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Evolution of Primary Liquid Products and Evidence of in Situ Structural Changes in Cellulose with Conversion during Hydrolysis in Hot-Compressed Water

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This study shows the dynamic evolution of the primary liquid products with conversion during the hydrolysis of both amorphous and crystalline cellulose in hot-compressed water (HCW). The results suggest that the dynamic changes in cellulose structure occur during conversion and strongly depend on reaction temperature. Results from a set of purposely designed two-step experiments further confirm at least two mechanisms which may be responsible for such structural changes. One is the selective consumption of the reactive components within the intrinsically heterogeneous cellulose at early conversions. This mechanism dominates during the hydrolysis of at low temperatures, e.g., 180−200 °C for amorphous cellulose and 230 °C for microcrystalline cellulose. The other is the combined effects of various parallel reactions during hydrolysis in HCW, including cleavage of hydrogen bonds, degradation reactions, and cross-linking reactions. Enhanced hydrogen bond cleavage increases the production of glucose oligomers. However, parallel degradation reactions and cross-linking reactions decrease the selectivity of glucose oligomers. The effect of cross-linking of cellulose in HCW appears to increase with temperature and becomes significant at 270 °C, leading to a structural condensation and hence a reduction in the specific reactivity of cellulose and the selectivity of glucose oligomers in the primary liquid products.

1. Introduction

In Australia, mallee biomass is regarded as a key second-generation feedstock for future sustainable production of chemicals and biofuels as it is a byproduct of dryland salinity management and complements food production.[1,2] Production of mallee biomass is known to be efficient,[3] cheap,[4] and close to carbon-neutral.[5] Recently, significant research and development has been devoted to the production of bioenergy and biofuels using mallee biomass as feedstock.[6–12] Similar to other lignocellulosic feedstocks, mallee biomass contains considerable amounts of cellulose and hemicellulose, which can be used to produce various sugars via hydrolysis or pyrolysis[10,13] for the production of biofuels. Due to the various advantages, a recent development in biomass/cellulose hydrolysis is to use hot-compressed water (HCW) as a reaction medium for feedstock pretreatment and sugar recovery.[14–28]

Hydrolysis of biomass/cellulose in HCW involves complex chemical and physical process which may include primary hydrolysis reactions on the surface of the reacting cellulose particles, the dissolution of primary hydrolysis products into HCW, and the secondary decomposition reactions of primary hydrolysis products in the aqueous phase.[16,19,22,27] Recent studies of our research group[26–28] provided new insights into the reaction mechanisms on cellulose hydrolysis in HCW. A new sampling and analytical method was developed[26] to characterize the glucose oligomers in the fresh liquid products via high performance anion exchange chromatography with pulsed amperometric detection (HPAEC-PAD). Using a semicontinuous reactor system,[27] a series of experiments were carefully designed to successfully obtain the primary liquid products of cellulose hydrolysis in HCW under various conditions with minimized secondary reactions in the aqueous phase. The results clearly showed that, on the surface of reacting cellulose particles, hydrolysis reactions dominate to produce glucose oligomers of a wide range of degrees of polymerization (DPs) while degradation reactions do occur but to a much less extent.[27] Both hydrolysis and degradation reactions were found to proceed on the particle surface in parallel and in a manner of randomness that is temperature-dependent.[27] Due to their structural differences, the amorphous and crystalline portions within microcrystalline cellulose also exhibit significant differences in hydrolysis behavior in HCW.[28]

Previous experimental data also suggested that the structure of cellulose might vary with conversion as hydrolysis reactions proceed in HCW.[19,28] While hydrolysis reactions proceed, the reacting cellulose particles may also experience parallel pyrolysis and/or other reactions, which can also dynamically alter the structure of the reacting cellulose particles and hence the characteristics of hydrolysis primary liquid products. This is expected to be important in batch or semicontinuous systems in which the reacting particles experience long residence times. However, little is known on how such structural evolution influences the formation of primary liquid products as a function of conversion during the course of cellulose hydrolysis in HCW. The significance of such an effect and its dependence on reaction temperature are also unknown. Fundamentally, these are all important aspects which need to be considered in the mechanistic understanding of cellulose hydrolysis behavior in HCW, the acquisition of cellulose hydrolysis reactivity data, and the design of hydrolysis reactor systems with maximized sugar recovery.

