# Characterization of Water-Soluble Intermediates and Solid Residues from Fast Pyrolysis of Cellulose in a Wire-Mesh Reactor

Biao Zhang, Erwei Leng, Yang Wang, Xun Gong,\* Yang Zhang, and Minghou Xu

The fast pyrolysis characteristics of cellulose were investigated in a wiremesh reactor, which minimized the secondary reactions between the solid residues and the evolved volatiles during pyrolysis and facilitated the collection of the primary intermediates and volatiles. The main component of the water-soluble intermediates was anhydrooligosaccharides with various degrees of polymerization (DP). The yields of cellotriosan and cellotetraosan in the intermediates were much higher than those of levoglucosan and cellobiosan in the early pyrolysis stage, indicating that the depolymerization of the cellulose chain occurred during a random cleavage process. Anhydro-oligosaccharides with DP up to 3, and partially decomposed sugar-ring-containing oligomers, were identified in the primary volatiles. Among the sugar-ring-containing oligomers, the compound with a relative molecular weight of 222 was considered to be the product of a reverse aldolization reaction. An analysis of the solid residues confirmed the occurrence of intramolecular dehydration during the cellulose pyrolysis.

Keywords: Cellulose; Fast pyrolysis; Wire-mesh reactor; Anhydro-oligosaccharides; Intramolecular dehydration

Contact information: State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, No. 1037, Luoyu Road, Wuhan, 430074, PR China; \*Corresponding author: gx@hust.edu.cn

# INTRODUCTION

Concerns about the energy crisis and the greenhouse effect have stimulated increased enthusiasm in searching for suitable substitutes for traditional fossil fuels. Biomass is an ideal candidate, as it is not only renewable, but it could also achieve zero emissions of CO<sub>2</sub>. Fast pyrolysis is a promising technology to make full use of biomass, transforming it into bio-oil, non-condensable gases, and solid char (Regalbuto 2009; Vispute *et al.* 2010). The bio-oil could be further upgraded to transport fuels through catalytic hydrogenation (Vispute *et al.* 2010), and the solid char can be used for soil amendment (Lehmann 2007; Wu *et al.* 2011a) or CO<sub>2</sub> neutral reductant in metallurgical applications (Griessacher *et al.* 2012).

As the most important product from the fast pyrolysis of biomass, bio-oil can take up to 85 wt.% of the biomass (Hoekstra *et al.* 2012; Westerhof *et al.* 2016). Therefore, the quality of bio-oil, to a great extent, determines the economic feasibility of fast pyrolysis technology. Unfortunately, the poor properties of bio-oil (*e.g.*, high acidity, instability, high ratio of O/C, *etc.*) make it far from meeting the quality requirements of the transportation fuel (Oasmaa and Czernik 1999). An adequate understanding of the biomass pyrolysis mechanism is helpful to maximize attainable quality of bio-oil. The effects of various pyrolysis parameters on the yields of bio-oil, char, and gas have been extensively studied (Várhegyi *et al.* 1997; Bridgwater 2012). However, the formation mechanisms of many important products are still unknown because of biomass' complex structure and the numerous reactions involved during fast pyrolysis.

