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# Differences in Water-Soluble Intermediates from Slow Pyrolysis of Amorphous and Crystalline Cellulose

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**ABSTRACT:** The paper reports the significant differences in the pyrolysis behavior between amorphous and crystalline cellulose. The strong hydrogen bonding networks in crystalline cellulose appear to preserve the sugar ring structure during pyrolysis so that the yield (a maximum of ~30% on a carbon basis at 250 °C) of water-soluble intermediates for amorphous cellulose is considerably higher than that (a maximum of ~3% on a carbon basis at 270 °C) of crystalline cellulose pyrolysis. Direct evidence was also provided to prove that various sugar oligomers (DPs: 1–14) present in water-soluble intermediates are indeed produced from some short glucose chain segments in amorphous cellulose during pyrolysis at a temperature as low as 140 °C. The weak hydrogen bonding networks in amorphous cellulose allow the liberation of these short glucose chain segments as pyrolysis intermediates. Compared to those from crystalline cellulose, the water-soluble intermediates from amorphous cellulose contain considerably more sugar oligomers and anhydro-sugar oligomers with a much wider range of degrees of polymerization (DPs), e.g., 1–14 and 1–16 for sugar oligomers and anhydro-sugar oligomers, respectively. Post-hydrolysis results, together with the yields of quantifiable sugar and anhydro-sugar oligomers, further suggest that water-soluble intermediates from amorphous cellulose pyrolysis at temperatures <270 °C are mainly contributed by high-DP sugar and/or anhydro-sugar oligomers, plus partially decomposed sugar-ring-containing oligomers, i.e., PDSRCOs. However, low-DP anhydro-sugar oligomers and PDSRCOs are the main products of water-soluble intermediates from crystalline cellulose pyrolysis. At higher temperatures (e.g., 300 °C), the water-soluble intermediates from amorphous cellulose are dominantly non-sugar products, largely due to the destruction of the sugar ring structures within the pyrolyzing amorphous cellulose.

## 1. INTRODUCTION

Biomass is a key renewable feedstock for future sustainable production of liquid fuels, chemicals, and carbon materials.<sup>1,2</sup> However, large-scale biomass utilization is limited by its fuel features.<sup>3,4</sup> The underlying chemical reactions during biomass thermochemical processing are also sophisticated due to the complex structure of lignocelluloses.<sup>5–8</sup> Pyrolysis is widely regarded as a promising process for converting solid biomass into bio-oil and biochar.<sup>1,9–12</sup> Despite its process advantages, the commercialization of the biomass pyrolysis process is largely hindered by various undesired properties of bio-oil as feedstock for biofuel production.<sup>10–14</sup>

Sugar compounds in bio-oil, as part of products from the pyrolysis of cellulose and hemicellulose components in biomass, are known to require attention in bio-oil upgrading and refining.<sup>15–17</sup> Therefore, a sound understanding of the cellulose pyrolysis mechanism is essential to the development of technologies for producing bio-oil with desired properties. Cellulose can be considered as a linear polymer of  $\beta$ -1,4-D-glucopyranose units linked together by glycosidic bonds.<sup>18,19</sup> Depending on the pattern of hydrogen bonding networks in the macromolecular structure, cellulose can be of a crystalline nature but may also contain various amounts of amorphous cellulose.<sup>20,21</sup> It has been reported that crystalline cellulose has well-packed long chains side by side via strong hydrogen bonding networks<sup>18</sup> while amorphous cellulose has much weaker hydrogen bonding networks and shorter chain length.<sup>21–23</sup> Such structural differences in hydrogen bonding pattern and chain length can be important in determining the chemical reaction behavior of cellulose. For example, a recent

study<sup>21</sup> by this research group clearly demonstrated that, under the same conditions, hydrolysis of amorphous and crystalline cellulose in hot-compressed water produces hydrolysis products containing glucose oligomers of significantly different characteristics. Surprisingly, in the open literature, little has been reported on the differences in the pyrolysis behavior between amorphous and crystalline cellulose.

Reports in the open literature<sup>24–33</sup> and recent advances<sup>34–37</sup> in the field suggest that cellulose fast pyrolysis may take place through a molten intermediate state and such reaction intermediates are reported to be water-soluble. Studies on reaction intermediates of cellulose slow pyrolysis are scarce because the prolonged temperature–time history under the conditions leads to very low survival of these species. Nevertheless, a recent study<sup>38</sup> of the same authors successfully characterized the water-soluble intermediates from microcrystalline cellulose slow pyrolysis at low temperatures. It was found that a wide range of sugar oligomers and anhydro-sugar oligomers with degrees of polymerization (DPs) up to 10, along with partially decomposed sugar-ring-containing oligomers (i.e., PDSRCOs) that are neither sugar nor anhydro-sugar oligomers, can be present in the water-soluble intermediates from cellulose slow pyrolysis at 100–350 °C.<sup>38</sup> Particularly, the formation of sugar oligomers with various DPs is in contradiction to the common perception that the primary

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reactions of cellulose pyrolysis mainly produce anhydro-sugars. It was speculated that the amorphous portion of the microcrystalline cellulose is responsible for the formation of sugar oligomers,<sup>38</sup> but no direct evidence was available.

Therefore, this study carries out an experimental program to investigate the differences between the pyrolysis of amorphous and crystalline cellulose under slow heating conditions. The water-soluble intermediates were characterized to provide new insights into substantial differences in the pyrolysis behavior of amorphous and crystalline cellulose. These results are also of significant importance to understanding the fundamental chemical reactions of amorphous and crystalline cellulose during pyrolysis.

## 2. EXPERIMENTS

**2.1. Cellulose Samples and Chemicals.** Microcrystalline cellulose (Avicel PH-101, Sigma-Aldrich) was sieved to prepare the size fraction of 75–106  $\mu\text{m}$  (i.e., raw cellulose), which was then used to prepare both amorphous and crystalline cellulose samples. Using a laboratory ball mill (Retsch Mixer Mill MM400), the amorphous cellulose was prepared via extensive ball milling of the raw cellulose—a method employed in our previous study.<sup>23,39</sup> Briefly,  $\sim 2$  g of raw cellulose was charged into the grinding cell, and the ball mill was operated at a grinding frequency of 15 Hz with a 15 mm ball for  $\sim 7$  h. As shown in the X-ray diffraction analysis,<sup>23</sup> the crystalline structure in raw cellulose was completely destroyed by ball milling under the conditions, resulting in the production of a completely amorphous cellulose sample. Crystalline cellulose was prepared by subjecting the raw cellulose to hot-compressed water extraction to remove the amorphous cellulose in a semicontinuous reactor, which is detailed elsewhere.<sup>40</sup> About 2 g of raw cellulose was loaded into a tubular reactor sandwiched by stainless steel gasket filters. Deionized water was delivered by an HPLC pump at a flow rate of 10  $\text{mL min}^{-1}$  and flowed through the reactor. The reactor cell was then rapidly heated to  $\sim 190$   $^{\circ}\text{C}$  in a gold image furnace. The pressure of the reactor system was controlled at 10 MPa by a back-pressure regulator. After holding for  $\sim 4$  h, the reactor cell is immediately cooled down and followed by another 1-h water washing at room temperature. After that, the cellulose was collected and air-dried at 40  $^{\circ}\text{C}$  in an oven. The standards of sugar and anhydro-sugar oligomers with DPs up to 5, together with other high purity reagents, were purchased for water-soluble intermediate analysis.