Therefore, the key objectives of this study are to carry out a systematic experimental study on the evolution of primary liquid products as a function of conversion during cellulose hydrolysis in HCW at various temperatures using a semicontinuous reactor system. Additionally, a set of novel two-step experiments was also carried out to illustrate the importance of in situ structural changes on the evolution of cellulose specific reactivity and primary liquid products during hydrolysis in HCW, considering both crystalline and amorphous cellulose.

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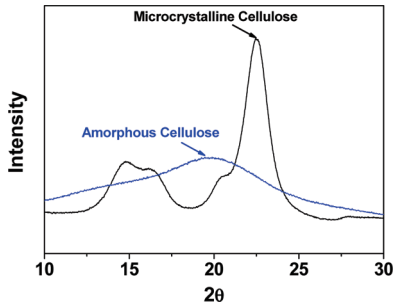

Figure 1. X-ray diffraction patterns of raw and ball-milled 7-h cellulose samples.

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 the experiments. X-ray diffraction (XRD) analysis shows that microcrystalline cellulose has a relative crystallinity index of 0.8 according to Segal's method.[29] A complete amorphous cellulose sample (no crystalline peaks found in the sample's XRD pattern, see Figure 1) was also prepared from the microcrystalline cellulose via ball milling for ~7 h using a laboratory ball mill. Glucose oligomer standards (i.e., glucose, cellobiose, cellotriose, cellotetraose, and cellopentaose), and high purity reagents for HPAEC-PAD analysis were also purchased from Sigma-Aldrich.

2.2. Hydrolysis Experiments. Hydrolysis of cellulose in HCW was carried out using a semicontinuous reactor system.[26–28] Experimental conditions were optimized to obtain the primary liquid products with minimized secondary reactions in the aqueous phase, following the method described elsewhere.[26,27] In this paper, all experiments were carried out at 10 MPa and at temperatures 180−270 °C, depending on the cellulose samples used. Another set of novel two-step experiments (a pretreatment step followed by an in situ hydrolysis step in HCW) were also conducted (as illustrated in Figure 2). For amorphous cellulose, the sample was first pretreated at 190 or 200 °C in HCW for 5 min and then in situ cooled to 180 °C for continuous hydrolysis reactions in HCW. The evolution of specific reactivity and primary liquid products obtained from the two-step experiments were then compared with that of hydrolysis of the raw sample at 180 °C directly at the same overall conversion levels (considering the conversions during both pretreatment and hydrolysis steps). Similar experiments and comparisons were also done for the microcrystalline cellulose, which was pretreated in HCW at 200 °C for 4 h, or at 250 or 270 °C for 5 or 10 min, and then in situ increased or cooled to 230 °C for subsequent hydrolysis.

2.3. Cellulose Conversion, Specific Reactivity, and Analysis of Liquid Products. Following a new sampling and characterization method,[26] the fresh liquid products were analyzed immediately after collection. The total carbon contents of liquid samples were analyzed using a total organic carbon (TOC) analyzer (Shimadzu TOC-V_{CPH}). The conversion level X of cellulose at a reaction time t, on a carbon basis, is calculated as $X = C_t/C_0$, where C_0 is the total carbon of the initial sample loaded into the reactor and C_t is the total carbon converted from the sample after a reaction time t. The value of C_t can be calculated from the sum of all carbon collected from the hydrolysis reactions commencing at $t = 0$, i.e., $C_t = \sum V_i C_i$, where V_i is the total liquid volume between two sampling intervals and C_i is the carbon concentration of that liquid. It should be noted that, for the two-step experiments, the overall conversion X consists of both the pretreatment and hydrolysis steps. The specific reactivity R of cellulose, on a carbon basis, was then determined as $R = -(1/C)(dC/dt)$, where C is the carbon content in the remaining cellulose at a reaction time t. The liquid samples were collected every 5 min so that the specific reactivity calculated is actually an average reactivity of cellulose during the collection time.

Following an established technique using HPAEC-PAD as described elsewhere,[26] all fresh liquid products were analyzed immediately after collection by HPAEC-PAD using a Dionex ICS-3000 ion chromatography (IC) system, within the instrument detector's linear response range. Comparisons of the selectivity of each glucose oligomer in various liquid products are made according to a method developed by the same authors.[27] The glucose oligomers are named according to DP values (e.g., glucose as C1, cellobiose as C2).