Cellulose is an important component of biomass and generally comprises up to 40% to 50% of dry biomass (Lédé 2012). To reveal the biomass pyrolysis mechanism, researchers have dedicated much effort to studying cellulose pyrolysis (Patwardhan et al. 2009; Shen and Gu 2009; Lédé 2012; Lin et al. 2012; Şerbănescu 2014; Westerhof et al. 2016). Researchers have reached a consensus that cellulose first passes through a watersoluble, liquid-phase intermediate before further formation of more volatile compounds (Diebold 1980; Di Blasi 1996; Boutin et al. 1998; Liu et al. 2008; Dauenhauer et al. 2009; Lédé 2012). Within the liquid phase, many complicated chemical reactions take place, such as depolymerization and dehydration (Mamleev et al. 2009; Teixeira et al. 2011). Revealing the components of the primary liquid-phase intermediates can provide great help in elucidating the formation routes of the pyrolysis products. However, clarifying the transformation process of nascent intermediates remains difficult work because of their brief lifetime and complex reactions, and the research is still in debate. Li et al. (2001) found that the FTIR (Fourier transform infrared) spectra produced from the pyrolysis of cellulose were similar to those produced from the pyrolysis of levoglucosan (Banyasz et al. 2001; Kawamoto et al. 2003). It is reasonable to speculate that levoglucosan was just the precursor of other products (Shoji et al. 2014). Bai et al. (2013) also found that the levoglucosan formed during cellulose pyrolysis could either evaporate or polymerize into oligosaccharides, which would further polymerize into polysaccharides or decompose into low-molecular-weight volatiles. It should be noted that these pyrolysis experiments were conducted either in fixed-bed reactors or via thermogravimetric analysis (TGA), where significant secondary reactions took place. The secondary reaction may obscure the primary reaction during pyrolysis, affecting the subsequent analysis results. Conversely, Lédé et al. (2002) reported that when cellulose was pyrolyzed in the image furnace, the main component of the liquid intermediates was anhydro-oligosaccharides with various degrees of polymerization (DPs). However, when using similar equipment as was used by Lédé et al. (2002), Liu et al. (2008) thought that the intermediates were composed of various reducing sugars (e.g., glucose, cellobiose, cellotriose, fructose, etc.), and that levoglucosan was derived from the secondary decomposition of these reducing sugars. Pyrolysis experiments in the image furnace are uncontrolled, as the pyrolysis temperature is only estimated, and the heating rate is unknown. Furthermore, primary solid residue is unavailable, restricting further exploration of cellulose pyrolysis.

The breakdown of the cellulose glucosidic chain is still currently an unsettled issue. Two dominant reaction schemes have been proposed: "unzipping" mode (Shafizadeh *et al.* 1979), and random cleavage mode (Byrne *et al.* 1966). According to the "unzipping" mode, the cellulose chain first depolymerized into a levoglucosan-end chain *via* transglycolation, and then the levoglusosan units were released from the levoglucosan-end chain one by one. The "unzipping" mode can well explain the experimental phenomena when cellulose is pyrolyzed under slow heating rate (Banyasz *et al.* 2001). However, some scholars thought that breakdown of the cellulose glucosidic chain is carried out by random mode (Mayes and Broadbelt 2012; Westerhof *et al.* 2016).

Given the above disputes on the mechanism of cellulose pyrolysis, the present study conducted a series of cellulose pyrolysis experiments in a wire-mesh reactor (WMR). A WMR can accurately control the heating rate even when it achieves 1000 °C/s, and it ensures that the collected solid residues and volatiles are products from the primary reaction. Because the previous studies have reported either anhydrooligosaccharides (including levoglucosan) or reducing sugars as the main component of the intermediates, this work paid great attention to these compounds. A quantitative analysis of the major components of both the intermediates and volatiles at different pyrolysis temperatures was performed to deduce the primary decomposition routes of cellulose. The solid residue structure was also analyzed in-depth to discover the possible pyrolysis reactions.

# EXPERIMENTAL

#### **Materials**

Cellulose (Avicel PH101), levoglucosan (AC1), cellobiose (C2), and glucose (C1) were purchased from Sigma-Aldrich (St. Louis, USA). Cellulose with particle sizes ranging from 100  $\mu$ m to 150  $\mu$ m was prepared for use in the pyrolysis experiments. Cellobiosan (AC2), maltosan, cellotriose (C3), cellotriosan (AC3), and cellotetraosan (AC4) were provided by Carbosynth Ltd. (Compton, England). Here C stands for celloligosaccharide (glucose, cellobiose, cellotriose), and AC stands for anhydrocelloligosaccharide (levoglucosan, cellobiosan, cellotriosan, cellotetraosan). The latter number indicates the degree of polymerization.

# Fast Pyrolysis Experiments of Cellulose in the WMR

The detailed structure of the WMR has been previously described (Wu *et al.* 2011b; Gui *et al.* 2013; Gong *et al.* 2014), and Fig. 1 shows its schematic structure.