**2.2. Pyrolysis Experiments.** Pyrolysis experiments of both amorphous and crystalline cellulose samples were conducted using a fixed-bed quartz reactor at 100–350  $^{\circ}\text{C}$  and 10  $\text{K min}^{-1}$ , following a similar procedure described elsewhere.<sup>38</sup> Briefly,  $\sim 2$  g amorphous or crystalline cellulose sample was charged into the reactor, which was then heated to a desired pyrolysis temperature at 10  $\text{K min}^{-1}$  under argon (UHP, 2.0  $\text{L min}^{-1}$ ), followed up with a further holding of 30 min at the pyrolysis temperature. Upon the completion of the pyrolysis program, the reactor was lifted out of the furnace immediately and cooled with argon continuously flowing through the reactor. The whole reactor (including the sample) was weighted before and after experiment. The weight loss of the sample was determined by the weight difference, taking into account the moisture in the samples.

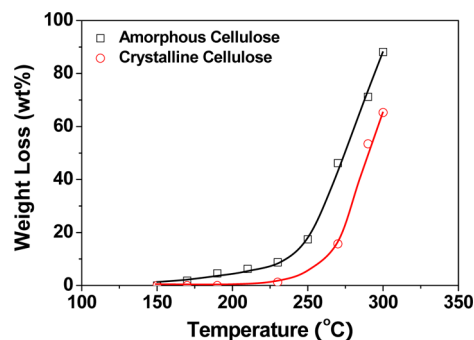
**2.3. Characterization and Analysis of Solid Samples.** The cellulose samples, along with the solid residues produced after various pyrolysis experiments, were subjected to Fourier transform infrared (FTIR) analysis (model: Perkin-Elmer Spectrum 100 ATR-FTIR spectrometer) for investigating the changes in functional groups in cellulose as results of pyrolysis reactions under various conditions. Post-hydrolysis was also carried for the cellulose samples and solid residues produced after various pyrolysis experiments to determine the total neutral glucose content in the samples, via acid hydrolysis according to an NREL method.<sup>41</sup> Briefly,  $\sim 300$  mg of sample was first hydrolyzed by sulfuric acid (72%) at 30  $^{\circ}\text{C}$  for 1 h, followed by adjusting acid concentration to 4% then treating the sample in an

autoclave for another 1 h at 121  $^{\circ}\text{C}$ . The solution was neutralized at room temperature before it was subjected to determine the glucose content in the solution using a high-performance anion exchange chromatography with pulsed amperometric detection (HPAEC-PAD, model: Dionex ICS-3000), following an isocratic method that elutes 100 mM NaOH at a flow rate of 0.5  $\text{mL min}^{-1}$ . The correction of sugar losses due to glucose degradation during acid hydrolysis was also considered.

**2.4. Characterization of Water-Soluble Intermediates from Amorphous and Crystalline Cellulose Pyrolysis.** Water-soluble intermediates were extracted from the solid residues produced from the pyrolysis of amorphous and crystalline cellulose by deionized water, following the procedure described elsewhere.<sup>38</sup> The contents of total organic carbon (TOC) in solutions after extraction were immediately analyzed using a TOC analyzer (model: Shimadzu TOC-V<sub>CPH</sub>). The yield of water-soluble intermediates was calculated on a carbon basis via normalizing the total water-soluble carbon to the total carbon in cellulose (amorphous or crystalline) fed into the reactor prior to pyrolysis reactions. The sugar oligomers and anhydro-sugar oligomers in the liquid samples were characterized by HPAEC-PAD analysis according to a gradient method,<sup>40</sup> using the Dionex ICS-3000 ion chromatography system. The identification of sugar oligomers and anhydro-sugar oligomers follows a similar approach as those used elsewhere.<sup>38,40,42</sup> For convenience, hereafter, sugar oligomers and anhydro-sugar oligomers are named according to the DP value (e.g., glucose as C1, cellobiose as C2, levoglucosan as AC1, cellobiosan as AC2, respectively). The sugar and anhydro-sugar oligomers with DPs of 1–5 can be directly quantified with standards using the isocratic method. Post-hydrolysis of the liquid samples was also carried out to quantify the total neutral glucose content in water-soluble intermediates.

## 3. RESULTS AND DISCUSSION

**3.1. Differences in Weight Loss and Structure Change during the Pyrolysis of Amorphous and Crystalline Cellulose.** Figure 1 presents the weight loss data of amorphous and crystalline cellulose samples during pyrolysis at different temperatures. Appreciable weight loss for amorphous cellulose during pyrolysis begins at  $\sim 170$   $^{\circ}\text{C}$  (443 K), which is much lower than that of crystalline cellulose, i.e.,  $\sim 230$   $^{\circ}\text{C}$  (503 K).



**Figure 1.** Weight loss of amorphous and crystalline cellulose as a function of pyrolysis temperature.

The reported temperature at which cellulose pyrolysis commences varies with heating rate, possibly due to the heat transfer limitation in the cellulose particle. For example, it was reported that in a thermogravimetric analyzer (TGA), cellulose pyrolysis commences at  $\sim 525$  K at 1  $\text{K min}^{-1}$ ,  $\sim 550$  K at 15  $\text{K min}^{-1}$ , and  $\sim 600$  K at 150  $\text{K min}^{-1}$ .<sup>43</sup> The reported temperatures are all higher than those obtained in this study, due to possibly two reasons. One is that previous studies used raw microcrystalline cellulose. The other is that the pyrolysis

experiments in this study include a further holding period of 30 min.

The data in Figure 1 also show that the weight loss of amorphous cellulose is always higher than that of crystalline cellulose at the same pyrolysis temperature. Substantial weight losses take place between 250 and 290 °C for amorphous cellulose and between 270 and 300 °C for crystalline cellulose, respectively. The weight losses are significant for both cellulose samples at 300 °C (~88% and ~65% for amorphous and crystalline cellulose samples, respectively). The results demonstrate that amorphous cellulose is more prone to decomposition and produces volatiles at a much lower temperature than crystalline cellulose. The data also suggest that amorphous cellulose pyrolysis has a different reaction pathway in comparison to crystalline cellulose. The macromolecular structures of amorphous and crystalline cellulose are mainly different in the hydrogen bonding networks, which appear to play an important role during cellulose pyrolysis.

