Characterization of Water-Soluble Intermediates from Slow Pyrolysis of Cellulose at Low Temperatures

3 AUTHORS, INCLUDING:

Yun Yu
Curtin University
44 PUBLICATIONS **777** CITATIONS

SEE PROFILE

Hongwei Wu
Yale University
91 PUBLICATIONS **2,335** CITATIONS

SEE PROFILE

Characterization of Water-Soluble Intermediates from Slow Pyrolysis of Cellulose at Low Temperatures

Yun Yu, Dawei Liu, and Hongwei Wu*

Department of Chemical Engineering and Fuels and Energy Technology Institute, Curtin University of Technology, GPO Box U1987, Perth WA 6845, Australia

ABSTRACT: This study reports the presence of both sugar and anhydro-sugar oligomers of a wide range of degrees of polymerization (1−10) as water-soluble intermediates in the solid residues produced from cellulose slow pyrolysis at low temperatures (100−350 °C) and a holding time of 30 min. These sugar and anhydro-sugar oligomers appear to be important precursors of volatiles formation during cellulose pyrolysis. Even at very low pyrolysis temperatures (e.g., 100 °C), sugar oligomers are found in the water-soluble intermediates. As the breakage of glycosidic bonds within cellulose chains is unlikely to take place under such low-temperature conditions, the results suggest that such sugar oligomers are likely to be produced from the short glucose chain segments that are hinged with crystalline cellulose via weak bonds (e.g., hydrogen bonds) in amorphous portions of microcrystalline cellulose. As the pyrolysis temperature increases, a wide range of anhydro-sugar oligomers start to appear while the sugar oligomers start to decrease. At temperatures <270 °C, water-soluble intermediates are dominantly (>78% based on total carbon) contributed by sugar oligomers, anhydro-sugar oligomers, and a large amount of partially decomposed sugar-ring-containing oligomers, i.e., PDSRCOs, but such contributions decrease substantially as the pyrolysis temperature increases to 300 °C. At higher pyrolysis temperatures (e.g., 325 °C), all sugar-ring-containing oligomers completely disappear, accompanied by substantial weight loss of cellulose. Together with those from the pyrolysis of sugar model compounds, such results further suggest that the production of anhydro-sugar oligomers are more likely due to the homolytic or heterolytic cleavage of glycosidic bonds of crystalline or amorphous cellulose within microcrystalline cellulose, rather than direct dehydration of sugar oligomers products within the intermediate phase.

1. INTRODUCTION

The declining fossil fuel reserves and increasing global energy demand require an inevitable switch of the energy supply from conventional fossil fuels to renewable and sustainable energy sources.[1] Biomass is abundantly available worldwide and is generally considered to be one of the key alternatives that will play an important role in the future sustainable energy supply, with significant benefits in energy security, environmental protection, and regional development.[2,3] Depending on the production system, some energy crops (e.g., mallee biomass[4−8] in Western Australia) can truly be a second generation feedstock for the development of a viable regional bioenergy industry without competing with food production.

Biomass conversion technology generally can be categorized into biochemical and thermochemical routes. Among the current technologies for biomass utilization, biomass pyrolysis is an attractive technology. Particularly, bio-oil production from biomass pyrolysis can be cheap and efficient. However, bio-oil as an end product itself suffers from several drawbacks, including instability (or aging),[9−11] high acidity,[9] coking,[12] low heating value,[9] and high viscosity.[13−15] A sound understanding of biomass pyrolysis mechanism is highly beneficial to developing advanced processes for addressing these issues.

Cellulose is a key component in biomass and can account for up to 50% of dry biomass. Extensive research was done on the pyrolysis of cellulose as a model compound of biomass since early last century,[16] evident by many reviews[17−23] and also some recent publications[24−28] (just to list a few). It has been widely reported that cellulose experiences an initiation stage of transformation before any measurable mass loss during pyrolysis.[19,23,29−31] At this initial stage, cellulose may rapidly decompose into some intermediates with a reduced average degree of polymerization (DP). Such low-DP intermediates are believed to constitute the so-called "active cellulose" in the well-known Broido−Shafizadeh (BS) model.[30,32] The rupture of cellulose molecules to form active cellulose is believed to take place at the crystalline−amorphous boundaries.[29] In the BS model, it is proposed that the active cellulose gives rise to two competitive first order global reactions: one produces condensable volatiles and the other produces char and gas fractions.[29]

The intermediates (e.g., active cellulose) from cellulose pyrolysis received significant attentions in the 1990s. Vladars-Usas[33] provided the evidence that, under fast heating conditions, depolymerization of cellulose can take place through a molten state, in which levoglucosan, cellobiosan, and anhydro-oligosaccharides can be found. Boutin et al.[34] found that radiant flash pyrolysis of cellulose proceeds through a yellowish short lifetime (a few tens of microseconds) intermediate phase, which is liquid at reaction temperature but becomes solid after rapid cooling. Those intermediates are reported to be soluble in water,[34] suggesting these are no longer cellulose but at least partially degraded cellulose. Piskorz et al.[35] further found that up to 44% of a water-soluble fraction can be obtained from recovered solid residues after flash

pyrolysis of cellulose in a drop-tube reactor at 850−1200 °C. Levoglucosan and anhydro-saccharides (DPs < 7) can be identified, while substantial oligomers with higher DPs appeared to also be produced but could not be identified (most likely due to the limitation of the analytical systems used). The formation of intermediate liquid compounds (ILC) was further investigated using radiant flash pyrolysis by Lédé et al.[36,37] High-DP (<7) anhydro-sugars were found to be present in both ILC and the trapped vapors with a great majority, while cellobiosan and levoglucosan are of minor importance.[37] Dauenhauer et al.[38] provided convincing proof of an intermediate liquid phase formed during cellulose fast pyrolysis by high speed photography. However, there is still considerable research scope for understanding the chemical compositions of intermediates during cellulose pyrolysis.

In the literature, there is one report[39] on the intermediates from cellulose pyrolysis under slow heating conditions, but little is known on the compositional analysis of such intermediates. This is largely due to the difficulty for characterizing the intermediates from cellulose slow pyrolysis. The main reason is that these intermediates would have experienced substantial evaporation and/or decomposition under slow heating pyrolysis conditions. Therefore, only small quantities of intermediates can be recovered from the solid residue, requiring a highly sensitive instrument for analysis. Additionally, due to the limitations of conventional analytical systems (e.g., high performance liquid chromatography (HPLC)[35]), it is still unknown if sugar and/or anhydro-sugars of high DPs (>6) are present in these intermediates. Recent research of this group developed a technique[40] for identifying sugar oligomers of a wide range of DPs up to 30, in aqueous solutions, paving the way for better characterization of the intermediates from cellulose pyrolysis. Therefore, the objective of this work is to provide some new data on the characteristics of water-soluble intermediates during cellulose pyrolysis at a slow heating rate (10 K min^{-1}), taking advantage of this advanced technique. In this study, cellulose pyrolysis experiments were carried out at low temperatures (100−350 °C) and a holding time of 30 min.

2. EXPERIMENTAL SECTION

2.1. Materials. Microcrystalline cellulose (Avicel PH-101, Sigma-Aldrich) was sieved, and the size fraction of 75−106 μm was used in this study. The cellulose was pretreated by double distilled water washing at room temperature to remove the water-soluble compounds that may have pre-existed in the sample. Dried cellulose samples were then used for pyrolysis experiments. A series of sugar and anhydro-sugar standards of DPs up to 5, as well as other high purity reagents, were purchased for water-soluble intermediate analysis.