Before the pyrolysis experiments, a small amount of cellulose samples (less than 10 mg) was evenly distributed within the circle (1-cm radius) between the two layers of wire mesh. Two pairs of thermocouples monitored the temperatures in the reaction center and the edge. The temperature difference between the two monitoring points was required to be lower than 10 °C to minimize the local temperature gradient; otherwise the experiment data was abandoned. During the pyrolysis experiments, the wire mesh was heated to the desired temperature (200 to 550 °C) by an electrical current at a heating rate of 100 °C/s. The holding time was zero, to maximize the yield of liquid intermediates. High purity N<sub>2</sub> (purity > 99.999%) was passed through the sample-hold wire mesh at a linear gas velocity of 0.1 m/s (corresponding flow rate was 4 L/min). Fast-flow-rate sweep gas rapidly took the volatiles produced during pyrolysis away from the pyrolysis zone (vapor residence time < 30 ms), which minimized the interactions between the volatiles and the particles. The volatiles that escaped from the pyrolysis zone were immediately quenched (0.2 to 0.3 s) by a liquid nitrogen-cooled trap so that the interactions of the volatiles were suppressed as well. Therefore, the volatiles condensed in the trap were primary volatiles, which were called bio-oil in the following section. The sweep gas also cooled the solid residues (solid products and unconverted cellulose left in the wire mesh after the experiments) to ambient temperature immediately (1 to 2 s) after the end of the pyrolysis experiment. The water-soluble portion of the solid residues was considered as the nascent intermediates, which were hereafter referred to as water-soluble intermediates. After the pyrolysis experiment, the bio-oil was washed with solvent, which was a mixture of chloroform and methanol, with a ratio of 4:1 by volume. The collected bio-oil was evaporated at 35 °C and in vacuum to remove the solvents. The bio-oil yield was determined on the original cellulose basis. The solid residue yield was calculated as the ratio of the weight of the solid residue to that of the original cellulose that was pyrolyzed.

In order to test the influence of the stacking effect of cellulose samples on the experimental results, cellulose with different sample weight (3mg, 5 mg, 8 mg, 10 mg) was pyrolyzed in the WMR (heating rate: 100 °C/s, final temperature: 550 °C, zero holding time), and solid residue yields were analyzed. These results are discussed in the section "Measurement Uncertainty". Each experiment was run in at least triplicate trials.



Fig. 1. The schematic structure of the WMR (Wu et al. 2011b; Gui et al. 2013)

## Methods

Characterization of the sugars in the water-soluble intermediates and bio-oil

To analyze the sugars in the water-soluble intermediates and bio-oil, another set of experiments was performed in the WMR under the same conditions. The pyrolytic solid residue and bio-oil collected by the three repeated pyrolysis experiments were washed with 15 and 20 mL of deionized water, respectively.

The filtered water solution was analyzed using a high-performance liquid chromatography-mass spectrometer (HPLC-MS) (Agilent 1100 LC-MSD-TRAP-XCT, Palo Alto, USA) as quickly as possible. The sugars in the water solutions were separated using a Sugar KS 802 column (Shimadzu, Kyoto, Japan) at 60 °C with a water-flow rate of 1 mL/min, and detected using a refractive index detector (RID) and mass spectrometry (MS) detector simultaneously. The MS was used in the electrospray ionization-negative (ESIN) mode, and the ionization agent was deionized water.

The ionization parameters were as follows: dry temperature was 280 °C, the pressure of the nebulizer was 0.276 MPa, the flow rate of dry gas was 10 L/min, the high voltage (HV) of the capillary was 3500 V, the voltage of the exit of the capillary was - 117.3 V, and the scan range of the m/z was 50 to 1500 Da. Standard curves for glucose (C1), levoglucosan (AC1), cellobiose (C2), cellobiosan (AC2), cellotriose (C3), cellotriosan (AC3), and cellotetraosan (AC4) were calibrated for identification and quantification of the products.

# Fast pyrolysis of the intermediates in the pyrolysis coupled with gas chromatography/mass spectrometry

To further establish the rationality of water-soluble intermediates reported in this work as the active cellulose, fast pyrolysis of one typical component in the water extract of cellulose pyrolyzed at 370 °C was conducted in the gas chromatography/mass spectrometer (Py-GC/MS). The Py-GC/MS was composed of a CDS5200 Pyroprobe (CDS Analytical, Oxford, USA) and a 7890A/5975C GC-MS (Agilent Technologies, Palo Alto, USA). The pyrolysis experiment was performed at 400 °C for 20 s with a heating rate of 100 °C/s. The products were analyzed by the GC/MS online, and the gas transmission pipeline and injection valve temperatures were set at 300 °C. The separation column in the GC/MS was DB-1701 (60  $\mu$ m × 250  $\mu$ m × 0.25  $\mu$ m). The split ratio of the injected pyrolysis volatiles into the GC was 1:100, with a constant flow rate of helium (99.999%). The GC temperature program was: 35 °C maintained for 3 min, then heated at the heating rate of 5 °C/min to 280 °C, and then held at this temperature for 8 min. The ion source temperature was 230 °C.