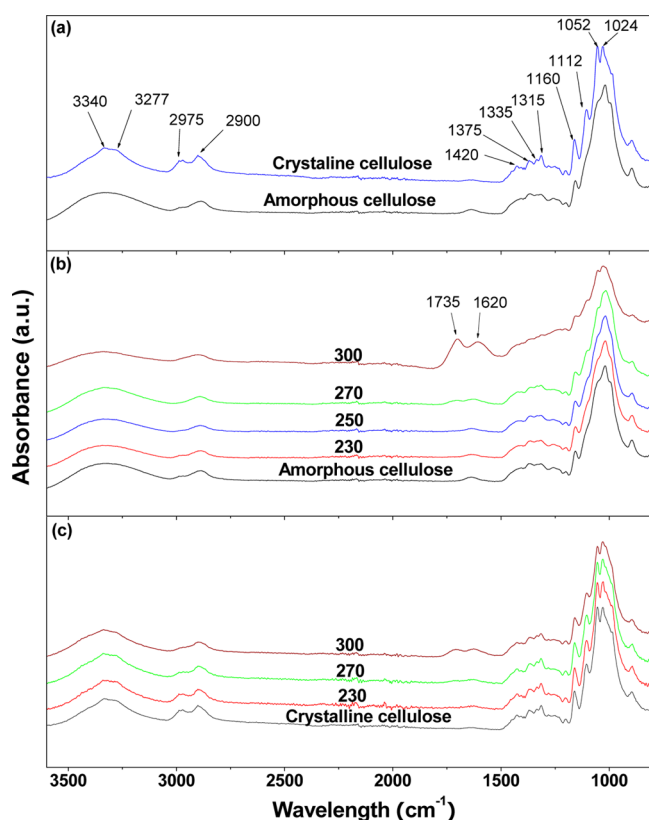
Figure 2a presents the FTIR spectra for the amorphous and crystalline cellulose samples. It can be seen that the hydrogen bonding networks in amorphous cellulose are indeed broken. This is clearly evident as the absorption ranges of 3230–3310  $\text{cm}^{-1}$  (representing intermolecular O(3)H...O(5) hydrogen bond<sup>44</sup>) and 3340–3375  $\text{cm}^{-1}$  (representing intramolecular O(3)H...O(5) hydrogen bond<sup>44</sup>) disappear. Additionally, other function groups representing strong hydrogen bonding networks (e.g., ~1278 and ~1375  $\text{cm}^{-1}$  for CH bending, ~1315  $\text{cm}^{-1}$  for CH<sub>2</sub> wagging, ~1335  $\text{cm}^{-1}$  for –OH in plane

bending, ~1420  $\text{cm}^{-1}$  for CH<sub>2</sub> bending vibration, and ~1112  $\text{cm}^{-1}$  for ring asymmetric stretching<sup>45,46</sup>) also disappear in the FTIR spectra of the amorphous cellulose. It is also noted that the response of aliphatic C–H stretch bands at 3000–2800  $\text{cm}^{-1}$  in crystalline cellulose appear to be increased after the raw cellulose was pretreated by hot-compressed water.<sup>47</sup>

Figure 2b and c further presents the FTIR spectra of the solid residues produced from the pyrolysis of amorphous and crystalline cellulose, respectively. For amorphous cellulose at 270 °C and above, there is a clear reduction in –OH group (3200–3600  $\text{cm}^{-1}$ ). It is also evident for the appearance of new peaks at ~1735  $\text{cm}^{-1}$  (known for C=O stretching<sup>47</sup>) and ~1620  $\text{cm}^{-1}$  (known for unsaturated C=C stretching<sup>47</sup>), indicating that the dehydration of the cellulose has occurred. It is interesting to see that dehydration of amorphous cellulose started at a lower temperature (~270 °C) than that of crystalline cellulose, which appears to commence at around 300 °C. Additionally, the absorption patterns at 1200–1400  $\text{cm}^{-1}$  were largely destroyed for amorphous cellulose during pyrolysis at 300 °C, suggesting that the sugar ring structure of cellulose was largely damaged under the conditions. This is in contrast to those for crystalline cellulose which the FTIR spectra clearly show the presence of abundant sugar ring structure in crystalline cellulose after pyrolysis at 300 °C. Again, such differences observed in macromolecular structures of solid residues produced from the pyrolysis of amorphous and crystalline cellulose samples suggest that the hydrogen bonding networks within cellulose play an important role in reactions during pyrolysis. The presence of strong hydrogen bonding networks appears to make the sugar ring structures within cellulose more resistant to dehydration reactions.

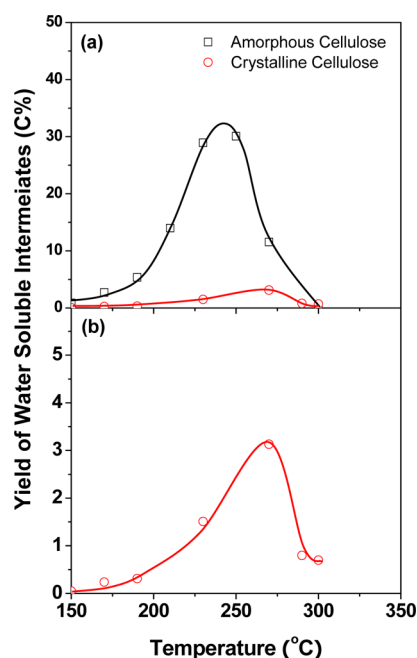
### 3.2. Difference in Yield of Water-Soluble Intermediates Produced from the Pyrolysis of Amorphous and Crystalline Cellulose.

The liquid samples of water-soluble intermediates were obtained via extraction of the solid residues after pyrolysis by deionized water at room temperature. Figure 3 presents the yield of water-soluble intermediates (expressed as the percentage of total carbon in cellulose) from the pyrolysis of both amorphous and crystalline cellulose samples at different pyrolysis temperatures. Clearly, pyrolysis of amorphous and crystalline cellulose exhibits substantial differences in the yield of water-soluble intermediates, with several important observations. First, water-soluble intermediates can be formed from the pyrolysis of amorphous cellulose at a temperature as low as 150 °C, at which no apparent weight loss was observed. However, for crystalline cellulose, the formation of water-soluble intermediates commences at 170 °C. Second, at any pyrolysis temperature, the yield of water-soluble intermediates from amorphous cellulose pyrolysis is considerably higher than that from crystalline cellulose. Third, in both cases, the yield of water-soluble intermediates increases with pyrolysis temperature, reaches a maximum, and then decreases with a further increase in pyrolysis temperature. The maximum yield for amorphous cellulose is ~30% (on a carbon basis), and the maximum occurs at ~250 °C; meanwhile, that for crystalline cellulose is only ~3%, and the maximum occurs at ~270 °C, which are similar to the previously reported values<sup>38</sup> (~3% at 270 °C) for raw cellulose. The substantially high yield of water-soluble intermediates in the solid residue from the pyrolysis of amorphous cellulose clearly suggests that amorphous cellulose follows a different mechanism to form intermediates during pyrolysis, in comparison to crystalline cellulose.



**Figure 2.** FTIR spectra of amorphous and crystalline cellulose, along those of solid residues from the pyrolysis of amorphous and crystalline cellulose at various temperatures: (a) amorphous and crystalline cellulose; (b) solid residues from the pyrolysis of amorphous cellulose; and (c) solid residues from the pyrolysis of crystalline cellulose.