2.2. Pyrolysis Experiments. Slow pyrolysis of microcrystalline cellulose was conducted in a fixed-bed quartz reactor at low temperatures ranging from 100 to 350 °C. The reactor is similar to the one used previously.[41] Briefly, approximately 2 g cellulose sample was first loaded into the reactor at room temperature. A stream of argon (UHP, 2.0 L min^{-1}) gas was used as a carrier gas. The reactor was then heated to a desired pyrolysis temperature at 10 K min^{-1}. After holding at the temperature for a further 30 min, the reactor was lifted out of the furnace immediately and cooled with argon continuously flowing through the reactor. The weight loss during cellulose pyrolysis in the experiment was determined by the difference in the weight of the reactor before and after experiment, considering the moisture contents of the feed and solid residue after pyrolysis.

2.3. Characterization of Solid Residues from Cellulose Pyrolysis. The cellulose and the solid residues after pyrolysis were subjected to a series of structure characterizations. Crystalline patterns of the samples were characterized by X-ray diffraction (XRD) using a Bruker AXS D8 Advance X-ray diffractometer. Briefly, the diffracted intensity of Cu Kα radiation was measured in a 2θ range from 10° to 30°. The changes in functional groups in cellulose as results of pyrolysis under different conditions were analyzed using a Perkin-Elmer Spectrum 100 ATR-FTIR spectrometer, following a similar procedure detailed elsewhere.[42]

Post-hydrolysis experiments of pyrolyzed cellulose were also conducted to determine the total neutral glucose content by acid hydrolysis, following a NREL method.[43] In a post-hydrolysis experiment, approximately 300 mg of solid sample was first hydrolyzed by sulfuric acid (72%) at 30 °C for 1 h, followed by treatment in an autoclave for another 1 h at 121 °C with the acid concentration adjusted to 4%. After neutralization of the sulfuric acid in the sample, the glucose content was analyzed by high-performance anion exchange chromatography with pulsed amperometric detection (HPAEC-PAD), following an isocratic method that elutes 100 mM NaOH at a flow rate of 0.5 mL min^{-1}. Glucose standards at different concentrations were also prepared for the correction of losses due to the degradation of glucose during acid hydrolysis.

2.4. Characterization of Water-Soluble Intermediates in Solid Residues from Cellulose Pyrolysis. The solid residues were washed by double distilled water, as the intermediates are reported to be water-soluble.[34] About 20 mg of pyrolyzed cellulose was immersed in ~21 mL water at ambient temperature and then thoroughly shaken for well mixing. The mixed sample was filtered to obtain the liquid sample containing the water-soluble intermediates in pyrolyzed cellulose. The solution samples were then analyzed by a total organic carbon (TOC) analyzer (Shimadzu Model TOC-V$_{CPH}$) to determine the total carbon contents of the liquid samples. The yield (on a carbon basis) of water-soluble intermediates can be calculated via normalizing the total water-soluble carbon in pyrolyzed cellulose to the total carbon in raw cellulose.

The oligomers in liquid samples were also characterized by HPAEC-PAD analysis, following a similar technique developed previously,[40] using a Dionex ICS-3000 ion chromatography (IC) system equipped with a CarboPac PA200 analytical column (3 × 250 mm) and guard column (3 × 50 mm). A gradient method was used, eluting 20−225 mM NaOAc and 100 mM NaOH over 30 min with a flow rate of 0.5 mL min^{-1}. The peaks detected by HPAEC-PAD were first identified with a series of sugar and anhydro-sugar oligomer standards with DPs up to 5. For high-DP (>5) sugar oligomers, an aqueous sample, which was produced from cellulose hydrolysis in hot-compressed water and known to contain dominantly glucose oligomers with a wide range of DPs, was used as a standard.[40] The identification of high-DP (>5) anhydro-sugar oligomers deployed a similar approach based on the elution order and peaks for the oligomer standards.[40,44] In this paper, the sugar and anhydro-sugar oligomers are named according to DP values (e.g., glucose as C1, cellobiose as C2; levoglucosan as AC1, cellobiosan as AC2).

Post-hydrolysis experiments of water-soluble intermediates of cellulose pyrolysis were also conducted to determine the total neutral glucose content. There is a little difference between the post-hydrolysis of solid resides and liquid intermediates of cellulose pyrolysis. For post-hydrolysis of intermediates, the liquid sample was only treated in an autoclave for 1 h at 121 °C and an acid concentration of 4%.

To better understand the decomposition of sugar oligomers during pyrolysis, some TGA experiments were conducted using model sugar compounds (glucose and cellobiose), following the same temperature−time history. For each TGA experiment, about ~3 mg sample was loaded in a Pt crucible. Then, the crucible was heated to a desired temperature (150−250 °C) in argon at a heating rate of 10 K min^{-1} with a further holding of 30 min at pyrolysis temperature. After pyrolysis, the whole crucible was mixed with double distilled water to dissolve any water-soluble compounds. The liquid solutions were then subsequently analyzed for quantification of water-soluble sugar compounds in the sample.

3. RESULTS AND DISCUSSION

3.1. Weight Loss and Structure Change of Cellulose during Pyrolysis.
Cellulose pyrolysis generally leads to the formation of char, tar, and gas, depending on the pyrolysis temperature and heating rate.[30,32,39,45,46] It is noted that, in this study, pyrolysis experiments were conducted at a low pyrolysis temperature for a holding time of 30 min. As shown in Figure 1,
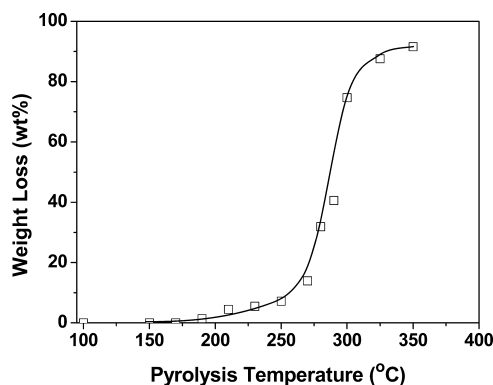

Figure 1. Weight loss of cellulose as a function of pyrolysis temperature.

the weight loss of cellulose during pryolysis begins at around 190 °C. A considerable amount of weight loss takes place within a narrow temperature range between 270 and 300 °C. Such a temperature range is slightly different from those reported elsewhere,[47,48] mainly due to different pyrolysis conditions (e.g., heating rate and holding time) used in this study.