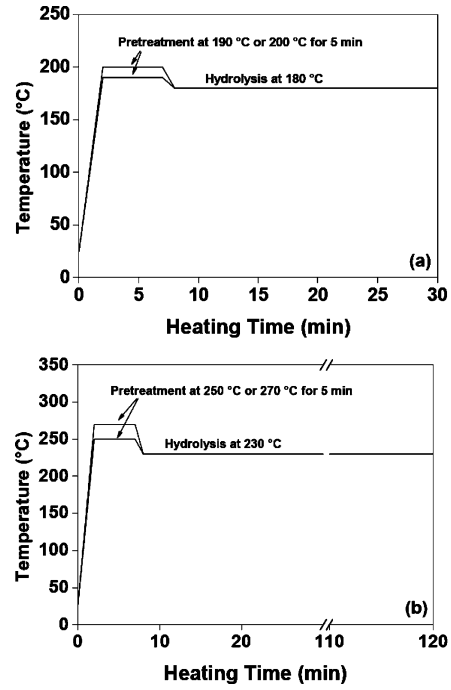

Figure 2. Two-step experiments including pretreatment and in situ hydrolysis (a) for amorphous cellulose and (b) for crystalline cellulose.

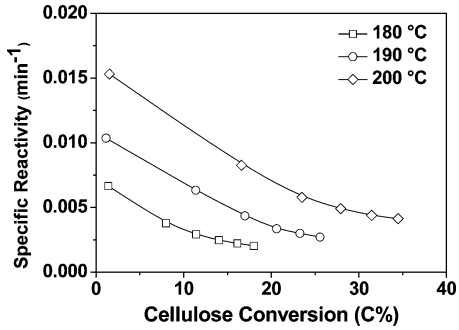

Figure 3. Evolution of specific reactivity of amorphous cellulose during hydrolysis in HCW at 180−200 °C and 10 MPa.

3. Results and Discussion

3.1. Evolution of Specific Reactivity as a Function of Conversion during the Hydrolysis of Cellulose in HCW. Figure 3 presents the evolution of specific reactivity as a function of conversion during the hydrolysis of amorphous cellulose at 180−200 °C. It can be seen in Figure 3 that the specific reactivity of amorphous cellulose decreases continuously with

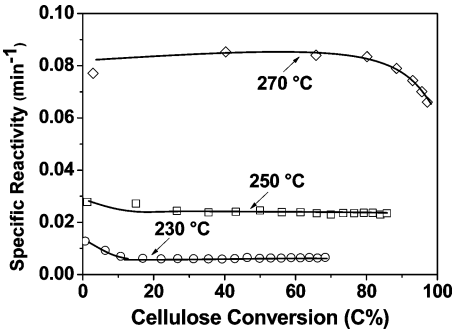

Figure 4. Evolution of specific reactivity of microcrystalline cellulose during hydrolysis in HCW at 230−270 °C and 10 MPa.

conversion. As shown in Figure 1, the amorphous cellulose is completely amorphous since no crystalline peak can be found in its XRD pattern. It is well-known that amorphous cellulose has a heterogeneous structure which consists of chain segments of various chain lengths.[30–32] Therefore, the decrease in specific reactivity as a function of conversion in Figure 3 is most likely due to the selective consumption of more reactive components at early conversions during hydrolysis.

Figure 4 presents the evolution of specific reactivity as a function of conversion during the hydrolysis of microcrystalline cellulose at 230−270 °C. As discussed previously,[28] at 230 °C there is an initial decrease in reactivity up to ∼20% conversion, corresponding to the selective conversion of the amorphous portion within the microcrystalline cellulose that has a relative crystallinity index of ∼0.8. After the amorphous portion is consumed, the specific reactivity of the crystalline portion remains relatively unchanged at conversion >20%. However, it is interesting to see that, at 250 and 270 °C, the decrease in the specific reactivity is not apparent at early conversions. It seems that, as far as specific reactivity is concerned, the structural differences between amorphous and crystalline portions within microcrystalline cellulose become less important at high temperatures. This also suggests that the strong hydrogen bonds in the microcrystalline cellulose can be broken very quickly at high temperatures. Another important point to make in Figure 4 is that, at 270 °C, there is a significant decrease in the specific reactivity of the reacting cellulose at high conversions. Such a decrease in specific reactivity clearly indicates the structural changes within the reacting cellulose. Such structural changes seem to involve the condensation of the structures, resulting in the reacting cellulose becoming more inert (or less reactive) as the conversion increases.