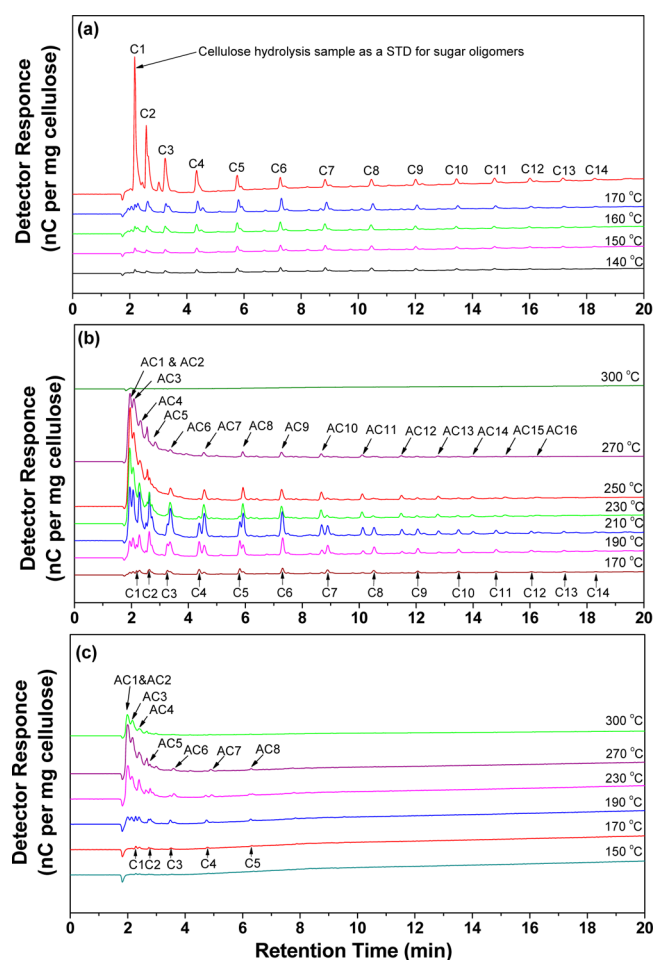




**Figure 3.** Yields of water-soluble intermediates (as a percentage of total carbon in cellulose before pyrolysis) from the pyrolysis of amorphous and crystalline cellulose at various temperatures: (a) a comparison of the yields between amorphous and crystalline cellulose; (b) yield for crystalline cellulose (as a close-up of panel a).

It should also be noted that although the yield of water-soluble intermediates from the pyrolysis of amorphous cellulose has a maximal yield of  $\sim 30\%$  at  $250\text{ }^{\circ}\text{C}$ , at the same temperature, the amorphous cellulose only experiences a weight loss of  $\sim 17\%$ . A further increase in pyrolysis temperature to  $270\text{ }^{\circ}\text{C}$  leads to a substantial decrease in the yield of water-soluble intermediates ( $\sim 12\%$ ) and a substantial increase in the sample weight loss ( $\sim 46\%$ ). This means that there are a substantial amount of water-soluble intermediates present in the pyrolyzing cellulose. These intermediates are difficult to evaporate/decompose to be released as volatiles at  $250\text{ }^{\circ}\text{C}$ , but an increase of  $20\text{ }^{\circ}\text{C}$  to  $270\text{ }^{\circ}\text{C}$  can substantially intensify the conversion of these intermediates into volatiles. On the contrary, for crystalline cellulose, the maximal yield is  $\sim 3\%$  at  $270\text{ }^{\circ}\text{C}$ , at which the crystalline cellulose experiences a weight loss of  $\sim 16\%$ . A further increase in the pyrolysis temperature leads to substantial reductions in the yields of water-soluble intermediates, together with substantial increases in weight loss. Obviously, the stability of water-soluble intermediates within the pyrolyzing cellulose determines the temperature at which the maximal weight loss occurs. It is clear that the water-soluble intermediates from amorphous cellulose seems less stable and easier to decompose/evaporate, with weight loss taking place mainly at  $250\text{--}290\text{ }^{\circ}\text{C}$ , in comparison to  $270\text{--}300\text{ }^{\circ}\text{C}$  for crystalline cellulose. Therefore, it can be concluded that the cellulose structure (mainly hydrogen bonding networks) significantly affects its thermochemical behavior, via controlling the formation of intermediates (hence, pyrolysis products e.g. volatiles) during pyrolysis.

**3.3. Distribution of Sugar Oligomers and Anhydro-sugar Oligomers in Water-Soluble Intermediates Produced from the Pyrolysis of Amorphous Cellulose.** The liquid samples of water-soluble intermediates were then analyzed by HPAEC-PAD to identify the oligomers present



**Figure 4.** IC chromatograms of water-soluble intermediates from the slow pyrolysis of amorphous and crystalline cellulose: (a) pyrolysis of amorphous cellulose at  $140\text{--}170\text{ }^{\circ}\text{C}$ ; (b) pyrolysis of amorphous cellulose at  $170\text{--}300\text{ }^{\circ}\text{C}$ ; (c) pyrolysis of crystalline cellulose at  $150\text{--}300\text{ }^{\circ}\text{C}$ .

in the water-soluble intermediates. Figure 4a presents the chromatograms of liquid samples prepared by room-temperature water extraction of solid residues from amorphous cellulose pyrolysis at various temperatures. Figure 4a compares the chromatograms of water-soluble intermediates samples from amorphous cellulose pyrolysis at  $140\text{--}170\text{ }^{\circ}\text{C}$ , together with a cellulose hydrolysis sample prepared in hot-compressed water as a standard for high-DP glucose oligomers. It is noted that at temperatures  $\leq 150\text{ }^{\circ}\text{C}$ , the cellulose sample experiences no weight loss. Therefore, the presence of the intermediates in the solid phase demonstrates that the changes occurred within cellulose macromolecular structure produce intermediates which were completely retained in the solid phase, without further conversion to be released as volatiles. Figure 4a clearly shows the presence of various glucose oligomers with a wide range of DPs of 1–14 in the water-soluble intermediates even at  $140\text{ }^{\circ}\text{C}$ . No anhydro-sugar oligomers are present in that sample. This demonstrates that amorphous cellulose pyrolysis produces glucose oligomers with a wide range of DPs at a temperature as low as  $140\text{ }^{\circ}\text{C}$ . As the glycosidic bonds in amorphous cellulose is not likely to break at such a low temperature, it can be concluded that these sugar oligomers are clearly produced from the liberation of these short glucose chain segments that are abundant in the amorphous cellulose.<sup>21</sup>

as results of the breakage of weak hydrogen bonds during pyrolysis at low temperature.