The XRD results of raw and pyrolyzed cellulose samples are presented for comparison in Figure 2. Coincident with the
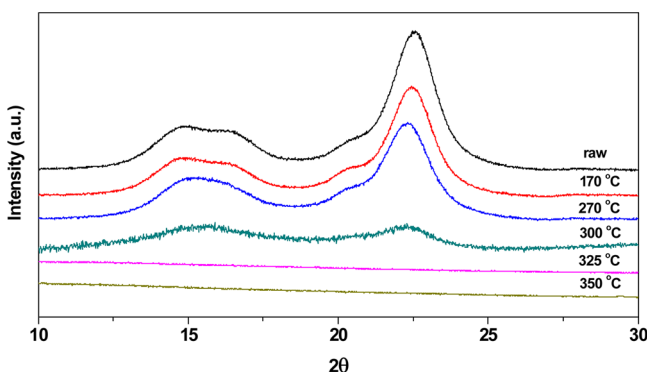

Figure 2. X-ray diffraction patterns of raw and pyrolyzed cellulose samples prepared at various pyrolysis temperatures.

substantial weight loss observed in Figure 1, the peak intensities exhibit substantial decrease between 270 and 300 °C. The data clearly demonstrate that the crystallinity of pyrolyzing cellulose reduces significantly as the pyrolysis temperature increases to above 270 °C, which transforms the structure of the pyrolyzing cellulose structure to be more amorphous. A further increase in the pyrolysis temperature to 325 °C or above leads to the complete disappearance of crystalline structure.

Figure 3 further presents the FT-IR (Fourier transform infrared) spectra for typical pyrolyzed cellulose samples prepared at various pyrolysis temperatures. It is clearly seen that, for raw cellulose and pyrolyzed cellulose at temperatures
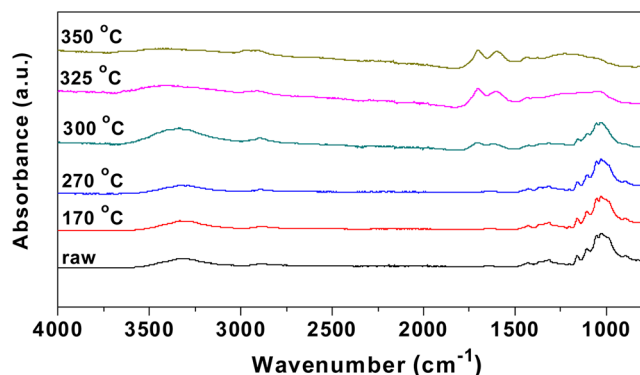

Figure 3. FT-IR spectra for typical pyrolyzed cellulose samples prepared at various pyrolysis temperatures.

<270 °C, there is no significant change in the FT-IR spectra acquired from the samples before and after pyrolysis. The OH groups exist in the broad absorption range within 3600−3200 cm^{-1}. As the pyrolysis temperature further increases to 300 °C, the pyranose structures of cellulose are still preserved due to the C−O stretching vibration at 1200−1000 cm^{-1}.[49] In addition, two new peaks appear in the region of 1850−1508 cm^{-1}. Generally, the 1800−1700 cm^{-1} region can be attributed to carbonyl structures (C=O) in unconjugated ketones and carbonyls, while the 1675−1655 cm^{-1} region is due to C=O stretching band in conjugated aldehydes and carboxylic acids.[42,50,51] Besides, possible olefinic C=C stretching bands are also known in the region of 1680−1620 cm^{-1}.[42] The appearance of C=O and C=C groups indicates the dehydration of water from the hydroxyl groups in the cellulose unit.[17] At a pyrolysis temperature of 350 °C, the formation of C=O groups and C=C groups become dominant in the solid residue after pyrolysis.

3.2. Formation of Water-Soluble Intermediates from Cellulose Pyrolysis.
It is clearly shown in Figure 1 that there is only a small weight loss during the pyrolysis of cellulose at temperatures lower than 270 °C, suggesting that most of the pyrolysis intermediates are still retained in the pyrolyzing cellulose. This also suggests that such intermediates cannot be released into the vapor phase unless these intermediates further decomposed into smaller compounds of low boiling points. To get some idea on the formation of intermediates during cellulose pyrolysis at such low temperatures, the pyrolyzed celluloses were then mixed with water to extract the water-soluble intermediates.

The water-soluble intermediates recovered from the solid residues of cellulose pyrolysis were first analyzed by TOC. Based on the carbon concentration of water-soluble intermediates, the yield of water-soluble intermediates was then calculated as the dissolved carbon normalized by the total carbon in raw cellulose, with the results presented in Figure 4. Indeed, the data in Figure 4 demonstrate the presence of organic compounds in the water-soluble intermediates recovered from the solid residues of cellulose pyrolysis. The data also show that the yield of water-soluble intermediates increases with pyrolysis temperature, and reaches a maximum (~3%) at 270 °C and then decreases substantially with further increase in the pyrolysis temperature. It is interesting to point out that the temperature at which the significant reduction in the yield of water-soluble intermediates takes place coincides with the temperatures at which cellulose experiences significant weight loss during pyrolysis. Therefore, the results suggest that
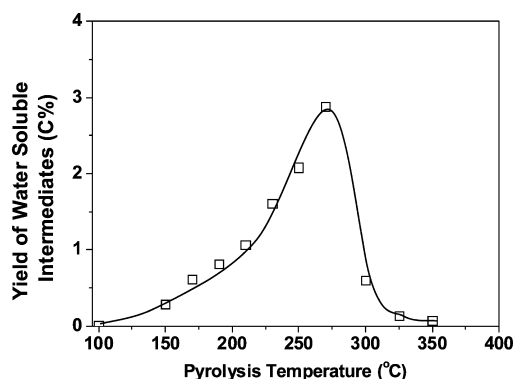
Figure 4. Yield of water-soluble intermediates on a carbon basis at various pyrolysis temperatures.

such water-soluble products are likely to be part of the pyrolysis reaction intermediates as important precursors for volatiles formation during pyrolysis. While the exact mechanisms are unknown, the reduction in the yields of such water-soluble intermediates may be due to the decomposition of these large compounds into more volatile compounds which can be readily released into gaseous phase (e.g., levoglucosan, hydroxyacetaldehyde), and/or due to the recombination of these intermediates into water-insoluble products in the solid phase. For example, as estimated by Suuberg et al.,[52] levoglucosan has a boiling point of ~260 °C. Therefore, it is likely that the evaporation of levoglucosan may be largely responsible for the reduction of water-soluble intermediates at 300 °C. As the water-soluble intermediates are instable and can be evaporated and/or decomposed,[34] the yield of water-soluble intermediates during pyrolysis is always low at such high temperatures. At 350 °C, those water-soluble intermediates are hardly detected.

It is also noted that the amount of water-soluble intermediates in solid residue from slow pyrolysis conditions in this study is much smaller than those under flash pyrolysis reported previously.[35] This is expected because the formation and survival of these water-soluble intermediates during pyrolysis are not favored at slow heating rates. A long holding time (30 min in this study, compared to <75 ms in flash pyrolysis[35]) would also favor further reactions that convert these intermediates into water-insoluble products in char and/

or decompose these intermediates into smaller compounds as part of volatiles. Nevertheless, the results reported in Figure 4 clearly confirm that cellulose pyrolysis does proceed through an intermediate phase, even at low temperature and low heating rate conditions.

3.3. Characterization of Water-Soluble Intermediates from Cellulose Pyrolysis. *3.3.1. Identification of Oligomers in Water-Soluble Intermediates.* The water-soluble intermediates of pyrolyzed cellulose were further characterized using HPAEC-PAD. Figure 5 presents the chromatographs of liquid samples prepared by water washing of the solid residues from cellulose pyrolysis at 170 and 250 °C, together with the liquid sample from cellulose hydrolysis as a standard for sugar oligomers. It is interesting to note that many peaks can be detected by HPAEC-PAD, leading to at least two important findings. One is the existence of anhydro-sugar oligomers with various DPs in the water-soluble intermediates. The other is that the water-soluble intermediates may also contain a large amount of glucose oligomers with various DPs, depending on pyrolysis temperature. For example, the water-soluble intermediates from pyrolyzed cellulose at 170 °C clearly contain the glucose oligomers with DPs of 1−10.