3.2. Evolution of Primary Liquid Products as a Function of Conversion during the Hydrolysis of Cellulose in HCW. It is expected that the structural changes of reacting cellulose should result in the differences in the primary liquid products at various conversions. Therefore, at the same hydrolysis temperature, the primary liquid products were then collected at various conversions and compared using an index called the "selectivity ratio". The selectivity ratio is defined as the ratio between the selectivity of a glucose oligomer in two liquid products, normalized to the total carbon contents of each liquid product.[27] Figures 5 and 6 present the selectivity ratios of glucose oligomers in the primary liquid products collected at various conversions for the hydrolysis of amorphous and microcrystalline cellulose in HCW. At a given hydrolysis temperature, if there is little structural change during conversion, the selectivity ratios for all glucose oligomers in the primary liquid products collected at various conversions should be 1. However, this is obviously not the cases in both Figures 5 and

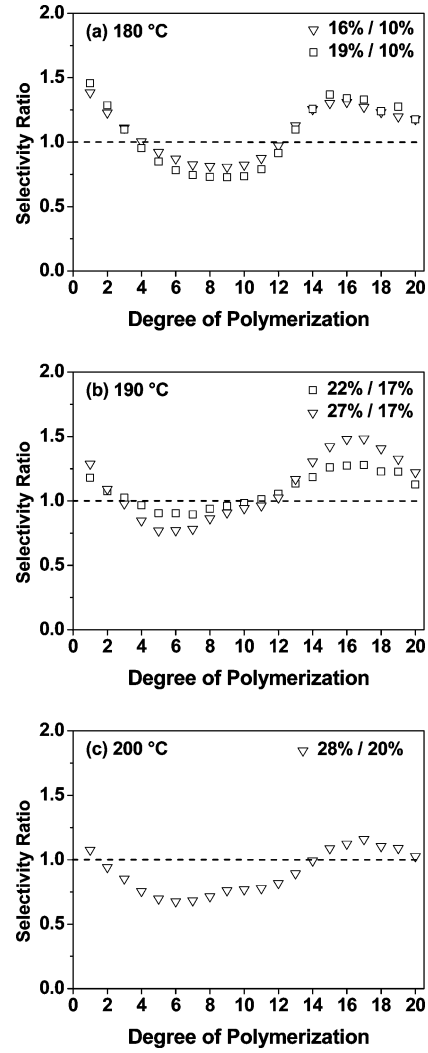

Figure 5. Evolution of primary liquid products of amorphous cellulose during hydrolysis in HCW at 180−200 °C and 10 MPa. (a) 180 °C; (b) 190 °C; (c) 200 °C.

6, which clearly show the significant changes in selectivities of glucose oligomers in the primary liquid products collected at various conversions at a given temperature. Therefore, there must be dynamic structural changes occurring in reacting cellulose particles as conversion increases during hydrolysis in HCW. A close examination of Figures 5 and 6 leads to several key observations.

First, for the amorphous cellulose at 180 °C, as the conversion increases, the selectivities of C3 to C13 decrease to below 1 while the low-DP glucose oligomers (DPs < 3) and high-DP glucose oligomers (DPs > 13) increase to above 1. The curves of the selectivity ratio have a similar shape at 190 and 200 °C. This is likely due to the heterogeneous structure of the amorphous cellulose. It is known that the chain segments of various lengths in amorphous cellulose are held together by isotropic intermolecular hydrogen bonds linked to the hydroxyl groups at the C-2 and C-3 positions,[31] with typically bent and twisted backbones, and the molecules are in a random coil conformation,[33–35] resulting in randomly distributed domain.[31] It was also found that the amorphous portion with microcrystalline cellulose contains various short-length chain segments (e.g., C3−C13).[28] For a completely amorphous cellulose sample, like the one used in this study, these short-length chain segments are expected to be more abundant. Therefore, those short chains would be progressively removed as conversion increases,