#### Analysis of solid residues

To investigate the possible decomposition reactions during cellulose pyrolysis, the elemental composition and surface structure of the solid residues obtained at different temperatures were analyzed. A Vario Micro Cube Element Analyzer (Elementar, Langenselbold, Germany) and an Axis-Ultra DLD-600W x-ray photoelectron spectrometer (Kratos, Japan) were used to measure the above-mentioned aspects.

The x-ray photoelectron spectroscopy (XPS) analysis was conducted under the following conditions: excitation source: AlK $\alpha$ , 15 keV, 10 mA, and the analysis of the vacuum was better than 5 × 10<sup>-9</sup> torr. Peak fitting was performed using XPSPeak 4.1 after subtraction of the Shirley background. The binding energy corresponding to C-C of C1's signals was set at 285 eV to correct the charge effects, and these fitting peaks had the same FWHM (Full Width at Half Maximum).

# **RESULTS AND DISCUSSION**

#### **Measurement Uncertainty**

Solid residue yields from fast pyrolysis of cellulose with different sample weights in the WMR are shown in Fig. 2. Whether the weight of cellulose samples was 3 mg or 10 mg, yield of solid residue was always about 2 wt%, which suggested that the particles could be considered as a monolayer even with the cellulose sample amount of 10 mg. The stacking effect could be ignored in the present pyrolysis conditions. It is worth noting that when the amount of cellulose samples pyrolyzed in the WMR was less, yield of solid residue was more unstable. In order to reduce the experimental error and facilitate the collection of pyrolytic products, 8 to 10 mg cellulose was pyrolyzed in the post pyrolysis experiments.



Fig. 2. Yield of solid residue from fast pyrolysis of cellulose with different weights in the WMR

#### Yields of Solid Residue and Bio-oil at Different Pyrolysis Temperatures

Figure 3 shows the solid residue and bio-oil yields at different temperatures from the fast pyrolysis of cellulose (8 to 10 mg) in the WMR. Weight loss was negligible when the temperature was below 300 °C, which was in accordance with its thermogravimetric curves (Chaiwat *et al.* 2009; Wang *et al.* 2013). However, the yield of solid residue at 550 °C was only approximately 2 wt%, which was much less than the results from the thermogravimetric experiments (approximately 10 wt%). Hoekstra *et al.* (2012) has found that solid residue yield was zero when cellulose was pyrolyzed in the wire-mesh reactor with much higher heating rate. Therefore, if the heating rate was fast enough, it could achieve zero yield of solid residue from cellulose pyrolysis in the WMR. There are two possible reasons for the lower solid residue yield in the wire-mesh reactor. One possible reason was that the fast heating rate promoted the formation of bio-oil. This simultaneously prevented the cellulose from producing solid product, whose formation required a low temperature or slow heating rate. The other possible reason was that the secondary reaction was minimized in the WMR, which worked against the solid product formation.



Fig. 3. Yields of solid residue and bio-oil from the fast pyrolysis (100 °C/s) of cellulose in the WMR

The bio-oil yield was too low to analyze its components with HPLC-MS when the pyrolysis temperature was below 400 °C. Thus, four temperature points (400, 450, 500, and 550 °C) were selected for the analysis of the bio-oil in the present study. For the same reason, the highest pyrolysis temperature used for the analysis of sugars in the intermediates was 450 °C.