The presence of glucose oligomers is not expected in the water-soluble intermediates and were not reported previously because it is widely accepted[23] that cellulose pyrolysis generally produces anhydro-sugars (e.g., levoglucosan, cellobiosan). To gain further understanding on this important aspect, the effect of pyrolysis temperature on the compositions of water-soluble intermediates of pyrolyzed cellulose was further investigated. As shown in Figure 6, a wide range of sugar and anhydro-sugar oligomers are present in the water-soluble intermediates recovered from the solid residues of cellulose pyrolysis at various temperatures. This indicates that cellulose pyrolysis randomly produces sugar and anhydro-sugar oligomers as reaction intermediates, which will further decompose to tar, char, and gas. The production of sugar oligomers with DPs of 1−10 increases with pyrolysis temperature from 100 to 190 °C, and then decreases with further increase in pyrolysis temperature. On the contrary, the anhydro-sugar oligomers with DPs of 1−10 keep increasing from 150 to 270 °C, as shown in Figure 6a, but further increase in the temperature will also lead to their reduction in the pyrolyzed cellulose (see Figure 6b). This indicates that significant decomposition of sugar and anhydro-sugar oligomers starts at ~190 and ~270 °C,
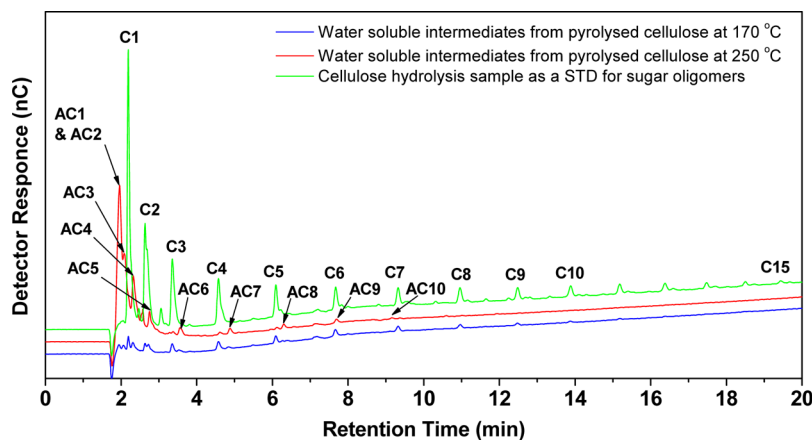

Figure 5. Comparison of water-soluble samples from pyrolyzed cellulose at 170 and 250 °C, with the liquid sample from cellulose hydrolysis at 230 °C as a standard.
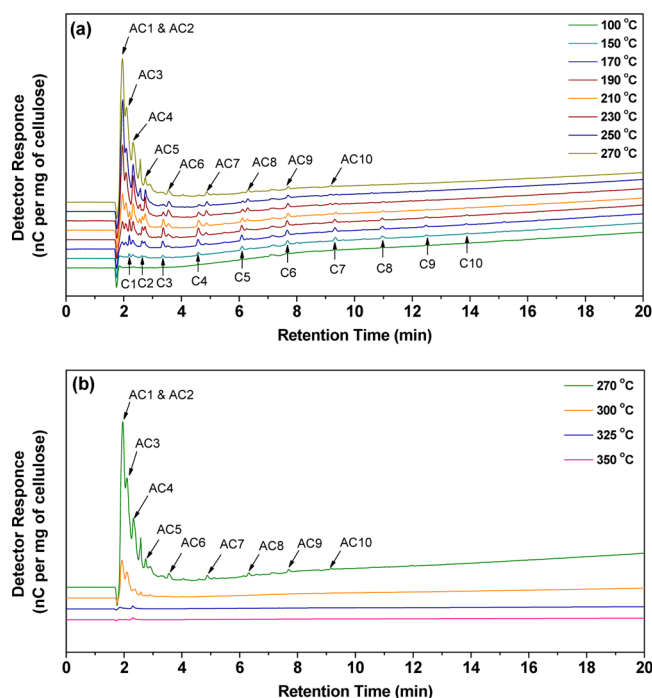
Figure 6. Effect of pyrolysis temperature on the composition of water-soluble intermediate samples from pyrolyzed cellulose at 100−350 °C: (a) 100−270 °C; (b) 270−350 °C. C1−10: glucose oligomers with DPs of 1−10. AC1−10: anhydro-glucose oligomers with DPs of 1−10.

respectively. It is important to note that while the sugar oligomers appear and also decompose at a lower temperature than anhydro-sugar oligomers and the reduction of sugar oligomers also coincide with the simultaneous increase of anhydro-sugar oligomers, there is no sufficient direct evidence to support that anhydro-sugar oligomers were converted from sugar oligomers (e.g., by dehydration). Furthermore, anhydro-sugars are known to be more stable than the sugars.[22] Yet, the data clearly show that most of the high-DP anhydro-sugars disappear at temperatures higher than 300 °C. Only a small amount of levoglucosan and cellobiosan are present in the water-soluble intermediates recovered from the solid residues of cellulose pyrolysis at 300 °C. Due to their high boiling points,[23] the high-DP anhydro-sugars would be difficult to evaporate into the vapor phase. As a result, their disappearances are more likely due to their decomposition into other more volatile compounds. The results also suggest that higher-DP anhydro-sugars are more susceptible to decomposition than lower-DP anhydro-sugars at the same temperature. This is consistent with the previous report that cellobiosan is less stable than levoglucosan.[53]

The interesting data in Figure 6 provide some important knowledge on the composition of intermediates in the solid phase. Particularly, the formation of glucose oligomers during pyrolysis of cellulose at low temperatures were not reported previously because glucose oligomers are generally considered to be products of cellulose hydrolysis (e.g., in hot compressed water).[54−57] While the exact mechanism is unknown at present, there are at least two possibilities that may be responsible for the formation of glucose oligomers during cellulose pyrolysis. One possibility is that the glucose oligomers are produced via the breaking of hydrogen bonding in amorphous portions of cellulose. It is known that the microcrystalline cellulose contains both amorphous and crystalline portions.[55] There

are some short glucose chain segments hinged with crystalline cellulose via weak bonds (e.g., hydrogen bonds) in amorphous portions of microcrystalline cellulose.[55] These weak bonds can be easily broken during thermal processing to release the short glucose chain segments as glucose oligomers. This is demonstrated by the hydrolysis of cellulose in hot compressed water, producing glucose oligomers with DPs of 4−13 at temperatures as low as 100 °C.[55] This possibility is supported by the data in Figure 6a that show no glucose was formed during cellulose pyrolysis at 100 °C, clearly indicating that the glucose oligomers are not produced from the breaking of glycosidic bonds in cellulose. The disappearance of glucose oligomers at high pyrolysis temperatures (>190 °C) suggests that those glucose oligomers may further decompose to anhydro-sugars or some other small compounds. Another possibility is that the anhydro-sugar and sugar oligomers may be produced via thermal cleavage of glycosidic bonds,[22] which deploymerizes a long cellulose chain into one chain with a levoglucosan end and another chain with a nonreducing end. Several mechanisms have been postulated to explain the thermal cleavage of glycosidic bonds during cellulose pyrolysis, including homolytic (free radical),[19,58] heterolytic (ionic),[18,19,22,59] and concerted mechanisms,[24,28] but no consensus has been reached yet. Further efforts are required to isolate those two possibilities to understand the formation mechanism of those sugar and anhydro-sugar oligomers as intermediates of cellulose pyrolysis.