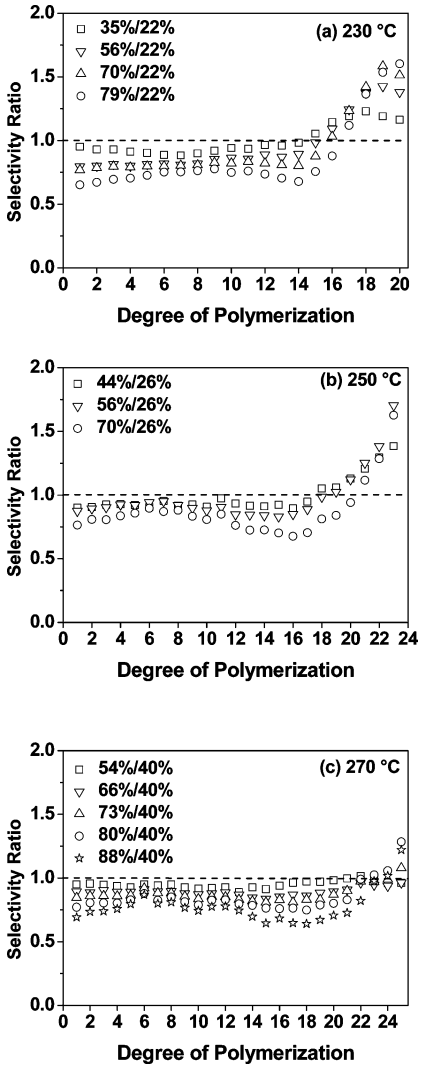

Figure 6. Evolution of primary liquid products of microcrystalline cellulose during hydrolysis in HCW at 230−270 °C and 10 MPa. (a) 230 °C; (b) 250 °C; (c) 270 °C.

resulting in a reduction in the selectivity ratios of C3 to C13 in the primary liquid products as cellulose conversion increases and an increase in the length of chain segments within the reacting amorphous cellulose. This is clearly shown in Figure 5a, that the selectivities of C3 to C13 decrease with increasing conversion of amorphous cellulose at 180 °C. Additionally, with increasing conversion, the reacting particles experience longer residence times in HCW, resulting in the continuous weakening of hydrogen bonds within the amorphous cellulose. As shown in Figure 5a, the hydrolysis of the reacting amorphous cellulose which has longer chain sizes at increased conversions would lead to an increase in the selectivities of low-DP glucose oligomers (DPs < 3) and high-DP glucose oligomers (DPs > 13). The data in Figure 5b,c also indicate that, compared to at 180 and 190 °C, the increase in high-DP glulose oligomers is less at 200 °C, suggesting that for amorphous cellulose the other parallel reactions of the chain segments within the reacting sample to form nonsugar products seem to be apparent even at 200 °C.

Second, for microcrystalline cellulose in Figure 6, the evolution of primary liquid products with increasing conversion follows a significantly different manner. At 230 °C, there are only small differences in the selectivities of the glucose oligomers in the primary liquid products at conversions less than 35%. Further increase in conversion leads to significant changes in the selectivity of the glucose oligomers in the primary liquid products. The selectivities of glucose oligomers with DPs of 1−14 are found to decrease significantly with conversion to be less than 1, while the selectivity of high-DP glucose oligomers (e.g., C17−C20) increases with conversion to be greater than 1. Also, the selectivity ratios of glucose oligomers larger than a certain DP (e.g., 14 at 230 °C) increases with the DP. The increasing selectivity of those high-DP glucose oligomers is possibly due to the change in hydrogen bonding. Crystalline cellulose consists of a complex network of intra- and intermolecular hydrogen bonds,[36] which can limit the accessibility of the glycosidic bonds within the chain and therefore the formation of high-DP glucose oligomers.[27] It is known that the structure of hydrogen bonds in crystalline cellulose is also drastically weakened at temperatures >220 °C.[37] Therefore, with increasing conversion, the reacting cellulose particles experience longer residence times and therefore continuous weakening of hydrogen bonds. The glycosidic bonds in cellulose residue are more accessible at higher conversions, therefore leading to an increase in the selectivity of those high-DP glucose oligomers in the primary liquid products.

Third, for microcrystalline cellulose, since the cleavage of accessible glycosidic bonds proceeds randomly on the surface of a reacting cellulose particle during hydrolysis in HCW,[27] one would expect that the glucose oligomers of low DPs (e.g., 1−14 at 230 °C) should also increase at higher conversion. However, the data in Figure 6 show that the selectivities of those low-DP glucose oligomers actually decrease with conversion to be less than 1. Therefore, there should be other mechanisms which induce in situ changes in the structure of the reacting crystalline cellulose residue, leading to less production of those low-DP glucose oligomers. One possibility is the parallel degradation reactions during cellulose hydrolysis in HCW. Parallel degradation reactions are known to occur randomly on the surface of reacting cellulose particles, albeit to much less extent in comparison to the hydrolysis reactions to produce glucose oligomers.[27] The other possibility is the parallel cross-linking reactions which condense the chain structure and lead to less production of glucose oligomers. Cross-linking reactions are known to be significant during cellulose hydrolysis at temperatures as low as 260 °C.[38] Figure 6b and Figure 6c show that the primary liquid products at different conversions for 250 and 270 °C have the same trends as those for 230 °C. However, at 270 °C, the selectivity ratios of almost all glucose oligomers at higher conversions are less than 1. Although higher reaction temperature increases the cleavage of hydrogen bonding, hence increasing the accessibility of glycosidic bonds, the selectivities of high-DP glucose oligomers at 270 °C do not increase significantly, as observed at lower temperatures. It seems that the formation of glucose oligomers from reacting cellulose particle is strongly affected by the competing mechanisms for dynamic structural evolution, i.e., increasing formation of glucose oligomers due to cleavage of hydrogen bonds and decreasing formation of glucose oligomers because of degradation and cross-linking reactions. The influence of cross-linking reactions becomes dominant with increasing reaction temperature, which leads to structural condensation. Indeed, such structural condensation results in a reduction in specific reactivity at high conversions at 270 °C as shown in Figure 4.

