Effect of Ball Milling on the Hydrolysis of Microcrystalline Cellulose in Hot-Compressed Water

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Ball milling leads to a considerable reduction in cellulose particle size and crystallinity, as well as a significant increase in the specific reactivity of cellulose during hydrolysis in hot-compressed water (HCW). Cryogenic ball milling for 2 min also results in a significant size reduction but only little change in cellulose crystallinity and specific reactivity during hydrolysis. Therefore, crystallinity is the dominant factor in determining the hydrolysis reactivity of cellulose in HCW while particle size only plays a minor role. Ball milling also significantly influences the distribution of glucose oligomers in the primary liquid products of cellulose hydrolysis. It increases the selectivities of glucose oligomers at low conversions. At high conversions, the reduction in chain length plays an important role in glucose oligomer formation as cellulose samples become more crystalline. An extensive ball milling completely converts the crystalline cellulose into amorphous cellulose, substantially enhancing the formation of glucose oligomers with high degrees of polymerization. © 2010 American Institute of Chemical Engineers *AIChE J,* 57: 793–800, 2011
Keywords: biomass, cellulose, hydrolysis, hot-compressed water, primary liquid products, ball milling

Introduction

The use of petroleum-based transport fuels leads to significant carbon dioxide emission and liquid biofuels are key alternatives for future sustainable development.[1] Mallee biomass in Australia is a byproduct of dryland salinity management[2,3] and has superb economic, energy, and environmental performances.[4–6] It is considered as a second generation renewable feedstock[7] for bioenergy and biofuels production in Australia.[8–14] Lignocellulosic ethanol production from mallee biomass is one of the key technical routes for producing liquid transport biofuels in Australia, if hemicellulose and cellulose in the biomass can be efficiently converted to fermentable sugars.

Hydrolysis in hot-compressed water (HCW) is an attractive way to recover sugars from cellulose or biomass. However, the mechanisms of cellulose hydrolysis in HCW are still not well understood.[15–26] The recent fundamental studies[27–30] by the same authors made progress to provide some new insights into the reaction mechanisms of cellulose hydrolysis in HCW. A new sampling and analytical method[27] has been established to analyze glucose oligomers in the liquid products using a high-performance anion exchange chromatography with pulsed amperometric detection (HPAEC-PAD). The fresh liquid products must be analyzed immediately after collection to avoid precipitation. Reaction conditions were also optimized to separate the primary hydrolysis reactions on the reacting cellulose particle surface from the secondary

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reactions in the aqueous phase.[28] Cleavage of hydrogen bond becomes fast at high temperatures hence increasing the accessibility of glycosidic bonds in cellulose chain. This considerably enhances the reaction rate of hydrolysis and alters the distribution of glucose oligomers in the primary liquid products.[28]

Cellulose may contain both amorphous and crystalline structures.[29,31] There are significant differences in the hydrolysis behavior of amorphous and crystalline portions within microcrystalline cellulose in HCW.[29] For the amorphous portion, as hydrogen bonds are weak,[32–36] the hydrolysis reactions are limited by the cleavage of glycosidic bonds and commence at ~150°C.[29] The crystalline portion has a network of strong intra- and intermolecular hydrogen bonds[37] which limit the accessibility of glycosidic bonds within the chain and hydrolysis reactions commence at ~180°C.[29] Therefore, converting crystalline cellulose into amorphous cellulose can be a good strategy to substantially increase cellulose hydrolysis reactivity so a reactor can be operated under mild reaction conditions to greatly reduce the degradation of sugar products.

Amorphous cellulose usually can be prepared from microcrystalline cellulose by ball milling of crystalline cellulose.[38,39] The crystallinity of cellulose decreases with milling time, suggesting that the hydrogen bonds in crystalline cellulose can be weakened substantially and converted to amorphous cellulose. Zhao et al.[39] reported the dilute acid hydrolysis of cellulose samples by ball milling and found that the glucose yield increased with ball milling time. In this study, the key objective is to investigate the behavior of ball-milled cellulose during hydrolysis in HCW. The effect of ball milling on the structure of cellulose was first investigated, followed by the behavior of ball-milled cellulose during hydrolysis in HCW. Finally, the primary liquid products obtained from ball-milled cellulose were characterized and compared to understand the effects of structural changes during ball milling on the formation of glucose oligomers.