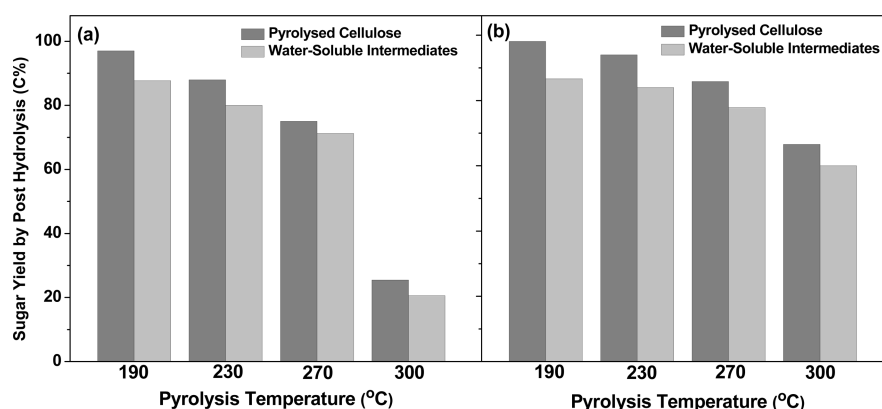
Figure 4b compares the chromatograms of water-soluble intermediates samples prepared by water extraction of solid residues from amorphous cellulose pyrolysis at 170–300 °C. As the chromatograms are normalized to the amount of cellulose sample loaded into the pyrolysis reactor, the heights for the same peak in chromatograms for different samples represent their concentrations in the liquid samples and can be directly compared. It is interesting to point out that at 170 °C, anhydro-sugar oligomers with DPs of 1–11 start to appear in the water-soluble intermediates, in addition to sugar oligomers with DPs of 1–14 that are observed in samples at lower temperatures. It is also clear that the concentrations of sugar oligomers increase with pyrolysis temperature, reach a maximum at ~210 °C, and then decrease with further increase in pyrolysis temperature. In addition, the concentrations of the anhydro-sugar oligomers increase with temperature from 170 °C, reach a maximum at ~230 °C, and then decrease with further increase in pyrolysis temperature. It is noteworthy that a higher pyrolysis temperature leads to the production of anhydro-sugar oligomers with higher DPs. For example, anhydro-sugar oligomers with DPs of 1–16 can be identified in the water-soluble intermediates at ~230 °C, in comparison to those with DPs of 1–11 at 170 °C. However, a too high pyrolysis temperature also results in the rapid decomposition of those sugar and anhydro-sugar oligomers. For example, at 270 °C, all the sugar oligomers have disappeared while anhydro-sugar oligomers can still be found in the water-soluble intermediates. At 300 °C, there is only a very small amount of anhydro-sugar oligomers in the water-soluble intermediates (see Figure 4b). The results in Figure 4b provide essential evidence for revealing the formation anhydro-sugar oligomers during the pyrolysis of amorphous cellulose. As the formation of levoglucosan is very small (<3%) during the pyrolysis of glucose and cellobiose,<sup>38</sup> anhydro-sugar oligomers from cellulose pyrolysis are not likely to be produced via direct dehydration reaction of sugar oligomers. Therefore, most of the anhydro-sugar oligomers are likely to be formed via the cleavage of glycosidic bond in cellulose.

**3.4. Distribution of Sugar Oligomers and Anhydro-sugar Oligomers in Water-Soluble Intermediates Produced from the Pyrolysis of Crystalline Cellulose.** Figure 4c presents the chromatograms of water-soluble intermediates samples prepared by water extraction of solid residues from crystalline cellulose pyrolysis at 150–300 °C. Compared to those from amorphous cellulose (see Figure 4a and b), there are several distinct differences in the compositions of water-soluble intermediates from the pyrolysis of amorphous and crystalline cellulose samples.

First, opposite to amorphous cellulose, no sugar oligomers of various DPs can be found in the liquid samples prepared from water extraction of the solid residue from crystalline cellulose pyrolysis at 150 °C. This suggests that most of amorphous cellulose within the raw microcrystalline cellulose have indeed been removed via the pretreatment method. This in turn demonstrated that the formation of sugar oligomers with various DPs observed in the pyrolysis of amorphous cellulose (see Figures 4a) at low temperatures are indeed results of the liberation of the short glucose chain segments in the amorphous cellulose, as results of the breakage of weak hydrogen bonds.

Second, it is surprising to observe the presence of a trace (but appreciable) amount of low-DP (up to 5) glucose oligomers in the water-soluble intermediates obtained from crystalline cellulose pyrolysis at 170 °C. As there are no anhydro-sugar oligomers present in the samples, the low-DP sugar oligomers that appear at 170 °C are most likely the products from cellulose hydrolysis, which was retained in the solid sample upon rapid cooling when preparing the crystalline cellulose from the raw cellulose using hot-compressed water pretreatment. However, this alone appears to be insufficient for explaining the increased production of low-DP sugar oligomers in the water-soluble product obtained from the pyrolysis of crystalline cellulose at 190 °C. Both anhydro-sugar oligomers and sugar oligomers can be produced via thermal cleavage of glycosidic bonds,<sup>31</sup> via the depolymerization of a long cellulose chain into one chain with a levoglucosan end (which could be anhydro-sugar oligomers) and the another chain with a nonreducing end (which could be sugar oligomers). Figure 4c shows that anhydro-sugar oligomers with DPs of 1–8 are already produced at 190 °C during crystalline cellulose pyrolysis, together with sugar oligomers with DPs of 1–5. Therefore, the depolymerization reactions by breaking the glycosidic bonds within the glucose chains start to take place during the pyrolysis of crystalline cellulose at ~190 °C, which is higher than the 170 °C for amorphous cellulose. This further demonstrates that the glycosidic bonds in amorphous cellulose are easier to break as the result of much weaker hydrogen bonding networks.

Third, the DPs of anhydro-sugar oligomers in the water-soluble intermediates from the pyrolysis of crystalline cellulose are much lower than those from amorphous cellulose. For example, the maximal DP of anhydro-sugar oligomers from crystalline cellulose is 8 at 270 °C, in comparison to 13 and 15 from amorphous cellulose at 270 and 250 °C, respectively. Again, it is known that the main differences between amorphous and crystalline cellulose samples lie in the chain length and hydrogen bonding networks.<sup>18,20,22</sup> Compared to amorphous cellulose, crystalline cellulose has strong and well-structured hydrogen bonding networks which connect long glucose chains to form crystalline structures. The results in this study clearly demonstrate that as results of such well-packed crystalline structure, the strong hydrogen bonding networks within crystalline cellulose offer protection to the glycosidic bonds, resulting in the requirement of higher temperatures for the pyrolysis reactions of crystalline cellulose to proceed. Even the glycosidic bonds are broken; the broken chain is still largely attached within crystalline cellulose as the strong hydrogen bonds are still intact. Therefore, only the lower-DP anhydro-sugars have a higher chance to be completely separated from crystalline cellulose. Oppositely, the hydrogen bonds within amorphous cellulose are very weak and easily broken during pyrolysis at low temperatures. The cleavage of glycosidic bonds in the individual glucose chains within amorphous cellulose can directly produce individual anhydro-sugar oligomers and other products that can be easily extracted from the solid residues. Due to the shorter glucose chain length in amorphous cellulose, there are more chances to produce high-DP anhydro-sugar oligomers from amorphous cellulose. Therefore, water-soluble intermediates from amorphous cellulose pyrolysis contain anhydro-sugar oligomers with a wider range of DPs and a higher maximal DP than those from crystalline cellulose pyrolysis under the same conditions. It can then be concluded that although the cleavage of glycosidic bonds within individual



**Figure 5.** Sugar yields by post-hydrolysis of solid residues and water-soluble intermediates samples from the pyrolysis of amorphous and crystalline cellulose at various temperatures: (a) amorphous cellulose; (b) crystalline cellulose.

glucose chains may proceed in a random manner, the yield of anhydro-sugar oligomers produced as pyrolysis intermediates largely depends on the hydrogen bonding networks within the cellulose sample.