3.3.2. Post-hydrolysis of Water-Soluble Intermediates. The pyrolyzed cellulose and water-soluble intermediates samples were also subjected to post-hydrolysis to measure the total neutral sugar yield on a carbon basis. As shown in Figure 7, the
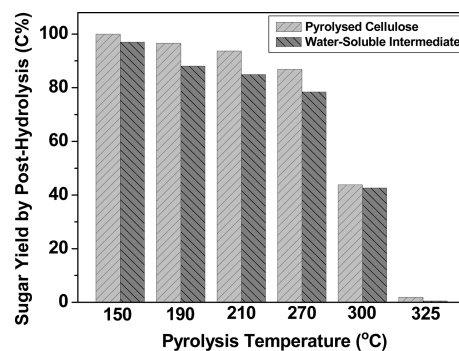

Figure 7. Sugar yields by post-hydrolysis of pyrolyzed cellulose and water-soluble intermediate samples at various pyrolysis temperatures.

sugar yields by post-hydrolysis of both pyrolyzed cellulose and water-soluble intermediates at 150 °C are close to 100%, indicating little degradation reactions occurs at low temperatures (<150 °C). As pyrolysis temperature increases, both sugar yields start to decrease. Substantial reductions in sugar yields are evident when the pyrolysis temperature increases to 300 °C or above. At a given pyrolysis temperature, the sugar yield for pyrolyzed cellulose is always higher than that for water-soluble intermediates, indicating that there are more degraded products in water-soluble intermediates. For example, at 270 °C, the sugar yield for pyrolyzed cellulose is ∼87% in comparison to ∼78% for water-soluble intermediates. Even at 300 °C, there is still ∼44% of the sugar compounds remaining in the pyrolyzed cellulose. However, at 325 °C, there are few sugar compounds left in the pyrolyzed cellulose. This is consistent with the FT-IR results (see Figure 3) of no sugar
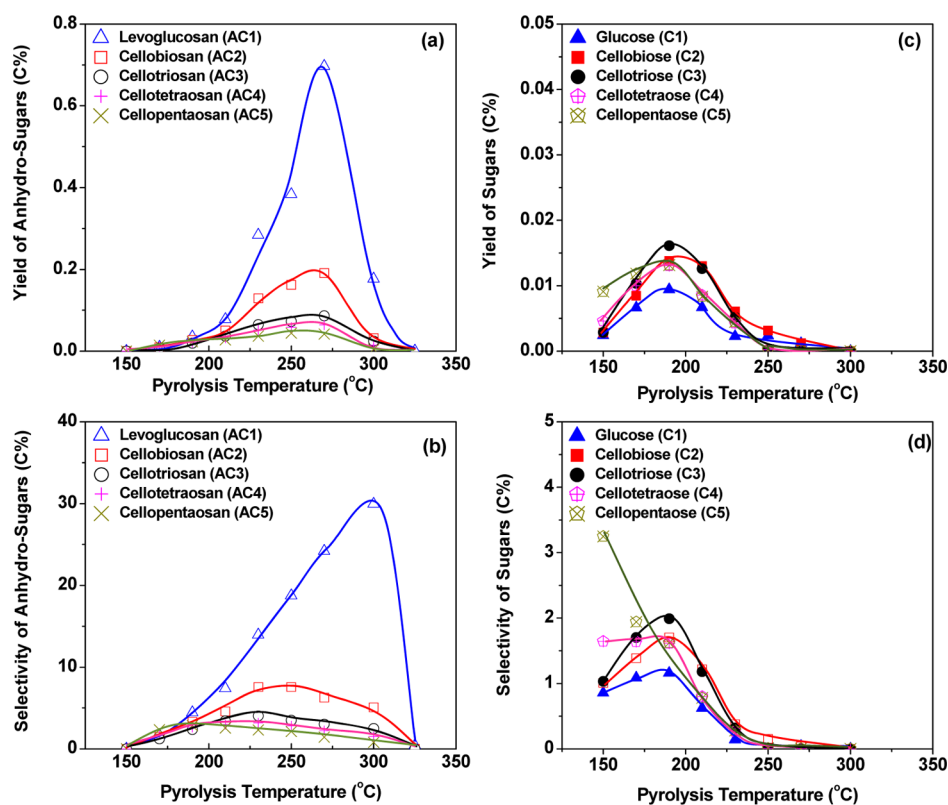
Figure 8. Yields and selectivities of quantifiable sugar and anhydro-sugar oligomers in the water-soluble intermediates at various pyrolysis temperatures: (a) yield of anhydro-sugar oligomers; (b) selectivity of anhydro-sugar oligomers; (c) yield of sugar oligomers; and (d) selectivity of sugar oligomers.

functional groups being observed for the solid residue after cellulose pyrolysis at 325 and 350 °C. Analysis of the water-soluble intermediate samples at 325 and 350 °C (see Figure 6b) also confirmed the absence of sugar compounds. Therefore, at these temperatures, there must be significant non-sugar compounds existing in the water-soluble intermediates of cellulose pyrolysis. Such non-sugar compounds contain no sugar rings, so no glucose can be produced during post-hydrolysis. Those non-sugar compounds could be the sugar-derived fragments[60,61] or the oligomers with cross-linked structures.[62] It is clear that the contribution of these non-sugar compounds to the water-soluble intermediates increases with pyrolysis temperature. It should also be noted that there is a substantial increase of non-sugar compounds in the water-soluble intermediates at temperatures >300 °C, at which extensive cleavage of the hydrogen bonding structure takes place, as shown in Figure 2.

3.3.3. Quantification of Low-DP Sugar and Anhydro-Sugar Oligomers in Water-Soluble Intermediates. The water-soluble intermediates were also analyzed to quantify the low-DP sugar and anhydro-sugar oligomers (i.e., with DPs of 1−5) by HPAEC-PAD. The yields of low-DP anhydro-sugars on a carbon basis of raw cellulose are shown in Figure 8a. It was found that the yield of levoglucosan reaches a maximum at 270 °C. A further increase in the pyrolysis temperature results in a reduction in the levoglucosan yield, most likely due to its evaporation (levoglucosan has a boiling point of ~260 °C[52]) as part of volatiles. This also coincides with the substantial reduction in the yield of water-soluble intermediates (see Figure 4). However, it is interesting to note that the yields of other anhydro-sugars (e.g., cellobiosan, cellotriosan, cellote-

traosan, and cellopentaosan) also reach maxima at 270 °C. The reductions in the yields of those larger-DP anhydro-sugars do not seem to result from evaporation, as these larger-DP anhydro-sugars are known to have much higher boiling points (e.g., ~581 °C for cellobiosan and 792 °C for cellotriosan[63]). Such reductions are more likely to result from reactions (e.g., decomposition) that produce other products (e.g., more volatile compounds). Figure 8b further presents the selectivities of those anhydro-sugars (on a carbon basis) in water-soluble intermediates. The results show that levoglucosan has the highest selectivity among of all the anhydro-sugar compounds, but the presence of levoglucosan is only evident at pyrolysis temperatures higher than 170 °C. The selectivity of levoglucosan increases with pyrolysis temperature and reaches the highest value of ~30% at 300 °C. For other anhydro-sugars, cellobiosan has the highest selectivity of ~7.6% at 250 °C, while cellotriosan has the highest selectivity of ~4.1% at 230 °C. It should be noted that levoglucosan has the highest selectivity at 300 °C rather than 270 °C, at which its yield reaches the highest, suggesting that levoglucosan is more stable than other higher-DP anhydro-sugars.