Experimental Section

Materials and experiments

Microcrystalline cellulose was purchased from Sigma-Aldrich (Avicel PH-101) and then sieved to prepare the size fraction of 75–106 μm for all experiments. 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. The ball-milled cellulose samples were prepared using a laboratory ball mill (Retsch Mixer Mill MM400). To prepare each sample, ~2 g sample was charged into the grinding cell and the ball mill operated at a grinding frequency of 15 Hz with a 15-mm ball. Various grinding times (1, 4, and 7 h) were used for preparing the samples with different contents of amorphous cellulose. Cryogenic ball milling was also used to prepare a cellulose sample with a significant reduction in particle size but little change in crystallinity. During cryogenic ball milling, the grinding cell was cooled with liquid nitrogen for 10 min before grinding in the ball mill, and a short milling time of 2 min was used.

Hydrolysis of the raw and ball-milled cellulose samples in HCW was carried out using a semicontinuous reactor system which was used in previous studies.[27–30] This reactor system can be optimized to minimize the secondary reactions of glucose oligomers in the aqueous phase, facilitating the collection of the primary liquid products during hydrolysis. The detailed description and operation procedure of the reactor system can be found elsewhere.[27] Briefly, in an experiment run, a thin bed of cellulose (10–30 mg) was loaded into a tubular reactor cell which was then placed in an infrared gold image furnace. Before heating, deionized water was delivered at a flow rate of 10 ml/min by an HPLC pump and flowed through the reactor cell. The furnace (and the reactor cell) was then rapidly heated to a desired reaction temperature within 2 min and held at the reaction temperature for a desired period. The liquid products were quickly quenched and collected periodically. In this study, all experiments were carried out at 10 MPa and 230°C. Such reaction conditions were carefully chosen due to several reasons. One is that cellulose samples after ball milling are very reactive at higher reaction temperatures, making the hydrolysis reaction more difficult to control. The other is that a low reaction temperature minimizes the secondary reactions and facilitates the collection of primary liquid products during cellulose hydrolysis. In addition, a low reaction temperature minimizes the parallel reactions (e.g., degradation and cross-linking reactions) of cellulose residue during hydrolysis.

Characterization of cellulose samples and liquid products

The particle size distributions of raw and ball-milled samples were first analyzed using a laser-diffraction particle size analyzer (Malvern Mastersizer 2000). The sample was mixed with sodium hexametaphosphate solution (10% w/v) to aid dispersion of fine particles before loading into the measuring chamber. Crystalline patterns of the cellulose samples were characterized by X-ray diffraction (XRD) using a Bruker AXS D8 Advance X-ray diffractometer. The diffracted intensity of Cu Kα radiation was measured in a 2θ range from 10° to 30°. Based the XRD results, relative crystallinity index of raw and ball-milled cellulose samples can be calculated according to Segal's method[40]

$$\mathrm{Cr}I = \frac{I_{(200)} - I_{\mathrm{am}}}{I_{(200)}},$$

where $I_{(200)}$ and I_{am} are the intensities of the 200 peak ($2\theta = 22.7°$) and the amorphous peak ($2\theta = 18°$), respectively. $I_{(200)}$ represents both crystalline and amorphous cellulose whereas I_{am} represents amorphous cellulose only.

The total carbon concentration of a fresh liquid sample was measured by a total organic carbon (TOC) analyzer (Shimadzu TOC-V_{CPH}). The cellulose conversions are expressed as a function of reaction time on a carbon basis. The specific reactivity of cellulose residue under different conditions was then determined by $R = -1/C \times dC/dt$, where C is the carbon content in the reacting cellulose residue at a reaction time t during hydrolysis in HCW. The analysis of liquid products follows an established method published elsewhere.[27] All fresh liquid products were also analyzed

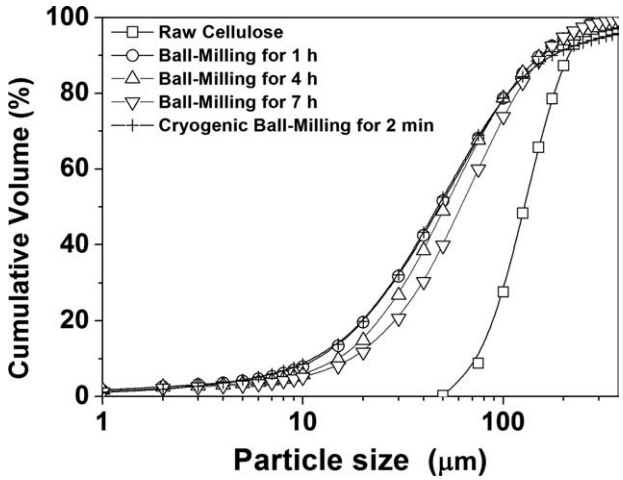

Figure 1. Particle size distributions of various cellulose samples.