Last, it is found that the water-soluble intermediates of amorphous cellulose pyrolysis at 300 °C contain little anhydro-sugar oligomers (see Figure 4b), which are still abundant in the water-soluble intermediates of crystalline cellulose pyrolysis at the same temperature. It is noted that there is still ~12% of unconverted solid product after the completion of amorphous cellulose pyrolysis at 300 °C. Therefore, the results suggest that in absence of strong hydrogen bonding networks, the anhydro-sugar oligomers from the cleavage of glycosidic bonds within pyrolyzing amorphous cellulose are difficult to survive at 300 °C, more likely due to the formation of cross-linked structure<sup>48</sup> of solid residue from amorphous cellulose at high temperatures.

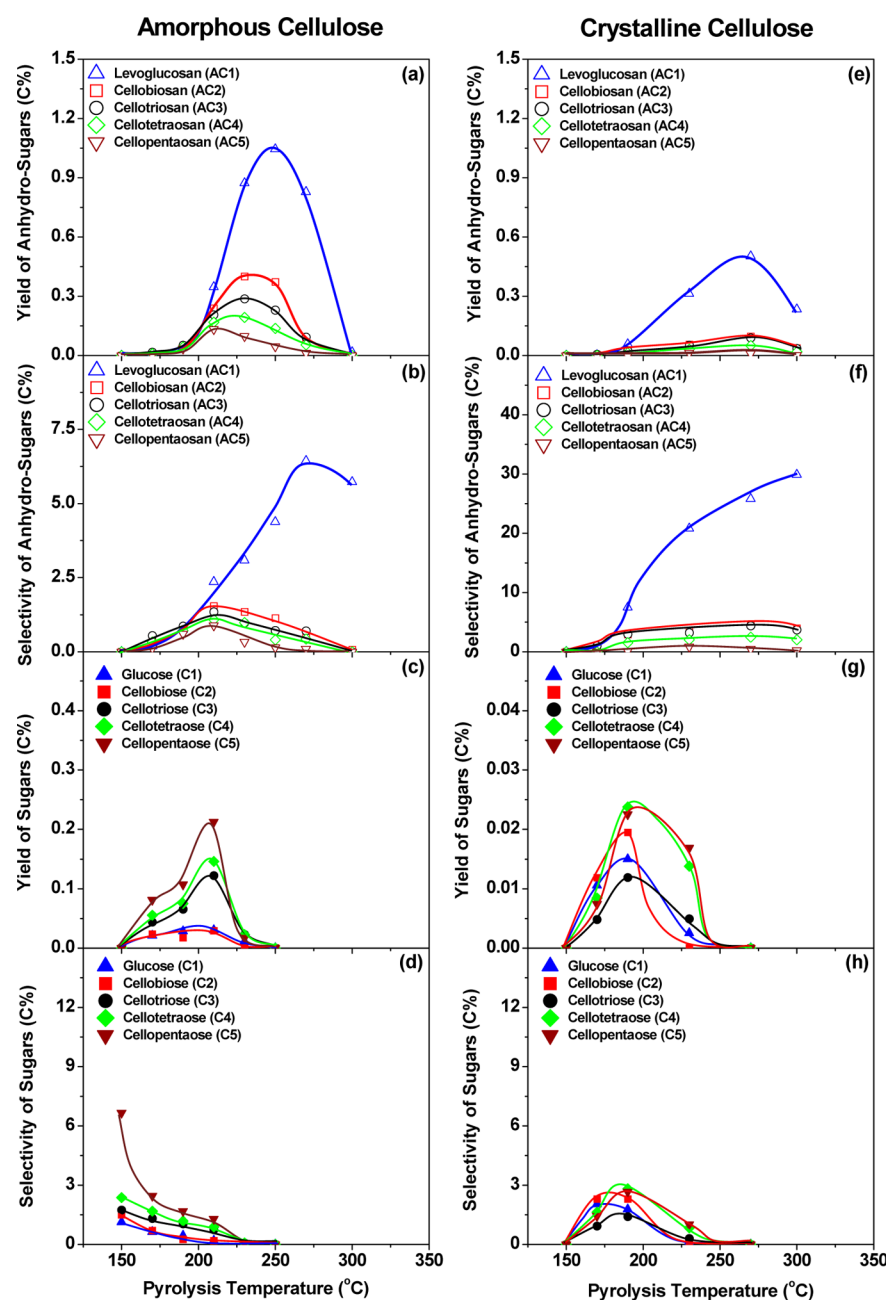
**3.5. Differences in the Total Hydrolyzable Sugars in Water-Soluble Intermediates Produced from the Pyrolysis of Amorphous and Crystalline Cellulose.** The water-soluble intermediates, together with the cellulose samples and the solid residues obtained from pyrolysis, were subject to post-hydrolysis, in order to obtain the total hydrolyzable sugar yields of these samples. The total hydrolyzable sugar yield is contributed by the glucose from the post-hydrolysis of various glucose-ring-containing oligomers, namely sugar oligomers (including glucose), anhydro-sugar oligomers (including levoglucosan), and the partially decomposed sugar-ring-containing oligomers (PDSRCOs). It is important to note that the PDSRCOs are neither sugar oligomers nor anhydro-sugar oligomers but contribute to glucose production during post-hydrolysis.

The total sugar yields (on a carbon basis) for various samples are presented in Figure 5. It can be seen that the total sugar yields of solid residues and water-soluble intermediates after pyrolysis all decreases with increasing pyrolysis temperature for both amorphous and crystalline cellulose. Additionally, the total sugar yield of a solid residue is always slightly higher than that of the water-soluble intermediate at the same pyrolysis temperature. This indicates that the water-soluble intermediates are more prone to further reactions for forming non-sugar products during pyrolysis, which is consistent with our previous work.<sup>38</sup>

There are also significant differences between the pyrolysis of amorphous and crystalline cellulose. For amorphous cellulose, a significant reduction in total sugar yield was observed at 300 °C in both solid residue and water-soluble intermediates. For

example, as pyrolysis temperature increases from 270 to 300 °C, the sugar yield reduces from ~75% to ~25% and ~71% to ~21% for solid residue and water-soluble intermediates, respectively. As aforementioned, there are very little anhydro-sugar oligomers in the water-soluble intermediates from amorphous cellulose pyrolysis at 300 °C (see Figure 4b). However, there is still about 25% sugar yield from post-hydrolysis of the solid residue from amorphous cellulose pyrolysis at 300 °C. This indicates that there is still a considerable amount of sugar ring structures in the solid residue from amorphous cellulose pyrolysis at 300 °C, in the form of structures from which it is difficult to produce anhydro-sugars via the cleavage of glycosidic bonds during pyrolysis. It is also plausible to believe that such structures are likely to be responsible for the formation of PDSRCOs in the water-soluble intermediates under the prevailing conditions. As for crystalline cellulose, the total sugar yield from post-hydrolysis decreases gradually as the pyrolysis temperature increases. Compared to those from amorphous cellulose, the total sugar yields of solid residues or water-soluble intermediates from crystalline cellulose pyrolysis are all higher under the same pyrolysis conditions. Particularly, for crystalline cellulose pyrolysis at 300 °C, the sugar yields from the solid residue and the water-soluble intermediates are ~67% and ~60%, respectively. These are considerably higher than those for amorphous cellulose (~25% and ~20%, respectively) under the same conditions. The results clearly suggest that while slowing down the pyrolysis reactions, the presence of strong hydrogen bonding networks within crystalline cellulose appears to also largely protect the sugar ring structure from being destroyed during pyrolysis at high temperatures. These results are consistent with the FTIR results in section 3.1.