Therefore, the significant variations in the compositions of the primary liquid products with conversion (as shown in Figures 3−6) suggest that structural changes have taken place within the reacting cellulose as hydrolysis progresses. At least two

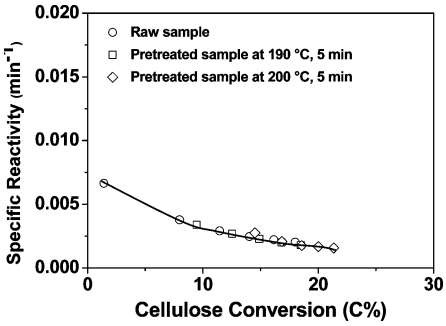

Figure 7. Effect of in situ pretreament of amorphous cellulose at 190 and 200 °C on the evolution of specific reactivity during hydrolysis in HCW at 180 °C and 10 MPa.

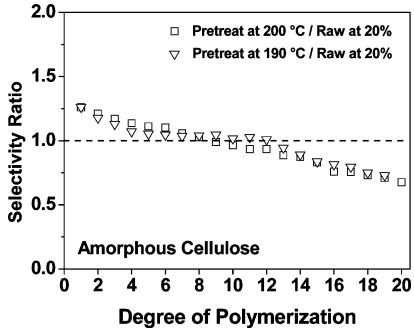

Figure 8. Effect of in situ pretreament of amorphous cellulose at 190 and 200 °C on the evolution of primary liquid product during hydrolysis in HCW at 180 °C and 10 MPa.

possible mechanisms may be responsible for such structural changes. One is the intrinsic heterogeneity of cellulose which leads to the selective consumption of the reactive amorphous portion at early conversions. This is particularly apparent at low temperatures (e.g., 180−200 °C for amorphous cellulose and 230 °C for microcrystalline cellulose). The other is as results from various parallel reactions, including hydrogen bond cleavage, degradation reactions, and cross-linking reactions during hydrolysis in HCW, which induce in situ structural changes within the reacting cellulose dynamically.

3.3. Effect of in Situ Pretreatment on the Evolution of Specific Reactivity and Primary Liquid Products with Conversion. An additional set of novel two-step experiments were then carried out to investigate the structural evolution during cellulose hydrolysis in HCW. The results are shown in Figures 7−10 for amorphous and microcrystalline cellulose, respectively. Figure 7 indicates that pretreatment of the amorphous cellulose at higher temperatures (190 and 200 °C) has little effect on the cellulose specific reactivity, considering the overall cellulose conversion including the pretreatment step at higher temperatures and the subsequent hydrolysis step at 180 °C. However, Figure 8 indicates that the pretreatment does have an effect on the glucose oliomgers in the primary liquid products produced at the same overall conversion. It can be seen that pretreatment increases the selectivities of low-DP glucose oligomers but decreases the selectivities of high-DP glucose oligomers in the primary liquid products at 180 °C. This may also be explained by the different thermochemical process which the amorphous cellulose experienced. The structure of amorphous cellulose is very reactive and is therefore prone to be influenced by pretreatment in HCW. It seems that, on the one hand, the pretreatment at 190 and 200 °C enhances the hydrogen bond weakening in the amorphous structure; therefore the selectivity of low-DP glucose oligomers is increased. On the

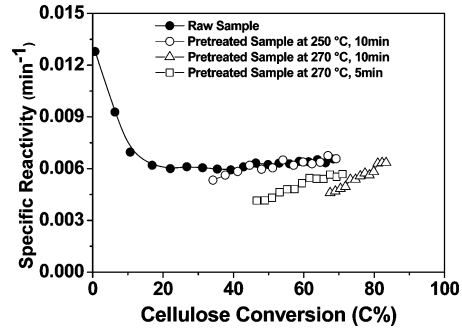

Figure 9. Effect of in situ pretreament of microcrystalline cellulose at 250 and 270 °C on the evolution of specific reactivity during hydrolysis in HCW at 230 °C and 10 MPa.