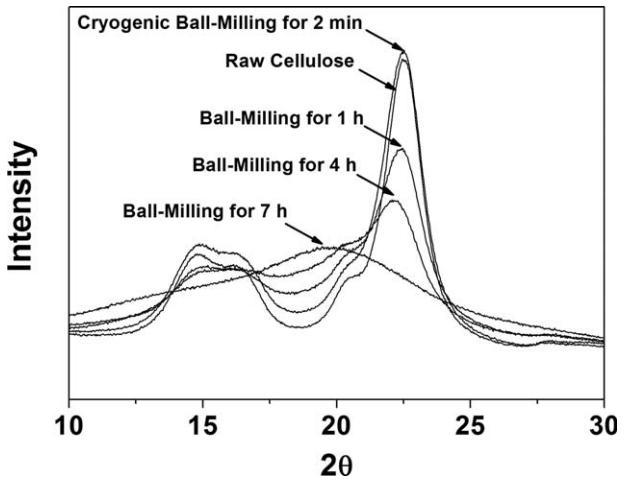

Figure 2. X-ray diffraction patterns of various cellulose samples.

immediately after collection via HPAEC-PAD using a Dionex ICS-3000 ion chromatography (IC) system within the detector's linear response range. Comparisons of the selectivity of each glucose oligomer in two liquid products are based on "selectivity ratio,"[28] which is defined as the ratio between the selectivity of a glucose oligomer in two liquid products. The selectivity of a glucose oligomer in a liquid product can be determined on a carbon basis as the carbon contained in the glucose oligomer normalized to the total carbon in the liquid product. Based on the method developed elsewhere,[28] the selectivity ratio can then be calculated as the ratio of the peak height of the glucose oligomer normalized by the carbon concentration of each liquid product, with the analysis of all the liquid samples being within the HPAEC-PAD detector's linear response range. In this article, the glucose oligomers are named according to the degree of polymerization (DP) values (e.g., glucose as C1, cellobiose as C2).

Results and Discussion

Changes in cellulose structure due to ball milling

Figure 1 presents the particle size distributions of the raw and ball-milled cellulose samples. Under normal conditions, 1 h ball milling of the raw cellulose sample results in a significant reduction in the particle size distribution of the cellulose sample. Further increasing ball milling time from 1 to 7 h leads to little further reduction in particle size therefore long ball milling is ineffective in reducing cellulose particle size. It is interesting to note that there is actually a slight increase in particle size, which is due to the agglomeration of fine particles as results of extensive ball milling. Figure 2 presents the XRD patterns of the raw and ball-milled cellulose samples. The crystalline peak decreases with increasing ball milling time. Further estimations of the relative crystallinity index for all samples were carried out using Segal's method. Indeed as shown in Table 1, the relative crystallinity index of cellulose reduced substantially from 0.79 for the raw sample to 0.58 for the 1 h ball-milled sample then to 0.38 for 4 h ball-milled sample. After 7 h ball milling time, the crystalline peak disappears totally, indicating all crystalline cellulose structures are transformed into amorphous cellulose structures. The results in Figures 1 and 2 are consistent with the previous findings that mechanical ball milling of microcrystalline cellulose decreases particle size, reduces the DP of cellulose, and increases the amorphous content of cellulose.[9,38,39] Clearly, the transformation of microcrystalline cellulose into amorphous cellulose suggests that ball milling has significantly weakened the hydrogen bonding networks within microcrystalline cellulose. Such changes are expected to have great influences on cellulose hydrolysis in HCW.