## **Evolution of the Sugars in the Water-Soluble Intermediates**

Previous research (Houminer and Patai 1969) has demonstrated that levoglucosan polymerization is easy to achieve. Also, the products were a mixture of various glucans having 1,3-, 1,4-, and 1,6- linkages, with  $\alpha$ - and  $\beta$ - orientations, amongst which maltosan was obtained in the largest yield. Maltosan and cellobiosan are isomers, and standard materials for them were analyzed by HPLC-MS. In the present study it was easy to distinguish them using HPLC-MS because of the differences in their second-order fragment ions (shown in Fig. 4) and retention time. No maltosan was detected in the present study. Therefore, the sugars in the water-soluble intermediates originated from the direct decomposition of cellulose, rather than levoglucosan polymerization.



Fig. 4. Second-order fragment ions of cellobiosan and maltosan

The corresponding MS spectra of various sugars in the water-soluble intermediates at different pyrolysis temperatures are shown in Fig. 5. Nothing was detected in the water-soluble intermediates when the pyrolysis temperature was 200 °C, while AC4 and AC3 appeared in the intermediates when the pyrolysis temperature reached 240 °C. Ponder and co-workers (1992) indicated that the cellulose chain began to depolymerize at approximately 230 °C, which was in agreement with the author's results. Because the polymerization of levoglucosan did not take place, and anhydrooligosaccharides such as AC2, AC3, and AC4 were identified, higher DP anhydrooligosaccharides were considered as anhydro-cellodextrans (cellopentaosan, cellohexaosan, and celloheptaosan). With increasing temperature, cellopentaosan (AC5), cellohexaosan (AC6), and celloheptaosan (AC7) also appeared in the water-soluble intermediates. Because of the limitations of the analytical instruments, the anhydrooligosaccharides with DP higher than 7, whose existence has been reported elsewhere (Yu et al. 2012), were not analyzed.

Glucose, cellobiose, and cellotriose were not detected in the intermediates at any pyrolysis temperatures. As the WMR could minimize the secondary decomposition of the intermediates, these sugars should not have broken down. As a result, they must have been formed only in a minimal amount, or not at all. The route that the cellulose decomposed *via* these reducing sugars as intermediates was inconsequential, and therefore, only anhydro-oligosaccharides are discussed in the following sections.



Fig. 5. The MS spectra of anhydro-oligosaccharides in the water-soluble intermediates

The yields of anhydro-oligosaccharides with DP up to 4 (on original cellulose basis) in the water-soluble intermediates are shown in Fig. 6. Variations in the yields of anhydro-oligosaccharides with DP from 2 to 4 were similar. The yields increased at first

as the temperature increased, and then they reached a maximum at 400 °C. In contrast, the yield of levoglucosan achieved its maximum at 370 °C. Levoglucosan is a rather stable compound with a boiling point of around 385 °C (Shoji et al. 2014). Levoglucosan was pyrolyzed in the WMR at 500 °C, employing a heating rate of 100 °C/s, and the recovery rate of levoglucosan was about 98.9%. Taking into account the collection loss, we thought that levoglucosan didn't decompose. Because the WMR suppressed further decomposition of levoglucosan produced during cellulose pyrolysis, and the pyrolysis temperature was much lower than 500 °C, the changes in the levoglucosan content in the intermediate phase were mainly related to physical evaporation. When the pyrolysis temperature was approximately 370 °C, the levoglucosan formation rate became slower than its evaporation rate, so the yield of levoglucosan decreased. The boiling points of AC2 and AC3 (Lédé 2012) were estimated to be 581 °C and 792 °C, respectively. In general, the boiling point of a polymer increased with increasing DP. Thus, the boiling points of anhydro-oligosaccharides with a DP above 1 were much higher than the pyrolysis temperature, which suggested that the changes in their contents in the intermediate phase were primarily associated with a chemical reaction. Because the yields of anhydro-oligosaccharides began to decrease as the temperature exceeded 400 °C, these anhydro-oligosaccharides likely depolymerized or decomposed quickly above 400 °C. Besides the chemical decomposition, larger DP anhydro-oligosaccharides could also escape the pyrolysis zone when temperature was high enough (Westerhof et al. 2016).