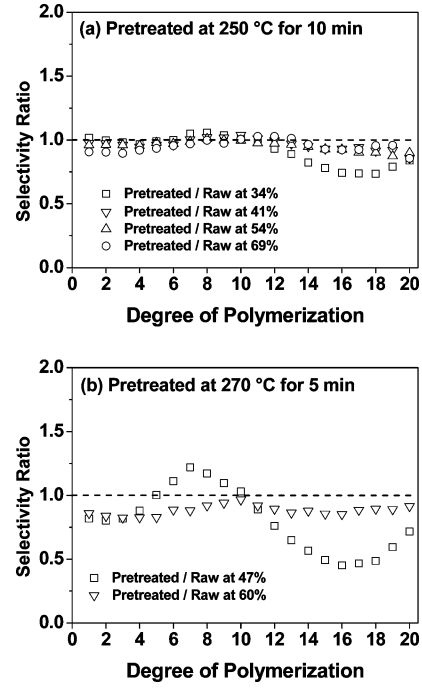

Figure 10. Effect of in situ pretreament of microcrystalline cellulose on the evolution of primary liquid products during the subsequent hydrolysis in HCW at 230 °C and 10 MPa. (a) 250 °C for 10 min; (b) 270 °C for 5 min.

other hand, the pretreatment at higher temperatures (e.g., 200 °C) also induced more degradation reactions of the chain segments within amorphous cellulose so that, during the subsequent hydrolysis of the pretreated cellulose at 180 °C, there are apparent reductions in the production of high-DP glucose oligomers in the primary liquid products. There is little change in the specific reactivity of amorphous cellulose as cross-linking reactions are not expected to take place at such a low temperature.

For crystalline cellulose, pretreatment at higher temperatures (250 and 270 °C) clearly has effect on the specific reactivity during the subsequent hydrolysis of the sample at 230 °C. Generally, as shown in Figure 9, pretreatment leads to a decrease in specific reactivity and such decrease becomes more significant at higher pretreatment temperatures (i.e., 270 °C). It is also clearly shown that at the same pretreatment temperature (i.e., 270 °C in Figure 9b), in comparison to a pretreatment time of 5 min, a longer pretreatment time of 10 min leads to a more significant decrease in specific reactivity of the crystalline cellulose. Accordingly, as shown in Figure 10, pretreatment also leads to a decrease in the selectivities of glucose oligomers in

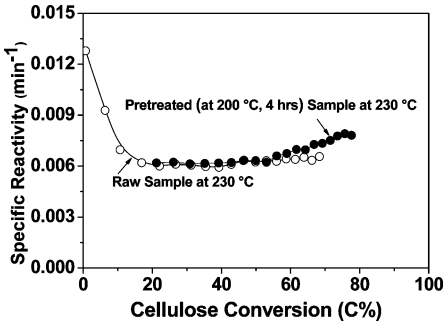

Figure 11. Effect of in situ pretreament of microcrystalline cellulose at 200 °C for 4 h on the evolution of specific reactivity during hydrolysis in HCW at 230 °C and 10 MPa.

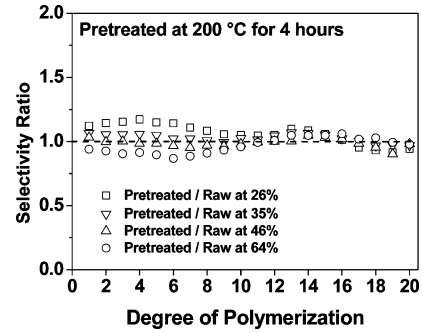

Figure 12. Effect of in situ pretreament of microcrystalline cellulose at 200 °C for 4 h on the evolution of primary liquid products during the subsequent hydrolysis in HCW at 230 °C and 10 MPa.

primary liquid products to be less than 1 during the subsequent hydrolysis of the pretreated samples at 230 °C. Such a decrease becomes more significant when the pretreatment temperature increases from 250 to 270 °C. Therefore, the data in Figures 9 and 10 are consistent with the discussion in the previous section and clearly demonstrate the significant influence of cross-linking reactions on the structure of reacting cellulose at 270 °C. Such cross-linking reactions lead to structural condensation, hence a significant reduction in specific reactivity of the pretreated sample and selectivities of glucose oligomers in the primary products during subsequent hydrolysis at 230 °C. Figure 10 also shows the clear evidence for the enhanced cleavage of hydrogen bonds during pretreatment as the selectivities of high-DP glucose oligomers do increase with DP, although the selectivity ratios of those glucose oligomers are <1 due to the dominant effect of cross-linking reactions.