Effect of ball milling on the evolution of specific reactivity of cellulose during hydrolysis in HCW

The conversion vs. time of cellulose hydrolysis in HCW at 230°C are shown in Figure 3. As expected, ball milling increases the reaction rate of cellulose hydrolysis in HCW significantly. For example, while the hydrolysis of the raw sample for 2 h only achieves ~56% conversion, that of the sample after 7 h ball milling achieves ~80% conversion for only 1 h. Obviously, this must be due to the physical or structural changes in the cellulose induced by ball milling. For example, the significant weakening of hydrogen bond network due to ball milling would make the glucose chains within microcrystalline cellulose more accessible.

The specific reactivity of various cellulose samples during hydrolysis in HCW at 230°C is therefore plotted in Figure 4, from which three important observations can be made. First, the specific reactivity curves of the raw cellulose and the samples after ball milling for 1 and 4 h have the same

Table 1. Relative Crystallinity Indices of the Raw and Ball-Milled Samples

		Normal Ball Milling			
Samples	Raw	1 h	4 h	7 h	Cryogenic Ball Milling for 2 min
Relative crystallinity index	0.79	0.58	0.38	–	0.78

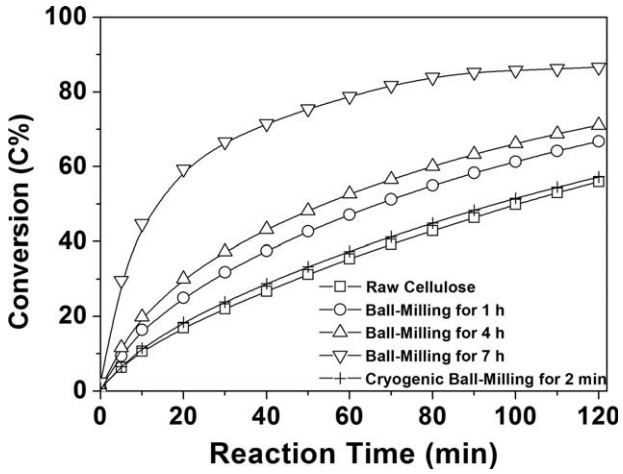

Figure 3. Conversion vs. time of various cellulose samples during hydrolysis in HCW at 230°C.

pattern, i.e., a continuous decrease till a certain conversion level X_c then levels off with further increasing conversion. The value of X_c increases with ball milling time, i.e., ~20%, ~40%, and ~55% for the raw cellulose and the samples after 1 and 4 h ball milling, respectively. The conversion X_c seems to be related to the samples' relative crystallinity indices which partially reflect the contents of crystalline portions within the cellulose samples. For ball-milled cellulose, the initial hydrolysis is mainly contributed by the reactions of amorphous cellulose and a small portion of crystalline cellulose as the hydrolysis of crystalline cellulose commences at ~180°C.[29] Second, it is noteworthy that the sample after 7 h ball milling shows continuous decrease in specific reactivity with conversion, as results of its complete amorphous nature. This in turn suggests that the structure of the amorphous cellulose itself is highly heterogeneous and as reaction progresses the remaining cellulose becomes less and less reactive. Last, at the same conversion, the specific reactivity of cellulose after ball milling increases significantly with increasing ball milling time. For example, at early conversions, the specific reactivity of the 4 h ball-milled sample is twice as that of the raw sample. At higher conversions, such difference in reactivity decreases because the remaining cellulose residue becomes more crystalline as hydrolysis proceeds.

Dominant role of crystallinity in cellulose reactivity during hydrolysis in HCW

The data in Figures 3 and 4 clearly show that mechanical ball milling is an effective method to substantially increase the specific reactivity of microcrystalline cellulose during hydrolysis in HCW. Fundamentally, this may be due to two mechanisms. One is the structural changes due to ball milling, including the destruction of hydrogen bonding networks and the reduction in DP of the microcrystalline cellulose. The other is the substantial decrease in the cellulose particle size. However, it is still unclear which of the two mechanisms (or both) play a dominant role in enhancing cellulose reactivity.