The yields of low-DP sugar oligomers and their selectivities in the water-soluble intermediates are also shown in Figure 8c and 8d. Compared to those of anhydro-sugar oligomers, the yields of sugar oligomers are much lower, thus leading to their lower selectivities in the water-soluble intermediates. The yields of low-DP sugar oligomers all achieve the maxima at 190 °C. A further increase in the pyrolysis temperature leads to their rapid decomposition, resulting in the reductions in both yields and selectivities of these low-DP sugar oligomers.

Further analysis was then carried out to work out the contribution of those quantifiable sugar oligomers and anhydro-sugar oligomers to the total hydrolyzable sugars in the water-soluble intermediates. Generally, there are three types of oligomers that contribute to glucose formation during post-hydrolysis of a solution: (a) sugar oligomers of various DPs including glucose; (b) anhydro-sugar oligomers of various DPs including levoglucosan; and (c) other oligomers which contain sugar ring(s) but with one or more glucose rings partially decomposed (hereafter denoted as partially decomposed sugar-ring-containing oligomers, i.e., PDSRCOs). While PDSRCOs are neither sugar oligomers nor anhydro-sugar oligomers, these compounds would contribute to glucose formation during post-hydrolysis. Figure 9 presents the data on the contribution of
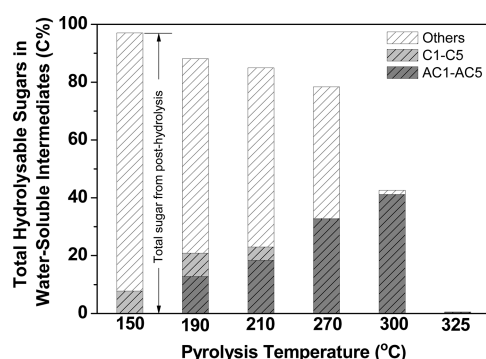

Figure 9. Contribution of small sugar oligomers (C1−C5) and anhydro-sugar oligomers (AC1-AC5) to the total hydrolyzable sugars in the water-soluble intermediates from pyrolyzed cellulose prepared at various pyrolysis temperatures.

various types of oligomers to the total hydrolyzable sugars in the water-soluble intermediates. Since only sugar and anhydro-sugar oligomers with DPs of 1−5 can be quantified, the category "others" in Figure 9 includes not only the contributions from sugar oligomers and anhydro-sugar oligomers with DPs > 5 but also those from the PDSRCOs. As shown in Figure 9, the contribution of sugar and anhydro-sugar oligomers with DPs of 1−5 increases from ∼7% at 150 °C to ∼41% at 300 °C. However, at low temperatures (<300 °C), such contributions are only a fraction of the total hydrolyzable sugar yields obtained from the post-hydrolysis of the solutions. Therefore, the remaining sugar (i.e., the category "others" in Figure 9) must be due to the contributions from unquantified sugar oligomers with DPs > 5, anhydro-sugar oligomers with DPs > 5, and PDSRCOs in the water-soluble intermediates. However, the contributions from sugar and anhydro-sugar oligomers with DPs > 5 are not expected to be significant. For example, for pyrolyzed cellulose at 150 °C, the sugar yield from post-hydrolysis is ∼97% and the contribution of sugar oligomers with DPs of 1−5 is only ∼7%. Since no anhydro-sugar oligomers were identified at 150 °C, the category "others" must be due to the contributions from sugar oligomers with DPs of 6−10 and PDSRCOs. As shown in Figure 8d, for sugar oligomers with DPs of 1−5, the selectivity of each sugar oligomer in the water-soluble intermediate is less than 5% on a carbon basis. Therefore, even the sugar oligomers with DPs of 6−10 contribute to additional 50% of sugars (i.e., with a maximal selectivity of 5% for each sugar oligomer), the balance (at least 40%) must be due to the contribution from PDSRCOs. Likewise, at 270 °C, the sugar yield from post-

hydrolysis is ∼78% while the total quantified sugar and anhydro-sugar oligomers with DPs of 1−5 only account for ∼34% of sugar. The data in Figure 8b show that the selectivity of anhydro-sugar oligomer decreases with DP and that of cellopentaosan (DP = 5) is below 5%. Therefore, at 270 °C, as no high-DP sugar oligomers were identified, considering a total contribution of 25% for high-DP anhydro-sugar oligomers (i.e., a maximal selectivity of 5% for each anhydro-sugar oligomer with DPs of 6−10), the balance (at least 19%) must be due to the contribution of glucose produced from PDSRCOs present in the water-soluble intermediates. Therefore, at pyrolysis temperatures of 150−270 °C, the water-soluble intermediates seem to contain a large amount of PDSRCOs that are partially decomposed but still contain glucose rings in their structures. The results also suggest that those PDSRCOs have very low detection responses, due to the limitations of the analytical system. Nevertheless, the existence of PDSRCOs is plausible to explain why the sugar yield from post-hydrolysis is much higher than the total quantifiable sugar and anhydro-sugar oligomers. Future work is certainly required to identify and quantify those PDSRCOs in the water-soluble intermediates from cellulose pyrolysis. It is also interesting to mention that the PDSRCOs seem to be converted into non-sugar products at 300 °C because the contribution of glucose produced from the post-hydrolysis of PDSRCOs is minimal (see Figure 9).

Based on this discussion, it can be concluded that, at pyrolysis temperatures <270 °C, the water-soluble intermediates in the pyrolyzed cellulose consist of not only sugar oligomers and anhydro-sugar oligomers but also some PDSRCOs. While at pyrolysis temperatures >325 °C, Figure 9 clearly shows that the water-soluble intermediates in the pyrolyzed cellulose are dominantly non-sugar compounds.