Additionally, it is interesting to note in Figure 9 that, during the subsequent hydrolysis at 230 °C, the specific reactivity of the pretreated samples actually increases with conversion. Accordingly, right after pretreatment, there is a significant change in the selectivities of glucose oligomers in the primary liquid products at the initial conversions during the subsequent hydrolysis of the pretreated samples. However, as conversion increases, the effect of pretreatment on the selectivity of glucose oligomers becomes much less and the selectivities of glucose oligomers become more similar to those from the hydrolysis of the raw sample. The results suggest that the effect of pretreatment seems to be limited to the outer layers of the reacting particles. It seems that the interactions between HCW and the sample did not penetrate throughout the reacting particle during pretreatment, possibly due to the short period of pretreatment time.

Another experiment was then conducted to pretreat the raw cellulose for a long period (4 h) at a suitable low temperature (200 °C) and then in situ heat the pretreated sample to 230 °C for continuous hydrolysis reactions in HCW. The specific reactivity and primary liquid products were compared with those at 230 °C for raw cellulose sample in Figures 11 and 12. Despite a prolonged pretreatment at 200 °C (4 h), there is little change in the specific reactivity of the pretreated sample initially. However, after reaction at 230 °C for 3 h, the pretreated sample actually exhibits a higher specific reactivity. The primary liquid products right after pretreatment showed a slight increase of the selectivities for low-DP glucose oligomers. With reaction proceeding further at 230 °C, the primary liquid products are almost the same as those for raw samples, until the conversion is higher than 55%. The selectivities of low-DP glucose oligomers start to decrease with conversion at higher conversions. The data in Figures 11 and 12 suggest that the cross-linking reactions are minimized as there is no reduction in the specific reactivity of the pretreated sample at 200 °C during the second step hydrolysis at 230 °C. Changes in hydrogen bonding and degradation reactions play more important roles. The slight increase of the selectivities of low-DP glucose oligomers for the in situ pretreated sample is likely due to the weakening and/or cleavage of hydrogen bonds within cellulose at 200 °C. The weakening and cleavage of hydrogen bonds seems to be mild because there is little increase in the selectivities of high-DP glucose oligomers. At higher conversions, the pretreated sample shows an increase in specific reactivity but not in the selectivities of glucose oligomers. This suggests that the increase in specific reactivity at 230 °C results from the formation of nonsugar products. It is possible that, as a result of prolonged reactions (it took an additional 70 min for the in situ pretreated sample to achieve 50% conversion), degradation reactions on the surface of reacting cellulose particles become more severe, leading to a slight increase in the formation of nonsugar products. Such a hypothesis is plausible because, even for the raw cellulose, there is also a slight increase (but less compared to the pretreated sample) in specific reactivity at conversions >55% (it took 120 min for the raw cellulose to achieve 55% conversion), as shown in Figure 11. Another possibility is that the long time of pretreatment partially changes the structure of glucose chains as a result of parallel degradation reactions. Such changes lead to the formation of some partially pyrolyzed residues and hence nonsugar products.

4. Conclusions

The specific reactivity and primary liquid products dynamically evolve during the course of cellulose hydrolysis in HCW at 10 MPa and 180−270 °C, suggesting the evolution of cellulose structure during conversion. The intrinsic heterogeneity of cellulose results in the selective consumption of reactive components at early conversions at low temperatures, e.g., 180−200 °C for amorphous cellulose and 230 °C for microcrystalline cellulose. Various parallel reactions, including hydrogen bond cleavage, degradation reactions, and cross-linking reactions, also contribute to the cellulose structure evolution during hydrolysis in HCW. While enhanced hydrogen bond cleavage increases the production of glucose oligomers, degradation reactions and cross-linking reactions have the opposite effect. The effect of cross-linking reactions becomes dominant at 270 °C, resulting in a structural condensation which significantly reduces both the specific reactivity of cellulose and the selectivities of glucose oligomers in the primary liquid products.

Acknowledgment

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