To clarify this important point, a new experimental method is required to separate the effect of the two mechanisms. This was achieved by cryogenic ball milling of the raw cellulose at a short time of 2 min and the results are presented in Figures 1–4. Indeed, after a short milling of 2 min under cryogenic conditions, the particle size of the milled sample reduced substantially to be even smaller than the sample which was prepared after 4 h ball milling under normal milling conditions (see Figure 1). However, it is interesting to see that the cellulose sample after 2 min cryogenic ball milling has a similar crystalline pattern (see Figure 2) as the raw cellulose. In fact, the relative crystallinity indices of the raw and cryogenic ball-milled samples are similar (see Table 1). Therefore, as shown in Figures 3 and 4, 2 min cryogenic ball milling leads to only a slight increase in conversion as a function of reaction time and the specific reactivity as a function of conversion. Those data clearly demonstrate that particle size plays only a minor role in the reaction of cellulose hydrolysis in HCW under current conditions. As the significant reduction in particle size also leads to a reduction in DP,[9,38,39] the data also clearly suggest that any such reduction in the DP of the cellulose after 2 min cryogenic ball milling plays a minor role in cellulose reactivity during hydrolysis in HCW. Therefore, the cellulose reactivity is dominantly controlled by the cellulose's crystallinity which is an indication of the presence of strong hydrogen bonding networks. It is known that a strong hydrogen bonding network limits the accessibility of the glycosidic bonds (by HCW) in the glucose chains within the crystalline structure.[28] The dominant role of crystallinity in cellulose reactivity in HCW is also clearly supported by the data in Figures 1–4. It can be seen that under normal ball milling conditions, further ball milling from 1 to 7 h leads to little further reduction in particle size but significant increase in the relative crystallinity and hence the specific reactivity of cellulose sample. The minor role of particle size in the conversion and specific reactivity of cellulose during hydrolysis also clearly suggests that a shrinking-core model, which was often used for describing the reaction kinetics of cellulose hydrolysis in subcritical and supercritical water,[23] is not applicable for modeling the overall hydrolysis reaction kinetics under conditions in this study.

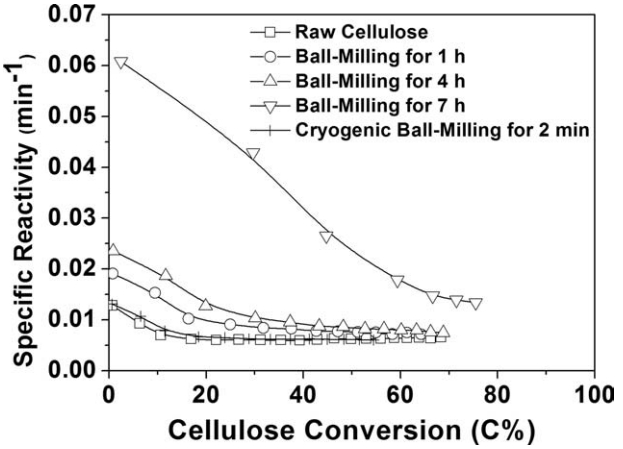

Figure 4. Specific reactivities of various cellulose samples during hydrolysis in HCW at 230°C.

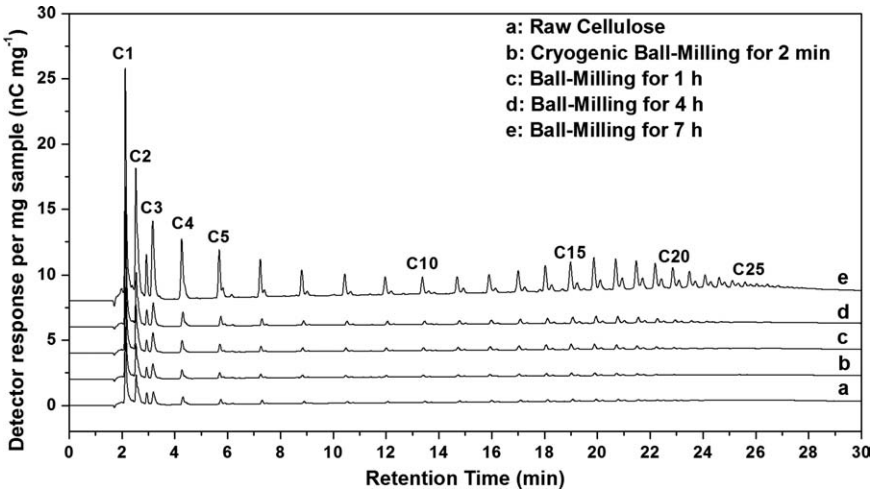

Figure 5. IC chromatograms of primary liquid products from various cellulose samples at 30% conversion during hydrolysis in HCW at 230°C.