3.4. Pyrolysis of Model Sugar Compounds. The results presented in this paper demonstrate the presence of sugar and anhydro-sugar oligomers with a wide range of DPs in the pyrolyzed cellulose under slow heating conditions, depending on pyrolysis temperature. However, the formation mechanism of those sugar and anhydro-sugars is still largely unknown. Some further work was then carried out to investigate the pyrolysis of model sugar compounds (glucose and cellobiose) in a TGA, in order to verify if anhydro-sugar oligomers can be directly produced from sugar oligomers. The maximal pyrolysis temperature used was carefully chosen to be lower than the boiling point of levoglucosan, in order to minimize the vaporization of levoglucosan if it is formed. The heating rate and holding time were same as those for cellulose pyrolysis. The results of pyrolysis of glucose and cellulose are shown in Table 1. It was found that glucose is almost completely decomposed at 200 °C after holding for 30 min, while

Table 1. Pyrolysis of Model Sugar Compounds in TGA

pyrolysis temp. (°C)	holding time (min)	conversion (wt %)	weight loss (wt %)	levoglucosan yield (wt %)
		Glucose		
150	30	1.1	0.5	not identified
170	30	53.4	5.7	not identified
200	30	98.5	17.9	2.4%
		Cellobiose		
150	30	0	0	not identified
170	30	0	0	not identified
200	30	0.3	2.0	not identified
250	30	83.9	30.8	2.8%

cellobiose still remains largely intact at the same pyrolysis temperature. When the pyrolysis temperature increases to 250 °C, ~84% of cellobiose is decomposed, but cellobiose decomposition only produces ~3% of levogluosan after 30 min holding at the pyrolysis temperature. Similarly, glucose decomposition only produces ~2% of levoglucosan after 30 min holding. The data show that while most of the sugars were already converted (at 200 °C for glucose, and at 250 °C for cellobiose), the weight loss of reactants were only ~18% for glucose at 200 °C and ~31% for cellobiose at 250 °C. The data clearly suggest that glucose and cellobiose have different pyrolysis mechanisms, which do not favor the formation of anhydro-sugars (e.g., levoglucosan) under the conditions. These results are consistent with those reported in the previous studies[64−66] and demonstrate that levoglucosan is not the major product from pyrolysis of glucose or cellobiose. It is known that levoglucosan is much more stable than glucose.[67] For this reason, levoglucosan has the highest selectivity among of all the compounds in water-soluble intermediates of cellulose pyrolysis, as supported by the data in this study. Therefore, it seems that those anhydro-sugar oligomers cannot be directly produced from sugar oligomers by dehydration, at least under the conditions of this study. Rather, those anhydro-sugar oligomers are more likely to be produced via thermal cleavage of either crystalline or amorphous cellulose within micro-crystalline cellulose.

4. CONCLUSIONS

Water-soluble intermediates were found to remain in the solid residue after slow pyrolysis of cellulose at low temperatures of 100−350 °C for 30 min. The yield of water-soluble intermediates increases first with pyrolysis temperature and has a maximal value of ~3% on a carbon basis at 270 °C. Further increase in the pyrolysis temperature leads to a significant reduction of water-soluble intermediates as well as solid residue during cellulose pyrolysis, indicating that water-soluble intermediates are important precursors of volatiles during cellulose pyrolysis. The presence of both sugar and anhydro-sugar oligomers with DPs of 1−10 in water-soluble intermediates was identified by HPAEC-PAD analysis. Sugar oligomers with a wide range of DPs appear at a temperature as low as 100 °C. Their production increases with pyrolysis temperature until ~190 °C and then further decreases, while anhydro-sugar oligomers with a wide range of DPs appear at ~150 °C and increase with pyrolysis temperature until 270 °C. Apart from sugar and anhydro-sugar oligomers, the water-soluble intermediates appear to also contain some partially decomposed sugar-ring-containing oligomers, i.e., PDSRCOs, which increases with pyrolysis temperature up to 270 °C then decreases drastically at higher temperatures. At 300 °C, the water-soluble intermediates consist of dominantly anhydro-sugars with low DPs. At higher pyrolysis temperatures (e.g., 325 °C), the sugar-containing oligomers completely disappear so that the water-soluble intermediates contain only non-sugar compounds. It is also noteworthy that the sugar oligomers present in the water-soluble intermediates even at low pyrolysis temperatures (e.g., 100 °C) are likely to be produced from the short glucose chain segments hinged with crystalline cellulose via weak bonds (e.g., hydrogen bonds) in amorphous portions of microcrystalline cellulose. The anhydro-sugar oligomers do not seem to be the products of direct dehydration of sugar oligomers within the intermediate phase; rather, these oligomers appear to be the products of homolytic or heterolytic

cleavage of glycosidic bonds of crystalline or amorphous cellulose within microcrystalline cellulose.

■ AUTHOR INFORMATION

Corresponding Author
*Tel.: +61-8-92667592. Fax: +61-8-92662681. E-mail: h.wu@curtin.edu.au.

Notes
The authors declare no competing financial interest.

■ REFERENCES

(1) IEA. *World Energy Outlook 2011*; International Energy Agency: Paris, France, 2011.
(2) Smeets, E. M. W.; Faaij, A. P. C.; Lewandowski, I. M.; Turkenburg, W. C. *Prog. Energy Combust. Sci.* **2007**, *33*, 56−106.
(3) Ladanai, S.; Vinterbäck, J. *Global Potential of Sustainable Biomass for Energy*; Department of Energy and Technology, Swedish University of Agricultural Sciences (SLU): Uppsala, Sweden, 2009.
(4) Bartle, J.; Olsen, G.; Cooper, D.; Hobbs, T. *Int. J. Global Energy Issues* **2007**, *27* (2), 115−137.
(5) Wu, H.; Fu, Q.; Giles, R.; Bartle, J. *Energy Fuels* **2008**, *22*, 190−198.
(6) Yu, Y.; Bartle, J.; Li, C.-Z.; Wu, H. *Energy Fuels* **2009**, *23*, 3290−3299.
(7) Yu, Y.; Wu, H. *Energy Fuels* **2010**, *24*, 5660−5668.
(8) Bartle, J. R.; Abadi, A. *Energy Fuels* **2010**, *24* (1), 2−9.
(9) Oasmaa, A.; Czernik, S. *Energy Fuels* **1999**, *13*, 914−921.
(10) Diebold, J. P. *A Review of the Chemical and Physical Mechanisms of the Storage Stability of Fast Pyrolysis Bio-oils*, NREL/SR-570-27613; National Renewable Energy Laboratory: Golden, CO, Jan. 2000.
(11) Oasmaa, A.; Sipilä, K.; Solantausta, Y.; Kuoppala, E. *Energy Fuels* **2005**, *19*, 2556−2561.
(12) Bertero, M.; de la Puente, G.; Sedran, U. *Energy Fuels* **2011**, *25*, 1267−1275.
(13) Bridgwater, A. V.; Meier, D.; Radlein, D. *Org. Geochem.* **1999**, *30*, 1479−1493.
(14) Mohan, D.; Pittman, C. U., Jr.; Steele, P. H. *Energy Fuels* **2006**, *20*, 848−889.
(15) Bridgwater, A. V. *Therm. Sci.* **2004**, *8*, 21−49.
(16) Picter, A.; Sarasin, J. *Helv. Chim. Acta* **1918**, *1*, 87−98.
(17) Tang, M. M.; Bacon, R. *Carbon* **1964**, *2*, 211−220.
(18) Shafizadeh, F.; Fu, Y. L. *Carbohydr. Res.* **1973**, *29*, 113−122.
(19) Golova, O. P. *Russ. Chem. Rev.* **1975**, *44*, 687−697.
(20) Shafizadeh, F. *J. Anal. Appl. Pyrolysis* **1982**, *3*, 283−305.
(21) Antal, M. J., Jr. *Advances in Solar Energy* **1983**, *1*, 61−111.
(22) Mamleev, V.; Bourbigot, S.; Bras, M. L.; Yvon, J. *J. Anal. Appl. Pyrolysis* **2009**, *84*, 1−17.
(23) Lédé, J. *J. Anal. Appl. Pyrolysis* **2012**, *94*, 17−32.
(24) Mayes, H. B.; Broadbelt, L. J. *J. Phys. Chem. A* **2012**, *116* (26), 7098−7106.
(25) Qu, T.; Guo, W.; Shen, L.; Xiao, J.; Zhao, K. *Ind. Eng. Chem. Res.* **2011**, *50* (18), 10424−10433.
(26) Zhang, X.; Li, J.; Yang, W.; Blasiak, W. *Energy Fuels* **2011**, *25* (8), 3739−3746.
(27) Zhang, X.; Yang, W.; Blasiak, W. *Energy Fuels* **2011**, *25* (10), 4786−4795.
(28) Assary, R. S.; Curtiss, L. A. *ChemCatChem* **2012**, *4* (2), 200−205.