In this study, the yields of AC4 and AC3 were much higher than that of levoglucosan in the early pyrolysis stage. However, if cleavage of the cellulose chain was ruled by the "unzipping" mode, the yield of levoglucosan was expected to be the largest, even in the early pyrolysis stage. Therefore, the random cleavage mode was more reasonable to explain the observations of the present study. This conclusion obtained in this paper was consistent with the previous work (Westerhof et al. 2016; Mayes and Broadbelt 2012). Generally, the weakest point of heterochain polymers is the bond linking the repeating unit (Pakhomov 1957). With the decrease in DP, the link bond could become more stable. For cellulose, the 1,4-glucosidic bond is the weakest, and it could have randomly broken down due to the difference in crystallinity, or other factors, that produced various DP anhydro-oligosaccharides. When the DP of anhydrooligosaccharides were reduced to approximately 4, perhaps further depolymerization became difficult and required longer residence time at a low temperature or a higher pyrolysis temperature. Thus, the "unzipping" mode was suitable to explain the phenomenon at the lower temperature pyrolysis of cellulose. However, it could not account for the results under the fast pyrolysis conditions, which was also found by Radlein et al. (1991).

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Fig. 6. Yields of anhydro-oligosaccharides (DP up to 4) in the water-soluble intermediates

#### Fast Pyrolysis of the AC2 in the Py-GC/MS

AC2 is a typical intermediate product, and fast pyrolysis of AC2 was conducted in Py-GC/MS. In order to facilitate comparative analysis, fast pyrolysis of cellobiose was also performed. Figure 7 shows the ion chromatograms of the main products from fast pyrolysis of AC2 and cellobiose. The fast pyrolysis of AC2 produced glycolaldehyde, furans (furfural, 5-hydroxymethylfurfural), and anhydro-oligosaccharides (levoglucosan, levoglucosenone, *etc.*), but the most important product was levoglucosan. Compared with AC2, cellobiose pyrolysis produces more furans and less levoglucosan. The product distribution from the fast pyrolysis of AC2 was more similar than cellobiose to that from the fast pyrolysis of cellulose (Patwardhan *et al.* 2009; Mettler *et al.* 2012), which further suggested that the main components of the intermediates were anhydro-oligosaccharides.



Fig. 7. Total ion chromatograms of the main products from the fast pyrolysis of AC2 (a) and cellobiose (b)

#### Formation Characteristics of Water-soluble Compounds in Bio-oil

Unlike the intermediates that contained anhydro-oligosaccharides with various DPs, three anhydro-oligosaccharides (AC1, AC2, and AC3) were identified in the bio-oil, and their yields at different pyrolysis temperatures are shown in Fig. 8. The yields of

these anhydro-oligosaccharides were essentially the same at 500 and 550 °C. As boiling points of AC2 and AC3 were higher than the pyrolysis temperature, high yields of AC2 and AC3 in the bio-oil at relative low pyrolysis temperatures could not be explained solely by their vapor pressure at these temperatures or levoglucosan repolymerization, from which the main product was maltosan (Houminer and Patai 1969).



Fig. 8. Yields of A1, AC2, and AC3 in the bio-oil produced at different pyrolysis temperatures

Perhaps the ejection mechanism proposed by Teixeira *et al.* (2011) was responsible for the existence of AC2 and AC3 in the bio-oil. The ejection mechanism could transfer the melted non-volatile compounds into the bio-oil. Anhydro-oligosaccharides with DP above 3, generally with higher melting points, likely did not melt, or they had broken down into light molecular compounds before melting, which led to their absence in the bio-oil.

Figure 9 shows the RID spectra of the sugars in the bio-oil produced at 500 °C. Although the compounds corresponding to peaks 3, 4, and 5 were unknown, their relative molecular weights were 274, 222, and 162, respectively, according to their MS spectra. Unfortunately, the compound represented by peak 3 has never been reported, and the detailed structure remains unknown. It may have been one of the partially decomposed sugar-ring-containing oligomers (Yu *et al.* 2012). Lomax and co-workers (1991) identified two products derived from the reverse aldolization reaction of the sugar ring to produce glycolaldehyde from the Curie-point pyrolysis of cellulose, and the simplest structure had a relative molecular weight of 222. The compound with a molecular weight of 222 that was detected in this study may have been the product reported by Lomax *et al.* (1991). Reverse aldolization fragmentation with higher DP was not detected in this study. Perhaps they cracked before entering into the bio-oil. Peak 5 possibly represented 1,6-anhydroglucofuranose, which has been reported by many researchers.