Comparisons between the primary liquid products produced from the raw and ball-milled cellulose during hydrolysis in HCW

To further understand the effect of structure change during ball milling on the formation of glucose oligomers during cellulose hydrolysis in HCW, the primary liquid products were collected from the hydrolysis of the raw and ball-milled cellulose samples at the same conversion level. The fresh liquid samples were analyzed by HPAEC-PAD immediately after collection, following the methodology described elsewhere.[27] First of all, the primary liquid products between the raw cellulose and the cryogenic ball-milled sample were compared to understand the effect of particle size on the primary hydrolysis reactions occurred on the surface of cellulose. As shown in Figure 5, the IC chromatograms of primary liquid products collected at 30% conversion from the two samples are very similar and the maximal DP of glucose oligomers in the primary liquid products are also same (20 for both samples). This is expected because the cryogenic ball milling has little effect on the crystallinity (i.e., the hydrogen bonding networks hence the accessibility of glycosidic bonds in the glucose chains) of the microcrystalline cellulose. However, for the samples prepared after prolonged ball milling under normal milling conditions (see Figure 5), there are significant differences in the IC chromatograms of the primary liquid products. The maximal DP of glucose oligomers in the primary liquid products increases substantially with ball milling time, from 20 for the raw sample to 22 for the ball-milled 4 h sample, then to 28 for the ball-milled 7 h sample. The data in Figure 5 are further evidence suggesting that the hydrogen bonds in crystalline glucose chains were substantially weakened and/or broken during the prolonged ball milling under normal conditions. As results, the cellulose becomes more amorphous and the glucose chains are therefore more accessible by HCW during hydrolysis under the same condition, leading to an increase in the maximal DP of glucose oligomers in the primary liquid products. Figure 5 also shows that the concentration of each glucose oligomer increases with ball milling time. Such an observation is in consistence with the increase in cellulose reactivity (see Figure 4).

To understand the effect of ball milling on the distribution of glucose oligomers in the primary liquid products, further study was then conducted to compare the selectivities of glucose oligomers in the primary products of the raw cellulose and various ball-milled samples, based on a method developed elsewhere.[28] The primary liquid products at three different conversions (15%, 30%, and 60%) were collected. For the 7 h ball-milled sample, only two liquid samples at 30% and 60% conversions were collected because it was difficult to collect the liquid sample at 15% conversion due to the fast reaction rate. The selectivity ratios of glucose oligomers from ball-milled samples and the raw sample are compared in Figure 6.

As shown in Figure 6, a 2 min cryogenic ball milling actually results in some changes in the distribution of glucose oligomers in the primary liquid products, although it leads to only slight changes in the specific reactivity and crystallinity (see Figures 2 and 4). At a low conversion (15%), the glucose oligomers have higher selectivities than those for the raw samples and the selectivity ratios for all the glucose oligomers are larger than 1. This indicates that the overall reactions favor more the production of various glucose oligomers via hydrolysis rather than the production of the sugar derivatives via degradation reactions. This is an interesting observation as it points to a way to use cryogenic milling to improve the selectivity of sugar products during hydrolysis. As discussed, the cellulose reactivity is dominantly controlled by the cellulose's crystallinity. The raw and cryogenic ball-milled samples have similar crystallinity, i.e., similar accessibility of glycosidic bonds of the glucose chains. It is known that the significant reduction in particle size also leads to a reduction in DP.[9,38,39] Although the crystallinity is similar in comparison with the cryogenic ball-milled sample, the glucose chains exposing on the surface of the reacting raw cellulose is longer, leading to increased possibilities for degradation reactions therefore more sugar derivatives being produced in the primary liquid products.