(29) Broido, A.; Javier-Son, A. C.; Barrall, E. M. *J. Appl. Polym. Sci.* **1973**, *17*, 3627−3635.

(30) Bradbury, A. G. W.; Sakai, Y.; Shafizadeh, F. *J. Appl. Polym. Sci.* **1979**, *23*, 3271−3280.

(31) Shafizadeh, F.; Bradbury, A. G. W. *J. Appl. Polym. Sci.* **1979**, *23*, 1431−1442.

(32) Broido, A.; Nelson, M. A. *Combust. Flame* **1975**, *24*, 263−268.

(33) Vladars-Uasa, A. *Thermal decomposition of cellulose*. PhD Thesis, University of Waterloo, Ontario, Canada, 1993.

(34) Boutin, O.; Ferrer, M.; Lédé, J. *J. Anal. Appl. Pyrolysis* **1998**, *47*, 13−31.

(35) Piskorz, J.; Majerski, P.; Radlein, D.; Vladars-Usas, A.; Scott, D. S. *J. Anal. Appl. Pyrolysis* **2000**, *56*, 145−166.

(36) Boutin, O.; Ferrer, M.; Lédé, J. *Chem. Eng. Sci.* **2002**, *57*, 15−25.

(37) Lédé, J.; Blanchard, F.; Boutin, O. *Fuel* **2002**, *81*, 1269−1279.

(38) Dauenhauer, P. J.; Colby, J. L.; Balonek, C. M.; Suszynski, W. J.; Schmidt, L. D. *Green Chem.* **2009**, *11*, 1555−1561.

(39) Wooten, J. B.; Seeman, J. I.; Hajaligol, M. R. *Energy Fuels* **2004**, *18* (1), 1−15.

(40) Yu, Y.; Wu, H. *Ind. Eng. Chem. Res.* **2009**, *48* (23), 10682−10690.

(41) Yip, K.; Tian, F.; Hayashi, J.-i.; Wu, H. *Energy Fuels* **2010**, *24*, 173−181.

(42) Wu, H.; Yip, K.; Kong, Z.; Li, C.-Z.; Liu, D.; Yu, Y.; Gao, X. *Ind. Eng. Chem. Res.* **2011**, *50* (21), 12143−12151.

(43) Sluiter, A.; Hames, B.; Ruiz, R.; Scarlata, C.; Sluiter, J.; Templeton, D.; Crocker, D. *Determination of Structural Carbohydrates and Lignin in Biomass*, Technical Report NREL/TP-510-42618; National Renewable Energy Laboratory: Golden, CO, 2008.

(44) Yang, B.; Wyman, C. E. *Bioresour. Technol.* **2008**, *99* (13), 5756−5762.

(45) Várhegyi, G.; Jakab, E. *Energy Fuels* **1994**, *8*, 1345−1352.

(46) Piskorz, J.; Radlein, D.; Scott, D. S.; Czernik, S. *J Anal. Appl. Pyrolysis* **1989**, *16*, 127−142.

(47) Di Blasi, C. *Prog. Energy Combust Sci.* **2008**, *34*, 47−90.

(48) Lin, Y.-C.; Cho, J.; Tompsett, G. A.; Westmoreland, P. R.; Huber, G. W. *J. Phys. Chem. C* **2009**, *113*, 20097−20107.

(49) Kloss, S.; Zehetner, F.; Dellantonio, A.; Hamid, R.; Ottner, F.; Liedtke, V.; Schwanninger, M.; Gerzabek, M. H.; Soja, G. *J. Environ. Qual.* **2012**, *41*, 990−1000.

(50) Schwanninger, M.; Rodrigues, J. C.; Pereira, H.; Hinterstoisser, B. *Vib. Spectrosc.* **2004**, *36*, 23−40.

(51) Pastorova, I.; Botto, R. E.; Arisz, P. W.; Boon, J. J. *Carbohydr. Res.* **1994**, *262*, 27−47.

(52) Suuberg, E. M.; Milosavljevic, I.; Oja, V. *Symp. (Int.) Combust.* **1996**, *26* (1), 1515−1521.

(53) Bridgwater, A. V.; Boocock, D. G. B. *Developments in Thermochemical Biomass Conversion*, Vol. *1*; Blackie Academic & Professional: London, 1996.

(54) Yu, Y.; Wu, H. *Energy Fuels* **2010**, *24* (3), 1963−1971.

(55) Yu, Y.; Wu, H. *Ind. Eng. Chem. Res.* **2010**, *49* (8), 3902−3909.

(56) Yu, Y.; Wu, H. *Ind. Eng. Chem. Res.* **2010**, *49* (8), 3919−3925.

(57) Yu, Y.; Wu, H. *AIChE J.* **2011**, *57* (3), 793−800.

(58) Kislitsyn, A. N.; Rodionoa, Z. M.; Savinykh, V. I.; Gusev, A. V. *Zh. Prikl. Khim. (Leningrad)* **1971**, *44*, 2518−2524.

(59) Ponder, G. R.; Richards, G. N.; Stevenson, T. T. *J. Anal. Appl. Pyrolysis* **1992**, *22*, 217−229.

(60) Arisz, P. W.; Lomax, J. A.; Boon, J. J. *Anal. Chem.* **1990**, *62*, 1519−1522.

(61) Matsuoka, S.; Kawamoto, H.; Saka, S. *Carbohydr. Res.* **2011**, *346*, 272−279.

(62) Chaiwat, W.; Hasegawa, I.; Tani, T.; Sunagawa, K.; Mae, K. *Energy Fuels* **2009**, *23*, 5765−5772.

(63) Léde, J.; Diebold, J. P.; Peacoke, G. V. C.; Piskorz, J.; Bridgwater, A. V.; Czernik, S.; Meier, D.; Oasmma, A.; Radlein, D. *Fast Pyrolysis of Biomass: A Handbook*; CPL Press: Newbury, U.K., 1999.

(64) Golova, O. P.; Andrievskaya, E. A.; Pakhomov, A. M.; Merlis, N. M. *Russian Chem. Bull.* **1957**, *6* (3), 399−401.

(65) Sanders, E. B.; Goldsmith, A. I.; Seeman, J. I. *J. Anal. Appl. Pyrolysis* **2003**, *66*, 29−50.

(66) Matsuoka, S.; Kawamoto, H.; Saka, S. *J. Anal. Appl. Pyrolysis* **2012**, *93*, 24−32.

(67) Tomasik, P.; Mieczyslaw, P.; Wiejak, S. *Adv. Carbohydr. Chem. Biochem.* **1989**, *47*, 203−278.