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**Fig. 9.** The RID spectra of the products in the bio-oil produced at 500 °C: 1: AC3, 2: AC2, 3: unknown compound, 4: unknown compound, 5: unknown compound, and 6: AC1

### Analysis of the Solid Residues Obtained at Different Pyrolysis Temperatures

The elemental composition of both the unreacted cellulose and the solid residues obtained at different temperatures are shown in Fig. 10 in the form of a Van Krevelen diagram. The red dashed line has a slope of 2, which indicates that the dehydration reactions resulted in the reduction of H and C at a molar ratio of 2:1.

Figure 10 illustrates that the elemental composition of the solid residues obtained with an increasing temperature moved along the dehydration line from the upper right corner to the lower left corner. This indicated that the dehydration reaction took place during cellulose pyrolysis. However, H/C and O/C decreased only slightly, even at 400 °C, which suggested that the dehydration of cellulose under the current pyrolysis conditions did not occur severely.



Fig. 10. Van Krevelen diagram for the solid residues produced at different temperatures

The XPS analysis results of the raw cellulose and solid residues are shown in Fig. 11. The XPS spectrum of raw cellulose contained three C1s peaks at 285 eV, 286.7 eV, and 288.3 eV, corresponding to C<sub>1</sub> (C-C or C-H), C<sub>2</sub> (C-O), and C<sub>3</sub> (O-C-O or C=O), respectively. As for the pyrolysis solid residues, an additional C1s peak appeared at 289.8 eV, arising from C<sub>4</sub> (O-C=O) (Johansson 2002). Table 1 presents the relative contents of these four C1s peaks for the raw cellulose and solid residues. As the temperature increased, the relative content of C<sub>2</sub> decreased, while the relative contents of C<sub>3</sub> and C<sub>4</sub>

increased. As  $C_2$  mainly represents C-OH in the raw cellulose, the change of the relative content of  $C_2$  reflected dehydration during pyrolysis. In general, dehydration during cellulose pyrolysis was divided into two types: intramolecular dehydration and intermolecular dehydration. Intramolecular dehydration in the sugar ring formed a C=O bond (Pastorova *et al.* 1993), while a C-O-C bond was formed by intermolecular dehydration. The XPS data showed that intramolecular dehydration occurred.



Fig. 11. The C1s spectra for raw cellulose and solid residues produced at different temperatures

Table 1. XPS Analysis of Raw Cellulose and Solid Residues Produced at	İ
Different Temperatures	

	Binding Energy (eV)			
Sample	<b>C</b> <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>
	285	286.7	288.3	289.8
RC <sup>1</sup>	8.30	76.68	15.01	0.00
270 <sup>2</sup>	7.99	68.70	20.58	2.96
330	7.80	67.75	21.64	3.05
400	8.30	54.50	29.01	8.94

Notes: 1- Raw cellulose, and 2- The solid residue obtained at 270 °C

# CONCLUSIONS

1. The yield of solid residue was negligible at 550 °C when the fast pyrolysis of cellulose was performed in a wire-mesh reactor. This suggested that the fast pyrolysis of cellulose could achieve a zero yield of solid product if the pyrolysis conditions were well controlled.

- 2. Anhydro-oligosaccharides with DP up to 7 were detected in the water-soluble intermediates. A quantified analysis of the anhydro-oligosaccharides with DP up to 4 in the intermediates showed that the yields of AC4 and AC3 were much higher than that of levoglucosan in the early pyrolysis stage. This finding indicated that the depolymerization of the cellulose chain was possibly through a random cleavage process.
- 3. Similarities between the pyrolysis product distributions of cellulose and cellobiosan also suggested that the anhydro-oligosaccharides were more likely to be the intermediates during cellulose pyrolysis.
- 4. Anhydro-oligosaccharides with DP up to 3, and partially decomposed sugar-ringcontaining oligomers, were identified in the bio-oil. Cellobiosan and cellotriosan were likely transferred into the bio-oil through ejection. Among the partially decomposed sugar-ring-containing oligomers, the compound with a relative molecular weight of 222 was assumed to be the product from the reverse aldolization reaction that produced glycolaldehyde.
- 5. Analysis of the solid residues based on the elemental composition and XPS revealed that the dehydration reaction was not severe, and that intramolecular dehydration took place during cellulose pyrolysis.

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