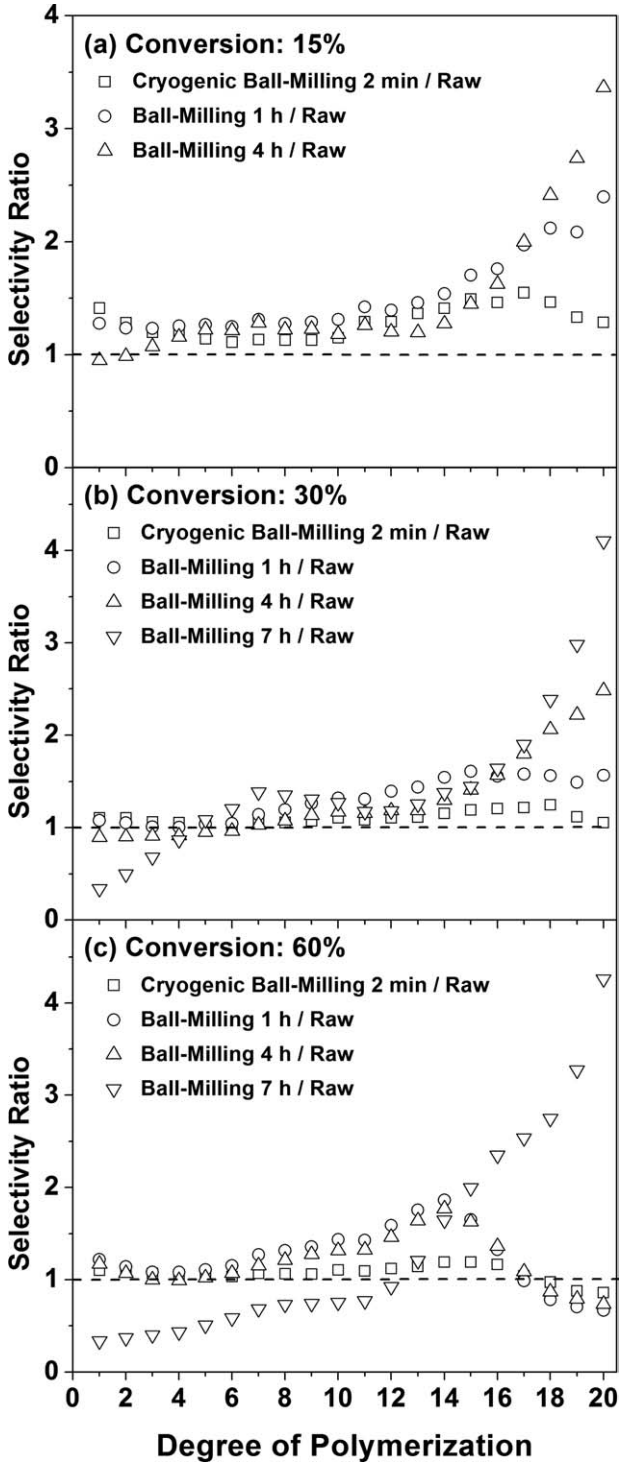

Figure 6. Selectivity ratios of glucose oligomers in the primary liquid products from various cellulose samples during hydrolysis in HCW at 230°C.

(a) At conversion of 15%; (b) at conversion of 30%; and (c) at conversion of 60%.

At higher conversions (30% and 60%), the selectivities of the glucose oligomers of cryogenic ball-milled sample becomes similar to those of the raw cellulose. This is mainly due to the fact that the amorphous portion has been removed so that the crystalline portion dominates the overall hydrolysis reactions. Additionally, it should also be noted that at all three conversions, there is an appreciably decrease in the selectivity ratio with DP of glucose oligomers from 16. This may be due to the significant reduction in particle size and the possible reduction in the length of glucose chains within the crystalline portion of the cellulose sample as results of ball milling, leading to a decrease in the selectivity ratio with DP for high-DP glucose oligomers.

Also illustrated in Figure 6, for the samples after 1 or 4 h ball milling under normal milling conditions, at conversions <60%, the selectivities of most glucose oligomers are higher than those for raw sample and the selectivity ratio of glucose oligomer also generally increases with DP, apparently due to the increased amorphous structures in these ball-milled samples. The relative crystallinity indices of the 1 h and 4 h ball-milled samples are 58% and 38%, respectively (see Table 1). Therefore, at conversions <60%, these samples mainly involve the hydrolysis of the amorphous portions. At 60% conversion, the crystalline portion would start to dominate the hydrolysis reactions for both 1 h and 4 h ball-milled samples. Therefore, a reduction in the selectivity of the high-DP glucose oligomers is shown in Figure 6, due to probably the same reasons as discussed for the cryogenic ball-milled sample.

