to form 5-HFM. Another chem-

Table 2
The molar fraction of the main compounds in the tar from the pyrolysis of hemicellulose under different temperature (feeding flow rate: 600 l/h).

Compounds	425 °C	475 °C	510 °C	570 °C	690 °C
Methanol	2.26%	2.59%	2.96%	3.12%	3.61%
Acetic acid	12.31%	11.28%	10.22%	8.82%	7.71%
Acetone	1.92%	2.23%	2.24%	2.76%	3.03%
Furfural	5.37%	5.9%	6.42%	7.89%	9.98%
1,4-Anhydro-D-xylopyranose	10.66%	8.78%	7.61%	5.54%	2.18%

ical pathway to produce 5-HMF is proposed as the pyran-ring of levoglucosan is broken to the hexose chain structure, followed by dehydration of the hydroxyl groups and sequential acetal reaction on C-2 and C-5 (Shafizadeh & Lai, 1972). No matter what the origin of the 5-HFM is, the furfural is reported to be produced from the secondary reaction of 5-HFM or 1-HFM, accompanying the evolution of formaldehyde (Liao, 2003).

The furfural is also regarded as a typical ring-containing product in the bio-oil from hemicellulose (Ponder & Richards, 1991; Shafizadeh et al., 1972). The yield of furfural improves as the temperature rises, indicating that high temperature promotes the formation of furfural (Table 2). The production of furfural is mainly ascribed to the cleavage of the hemiacetal bond on the depolymerized xylan unit, followed by the dehydration between the hydroxyl groups on C-2 and C-5 position. Another possible chemical pathway for the formation of furfural is proposed as the cleavage of the 1,2-glycosidic bond between the xylan unit and 4-O-methylglucuronic acid unit, followed by the ring-opening reaction and rearrangement of the 4-O-methylglucuronic acid after the elimination of CO_2 and methanol.

3.3.3. The low molecular weight products (C<4)

Hydroxyacetaldehyde (HAA) and hydroxyacetone (HA) are taken as the major C2-3 oxygenated products in the bio-oil from the cellulose (Bridgwater, 2008; Hosoya et al., 2007a, 2007b), the formation of them are enhanced by the elevated temperature. Piskorz et al. (1986) reports that the ring hemiacetal bond is very active under thermal radiation and the bond between C-2 and C-3 is longer than other positions of the ring, representing its instability. Hence, the formation of HAA on the C-1 and C-2 is favoured by the ring-opening through the cleavage of the above two active bonds, along with the evolution of a four-carbon fragment. Liao (2003) suggests that almost all of the carbons on the pyran-ring could contribute to the formation of HAA, even on the C-5 and C-6 through the cleavage of the rearranged four-carbon fragment. The HA is probably produced through the cleavage of the rearranged four-carbon fragments from the direct conversion of the cellulose molecules, where the tetrose fragment is initially dehydrated on C-5 and C-6 and then broken to CO and HA by the decarbonylation on C-3 (Piskorz et al., 1986).

Comparatively the acidic compounds are commonly detected in the bio-oil from the hemicellulose (Table 2). The yield of acetic acid decreases at elevated temperature, indicating that the formation of acetic acid is retarded at high temperature. The formation of acetic acid is referred to the primary elimination of the active O-acetyl groups linked to the xylan chain on C-2 position (Fig. 1). Another chemical pathway for the acetic acid production is ascribed to the ketene structure of the fragment from the 4-O-methylglucuronic acid unit after the elimination of the carbonyl and O-methyl groups. The former formation pathway of acetic acid is comparatively predominant over the other pathway, since the acetyl groups are in larger proportion than the 4-O-methylglucuronic acid units in the material.

Table 2 shows an increased yield of methanol and acetone according to temperature. The formation of methanol is mainly attributed to the elimination of the O-methyl group on C-4 position of 4-O-methylglucuronic acid unit. The yield of methanol changes slightly at the elevated temperature, due to no competitive reaction consuming the O-methyl groups. The formation of acetone should be complicated, as almost each unit (Fig. 1) could be decomposed to acetone. Since the acetic acid produced from the O-acetyl-xylan unit (**6** in Fig. 1) accompanying the evolution of acetone decreases at elevated temperature, the acetone produced from the other xylan units (**5**, **7** in Fig. 1) should be more prevalent under high temperature.

4. Conclusions

The pyrolytic mechanisms of two main polysaccharide components in biomass, cellulose and hemicellulose, are extensively studied using TG and Py-GC–MS/FTIR. The results are summarized as the following points:

- An "abrupt mass loss stage" is observed from the TG curve of cellulose, while the mass loss stage of hemicellulose is relatively steady. The mass loss for hemicellulose starts earlier than that of cellulose, due to the thermally unstable xylan-content in hemicellulose.
- The char residue obtained at the low heating rate for hemicellulose is more active than that at the high heating rate, while the thermal stability of the char residue from hemicellulose varied unremarkably with the heating rate.
- For the fast pyrolysis experiment, the yields of gas, tar and char from cellulose change more pronouncedly at the elevated temperature, compared to those from heimcellulose. Cellulose is the main contributor to the bio-oil production (the maximum value of 72% at 580 °C), while the hemicellulose acts as a significant precursor for the char production (about 25%).
- Levoglucosan, the main compound in bio-oil from hemicellulose, is less produced at elevated temperature, presenting the competition with the formation of other fragments. The hydroxyacetaldehyde and hydroxyacetone are also prevalently produced from the cellulose pyrolysis, while acidic products (such as acetic acid and formic acid) are the major compound in the bio-oil from hemicellulose due to its sufficient content of acetyl groups.
- The production of CO_2 is not varied substantially according to temperature, while higher yield is found for hemicellulose. Comparatively, the formation of CO from the two polyssacharides is enhanced under the high temperature where the secondary reactions are greatly favoured.

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