**3.6. Differences in Yields and Selectivities of Sugar Oligomers and Anhydro-sugar Oligomers in Water-Soluble Intermediates Produced from the Pyrolysis of Amorphous and Crystalline Cellulose.** Further efforts were then taken to quantify the sugar oligomers and anhydro-sugar oligomers with DPs of 1–5 in water-soluble intermediates according to HPAEC-PAD analysis because those standards are available. The yields and selectivities of these sugar oligomers and anhydro-sugar oligomers, expressed on a carbon basis, are presented in Figure 6. For anhydro-sugar oligomers (see Figure 6a and e), the effect of pyrolysis temperature on their yields generally follows a similar trend, i.e., increasing with pyrolysis temperature initially, reaching a maximum at a certain temperature, then decreasing with further increase in pyrolysis

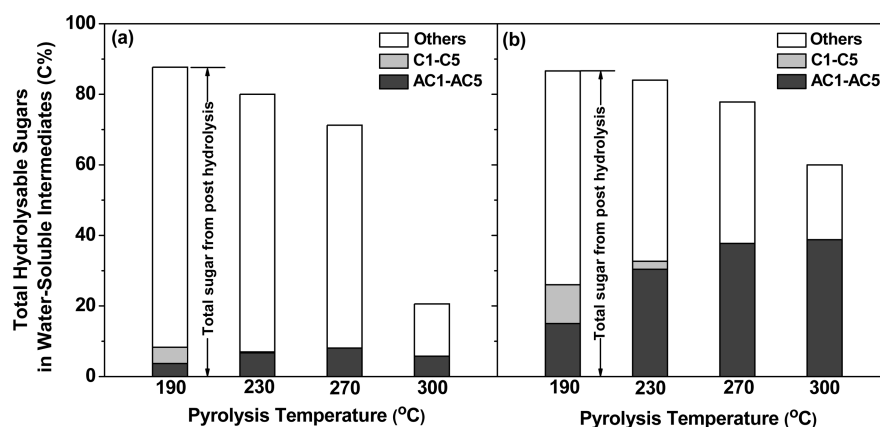


**Figure 6.** Yields and selectivities of quantifiable anhydro-sugar and sugar oligomers in the water-soluble intermediates from the pyrolysis of amorphous and crystalline cellulose samples at various temperatures: (a) yield of anhydro-sugar oligomers for amorphous cellulose; (b) selectivity of anhydro-sugar oligomers for amorphous cellulose; (c) yield of sugar oligomers for amorphous cellulose; (d) selectivity of sugar oligomers for amorphous cellulose; (e) yield of anhydro-sugar oligomers for crystalline cellulose; (f) selectivity of anhydro-sugar oligomers for crystalline cellulose; (g) yield of sugar oligomers for crystalline cellulose; and (h) selectivity of sugar oligomers for crystalline cellulose.

temperature. For amorphous cellulose, the lower-DP anhydro-sugar oligomers reach the maximal yield at a higher pyrolysis temperature and the maximal yield is also higher. For example, levoglucosan reaches the maximal yield of  $\sim 1.0\%$  at  $\sim 250^\circ\text{C}$ , in comparison to cellobiosan of  $\sim 0.4\%$  at  $\sim 240^\circ\text{C}$ , cellotriosan of  $\sim 0.3\%$  at  $\sim 230^\circ\text{C}$ , cellotetraosan of  $\sim 0.2\%$  at  $\sim 220^\circ\text{C}$ , and cellopentaosan of  $\sim 0.15\%$  at  $\sim 210^\circ\text{C}$ . As the effect of hydrogen bonding is insignificant in the case of amorphous cellulose, the data suggest that the stabilities of anhydro-sugar oligomers present in the pyrolyzing amorphous cellulose decrease with increasing DP. The instable high-DP anhydro-sugar oligomers may also decompose into low-DP anhydro-sugar oligomers, contributing to their high maximal yields. For

crystalline cellulose, the value of the maximal yield also decreases with the DP of the anhydro-sugar oligomers. However, at the same temperature, the maximum reached is considerably lower than that for amorphous cellulose. Such differences clearly demonstrate the critical roles of the strong hydrogen bonding networks within crystalline cellulose. At the same temperature, the strong hydrogen bonding networks within crystalline cellulose make it more difficult for the pyrolysis reactions to proceed, leading to much lower yields of anhydro-sugar oligomers at the same pyrolysis temperature. Furthermore, as shown in Figure 6e, for crystalline cellulose, the maximal yields for all anhydro-sugar oligomers reach at the same temperature ( $\sim 270^\circ\text{C}$ ). The results suggest that the





**Figure 7.** Contribution of sugar oligomers with DPs of 1–5 (i.e., C1–C5) and anhydro-sugar oligomers with DPs 1–5 (i.e., AC1–AC5) to total hydrolysable sugars in the water-soluble intermediate samples produced from the pyrolysis of amorphous and crystalline cellulose samples at various temperatures: (a) amorphous cellulose; (b) crystalline cellulose.

dominant roles of strong hydrogen bonding networks in pyrolysis reactions, making the difference in the pathways of producing anhydro-sugars with different DPs become less important.

As shown in Figure 3, the yield of water-soluble intermediates during amorphous cellulose pyrolysis (~30% max) is substantially higher than that of crystalline cellulose (~3% max), by 1 order of magnitude. However, Figure 6a shows that the yields of anhydro-sugar oligomers with DPs of 1–5 from amorphous cellulose is only several times (e.g., twice for levoglucosan, 4 times for cellobiosan, 3 times for cellotriosan) higher than those from crystalline cellulose. This leads to considerably lower selectivities for anhydro-sugars with DPs of 1–5 in water-soluble intermediates from amorphous cellulose. As shown in Figure 6b and f, the maximal selectivity for levoglucosan from amorphous cellulose is only ~6% at 270 °C, compared to ~26 and 29% from crystalline cellulose at 270 and 300 °C, respectively. This indicates that the low-DP anhydro-sugars are not the main products in the water-soluble intermediates from amorphous cellulose pyrolysis, while these products are indeed main products in the water-soluble intermediates from crystalline cellulose pyrolysis. The data again suggest the important roles of strong hydrogen bonding networks within crystalline cellulose during pyrolysis. Even for the anhydro-sugar oligomers produced during pyrolysis, as part of pyrolysis intermediates within the matrix of crystalline cellulose, the presence of strong hydrogen bonding networks (maybe already partially destructed under the conditions) appear to also have a shield effect that makes the further conversion reactions of these intermediates more difficult to proceed.