Figure 6 also shows that for the 7 h ball-milled sample, the selectivity ratio always increases with DP. The selectivity ratios for high-DP glucose oligomers are significantly higher than 1. Table 1 shows that due to prolonged ball milling the sample is completely amorphous and there is no crystalline portion remaining in the sample. Therefore, in comparison with the raw cellulose, the hydrogen bonding networks within the 7 h ball-milled sample would be destroyed considerably and the length of the glucose chains would also be shorter, leading to the production of more high-DP glucose oligomers (see Figure 5). In addition, the short glucose chains would also be more easily and quickly removed during hydrolysis in HCW, reducing the probability of those chains to be further hydrolyzed to produce lower-DP glucose oligomers. This is indeed shown in Figure 6c where the selectivites of those glucose oligomers are actually less than 1 and the effect is more significant at a high conversion (i.e., 60%).

Further discussion on mechanisms of cellulose hydrolysis in HCW

The above data and discussion lead to important knowledge on the mechanisms of cellulose hydrolysis in HCW. First of all, the maximal DP of the glucose oligomers in the primary liquid products is determined by the longest length of glucose chain within the cellulose accessible by HCW. Weakening and destruction of the hydrogen bonding networks by ball milling can significantly increase the accessibility of long glucose chains in microcrystalline cellulose. A related study previously reported that the maximal DP of glucose oligomers in the primary liquid products for the raw sample increases with temperature from 23 at 230°C to 28 at 270°C.[28] However, for the 7 h ball-milled cellulose sample in this study, the maximal DP of glucose oligomers in the primary liquid product is 28 even at 230°C. This further

proves that the increase in the maximal DP with reaction temperature during the hydrolysis of microcrystalline cellulose is indeed due to increased accessibility of longer glucose chains as results of faster breaking of hydrogen bonds at higher temperatures. Second, the distribution of glucose oligomers in the primary liquid products is significantly influenced by the distribution of accessible glucose chains of various lengths. Such distributions are determined by key properties of cellulose, particularly hydrogen bonding pattern, length of chain segments, crystallinity, and DP. Third, the reaction rate of microcrystalline cellulose during hydrolysis in HCW is also determined by the accessibility of chain segments within the microcrystalline cellulose. An increase in reaction temperature can significantly increase the reaction rate as the crystalline cellulose becomes more accessible due to the faster breaking of hydrogen bonds at elevated temperatures. Ball milling also increases the reaction rate as ball milling significantly weakens or even destroys the hydrogen bonding networks within the microcrystalline cellulose. A substantial reduction in particle size, e.g., after 2 min cryogenic ball milling, has only resulted in a minor increase in the reaction rate, because there is little improvement in the overall accessibility of glucose chain segments.

Therefore, the pattern of hydrogen bonding networks within microcrystalline cellulose plays an essential role in the hydrolysis behavior in HCW. There are at least two pretreatment methods which may be used to weaken and/or destroy the hydrogen bonds within microcrystalline cellulose. One is to pretreat the cellulose at high temperatures, which may lead to the crystalline-to-amorphous transformation of cellulose, as reported previously in HCW at $\sim$300°C.[41] The other is to pretreat the cellulose via ball milling. From the viewpoint of maximizing sugar production, a low-temperature pretreatment condition is preferred to minimize the degradation of sugar products. Therefore, ball milling seems to be a good strategy for improving cellulose hydrolysis reactivity although energy consumption during milling should also be considered. Future studies are required to develop the efficient, effective, and cheap pretreatment methods to break the hydrogen bonding networks within microcrystalline cellulose.

Conclusions

This article reports the effect of ball milling as pretreatment on cellulose hydrolysis in HCW. Cellulose samples after ball milling under normal conditions exhibit a significant decrease in particle size and crystallinity therefore a significant increase in the specific reactivity during hydrolysis in HCW. Cryogenic ball milling for 2 min results in a considerable reduction in the particle size of cellulose but only little change in the crystallinity and hydrolysis reactivity. The data clearly suggest that particle size only plays a minor role in the reactivity of cellulose hydrolysis in HCW and crystallinity is the dominant factor. Ball milling can significantly influence the selectivities and distributions of glucose oligomers in the primary liquid products. It increases the selectivities of glucose oligomers at low conversions while at high conversions, the reduction in chain length starts to play an important role on glucose oligomer formation since cellulose samples become more crystalline. After sufficient long time ball milling, the crystalline cellulose can be completely converted to amorphous cellulose, resulting in a significant increase in the formation of high-DP glucose oligomers during hydrolysis in HCW.

Acknowledgments

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