For sugar oligomers (see Figures 6c and g), the yields from amorphous cellulose are much higher than those from crystalline cellulose. For example, the maximal yields of cellopentaose, which were reached during the pyrolysis of both amorphous and crystalline cellulose at 210 °C, are ~0.2% and ~0.02%, respectively. It is noted that for amorphous cellulose pyrolysis, although the yields of sugar oligomers increase as pyrolysis temperature increases to ~210 °C, the selectivities of these sugar oligomers actually decrease with increasing temperature, suggesting that more of other products (e.g., high-DP sugar oligomers and anhydro-sugar oligomers as shown in Figure 4b) are produced at increased temperature. The low selectivities of low-DP sugar oligomers (see Figure 6d)

indicate that these compounds are also not the main products in the water-soluble intermediates from amorphous cellulose. Additionally, opposite to anhydro-sugar oligomers with DP of 1–5 (see Figure 6a), the yield of sugar oligomers increases with DP for amorphous cellulose. However, for crystalline cellulose, this trend is not obvious (see Figure 6g and h). The different patterns of sugar oligomer formation between amorphous and crystalline cellulose may indicate the different formation mechanisms of these sugar-oligomers between amorphous and crystalline cellulose. For example, for amorphous cellulose, these sugar oligomers can be formed via easily breaking the weak hydrogen bonds to release the glucose chain segments of various DPs within amorphous cellulose, at relatively lower temperatures and higher yields. However, for crystalline cellulose, the formation of these sugar-oligomers requires the breakage of both strong hydrogen bonds and glycosidic bonds in glucose chains at higher temperatures at which these sugar oligomers are also prone to further decomposition, leading to generally lower yields. It should also be noted that although the yields of sugar oligomers with DPs of 1–5 from amorphous cellulose are much higher than those from crystalline cellulose, the selectivity (see Figures 6d and h) are quite similar when the pyrolysis temperatures are >170 °C. This in turn suggests that these sugar oligomers are prone to decomposition at higher temperatures.

Figure 6 clearly shows that the selectivities of sugar oligomers and anhydro-sugar oligomers with DP of 1–5 are low in water-soluble intermediates from both amorphous and crystalline cellulose samples. Therefore, further efforts were taken to compare the contribution of those quantifiable sugar oligomers and anhydro-sugar oligomers to the total hydrolysable sugars in the water-soluble intermediates from both amorphous and crystalline cellulose. As mentioned before in section 3.5, three types of glucose-ring-containing oligomers, i.e. sugar oligomers (including glucose), anhydro-sugar oligomers (including levoglucosan), and the PDSRCOs, contribute to the total hydrolysable sugars in a sample. The PDSRCOs contain sugar rings but are neither sugar oligomers nor anhydro-sugar oligomers, having low detector responses using the analytical system in this study. As shown in Figure 7, the total sugar and anhydro-sugar oligomers with DPs of 1–5 only contribute <10% of total carbon in water-soluble intermediates from amorphous cellulose. Figure 4b indicates that there are various peaks of sugar oligomers and anhydro-sugar oligomers with DP

> 5 in the water-soluble intermediates from amorphous cellulose. Therefore, it is expected that at least some of the total hydrolyzable sugar would have been contributed by those sugar oligomers and anhydro-sugar oligomers with DP > 5. However, the detailed contribution of PDSRCOs cannot be quantified, due to the unavailability of the sugar and anhydro-sugar oligomers standards. For amorphous cellulose, Figure 7a also shows that even at 300 °C, the hydrolyzable sugar yield is ~21% from post-hydrolysis of water-soluble intermediates. According to Figure 4b, the sample only contains anhydro-sugar oligomers with DPs of 1–3, without sugar oligomers or higher-DP anhydro-sugar oligomers. On the basis of the data in Figure 6a, the total yield of anhydro-sugars with DPs of 1–5 only accounts for ~6% of total carbon in water-soluble intermediates. Therefore, the shortfall of ~19% carbon in the water-soluble intermediates should be contributed by PDSRCOs. Therefore, the data provide direct evidence to prove that there are substantial PDSRCOs present in the water-soluble intermediates from amorphous cellulose pyrolysis. In fact, Figure 7a shows that the majority of the water-soluble intermediates are contributed by non-sugar products during amorphous cellulose pyrolysis at high temperatures. For example, non-sugar products accounts for ~80% of carbon in water-soluble intermediates at 300 °C. The non-sugar products are more likely produced from the decomposition of instable sugar oligomers in the intermediate phase from amorphous cellulose pyrolysis. As for crystalline cellulose, sugar oligomers may also contribute to the water-soluble intermediates but only at low temperature (e.g., ~10% at 190 °C). Anhydro-sugars are clearly part of the main products in the water-soluble intermediates. The direct evidence on the presence of substantial PDSRCOs can be seen at 300 °C, with a contribution of ~20% of total carbon in water-soluble intermediates. The contribution of non-sugar products (~40% on a carbon basis) for crystalline cellulose is much lower, compared to that (~80% on a carbon basis) for amorphous cellulose at 300 °C.

#### 4. CONCLUSIONS

This study compares the pyrolysis behavior between amorphous and crystalline cellulose under slow heating conditions and provides a comprehensive analysis on the water-soluble intermediates from amorphous and crystalline cellulose pyrolysis at 150–300 °C. The results demonstrate the critical importance of hydrogen bonding networks in the pyrolysis behavior of cellulose. Some main conclusions can be drawn as follows:

1. The temperature at which pyrolysis commences is lower for amorphous cellulose than crystalline cellulose, resulting from the absence of strong hydrogen bonding networks within amorphous cellulose.
2. Due to the short glucose chain length with weak hydrogen bonding networks in amorphous cellulose, some short glucose chain segments present in amorphous cellulose can be directly released as sugar oligomers with various DPs, as part of water-soluble intermediates at a temperature as low as 140 °C. Oppositely, under the same pyrolysis conditions, the sugar ring structure in crystalline cellulose is largely preserved due to the protection of its strong hydrogen bonding networks.

3. Under the same pyrolysis conditions, the yield of water-soluble intermediates for amorphous cellulose is considerably higher than that of crystalline cellulose pyrolysis. For example, the maximal yield from amorphous cellulose is ~30% on a carbon basis at 250 °C, while that value from crystalline cellulose is ~3% at 270 °C. This clearly suggests that the strong hydrogen bonding networks have significantly changed the cellulose pyrolysis reaction mechanism.
4. The short glucose chain length and weak hydrogen bonding networks in amorphous cellulose also lead to the formation of considerably more anhydro-sugar oligomers and sugar oligomers with a wider DP range of 1–16 and 1–14, respectively, compared to a narrower DP range of 1–8 and 1–5 for anhydro-sugar oligomers and sugar oligomers from crystalline cellulose, respectively.
5. At temperatures <270 °C, the water-soluble intermediates from the pyrolysis of amorphous cellulose are mainly contributed by high-DP sugar oligomers and/or anhydro-sugar oligomers, as well as a substantial amount of partially decomposed sugar-ring-containing oligomers, while those at higher temperatures (e.g., 300 °C) are dominantly non-sugar products.
6. For crystalline cellulose, low-DP anhydro-sugar oligomers and those partially decomposed sugar-ring-containing oligomers are the main compounds in the water-soluble intermediates. The contribution of non-sugar products reduces significantly at high temperature (e.g., 300 °C), compared to that for amorphous cellulose.

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##### Notes

The authors declare no competing financial interest.

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