Decomposition behaviors of various crystalline celluloses as treated by semi-flow hot-compressed water

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Abstract

Various types of crystalline celluloses consisted of group I (Cell I, III_I, IV_I) and group II (Cell II, III_{II}, IV_{II}) prepared from cotton linter were adjusted for their degree of polymerization (DP) as starting materials. These celluloses were, then, treated by semi-flow hot-compressed water (HCW) at 230-270˚C/10MPa/2-15min to study their decomposition behaviors. The treatments performed resulted in the residues of celluloses and water-soluble (WS) portions. Consequently, the crystallinity of the residues was found to remain the same, but the DP was reduced as temperature increased. Additionally, the X-ray diffractometry (XRD) and Fourier transform-infrared (FT-IR) analyses demonstrated that the crystallographic changes were occurred for residues of Cell III_I, IV_I and III_{II}. Despite of these changes, the overall results of the residues showed that group I has higher resistance to be decomposed than group II. As for the WS portions, the yields of the hydrolyzed and degraded products were more in group II as compared with group I, indicating that group II are lesser in resistance for their decomposition by HCW treatment. Both results on the residues and WS portions are in agreement with each other, concluding that the degree of difficulty for decomposition was higher in group I compared with group II. Therefore, the decomposition behaviors of the celluloses are due to the differences in crystalline forms.

Keywords *Cellulose • Cotton linter • Crystalline structure • Hydrolysis • Semi-flow hot-compressed water*

Introduction

Cellulose together with hemicelluloses is often encrusted with lignin in a complex composite known as lignocellulose. Such lignocellulose is not easy to separate and dissolve in almost any solvents, making them resistant to enzymatic hydrolysis (O'Sullivan 1997). Cellulose is a crystalline homopolysaccharide composed of D-glucopyranose linked together by β-1,4-glucosidic bonds. The β-1,4 linkages in cellulose form linear chains that are highly stable and resistant to chemical attack because of the high degree of intra- and inter-molecular hydrogen bondings (Nishiyama et al. 2002).

There are six known polymorphs of celluloses (I, II, III_I, III_{II}, IV_I, and IV_{II}) identified by their characteristic X-ray diffraction (XRD) patterns as well as ^{13}C nuclear magnetic resonance (NMR) spectra. This crystalline structural arrangement of one allomorph can be converted to the other by treating it with chemicals through various processes such as mercerization, hydrothermal processes etc (Isogai 1994).

Cellulose I, known as native cellulose, is abundant in nature and can be further classified into two polymorphs, celluloses I_α and I_β (Atalla et al. 1984; Sugiyama et al. 1991), whose detailed structures have been established through synchrotron X-ray and neutron fiber diffraction studies (Nishiyama et al. 2002; 2003). Cellulose I_α is metastable and converted irreversibly into cellulose I_β by hydrothermal treatment, without losing its crystallinity (Yamamoto et al. 1993; Wada et al. 2004).

Cellulose II can be prepared by two distinct routes: mercerization by alkali treatment and regeneration through solubilization and subsequent recrystallization. It is thermodynamically more stable in structure with an anti-parallel arrangement of the strands and some inter-sheet hydrogen bondings. On the other hand, celluloses III_I and III_{II} can be prepared from celluloses I and II, respectively, by treatment with liquid ammonia or some amines. The swelling of cellulose in liquid ammonia or some amines is a simple and classical way to increase the accessibility of crystalline cellulose (Da Silva Perez et al. 2003), while celluloses IV_I and IV_{II} can be obtained by heating celluloses III_I and III_{II}, respectively, at 260˚C in glycerol (O'Sullivan 1997; Zugenmaier 2008).

Acid/alkali treatment and acid/alkali pretreatment followed by enzymatic hydrolysis are conventional methods to produce glucose from cellulose (Camacho et al. 1996; Karr et al. 2000). The obtained glucose can be used to synthesize various specialty chemicals or fermented to produce bioethanol. However, these treatments are associated with serious economic and environmental constraints due to the heavy use of chemicals (Hsu 1996). Furthermore, cellulose utilization is still seen to be restricted by its resistance against hydrolysis due to the encrusted structure with lignin (Grous et al. 1986; Mes-Hartree et al. 1988).

For the past three decades, hot-compressed water (HCW) treatments have attracted much attention because of their suitability as a non-toxic, environmentally benign, inexpensive medium for lignocellulose hydrolysis without any catalysts (Bobleter et al. 1976; Bobleter et al. 1983; Yu et al. 2010). The HCW treatment system can be categorized into batch-type or flow-type arrangements. Due to significant decomposition reactions occurred in batch-type treatment, flow-type HCW treatment was preferred to hydrolyze and fractionate lignocellulose (Ehara et al. 2002; Lu et al. 2009; Phaiboonsilpa et al. 2010; 2011).

About 4-22% of cellulose decomposed in HCW (200-230˚C/34.5MPa/15min) by using flow-type treatment (Mok et al. 1992). Another configuration of HCW system is a semi-flow HCW treatment. It resulted in the better digestible cellulose (Xiao et al. 2011), greater removal of lignin (Tirtowidjojo et al. 1988), higher

sugar recovery from hemicelluloses (Bobleter et al. 1983) and less inhibitors in the hydrolyzed liquid as compared with the conventional batch and co-current flow systems (Liu et al. 2003). Recently, the two-step semi-flow HCW treatments were used to study the chemical conversion of lignocellulose biomass (Lu et al. 2009; Phaiboonsilpa et al. 2010; 2011) and it revealed that 230˚C/10MPa/15min and 270˚C/10MPa/15min were optimum conditions for decomposition of hemicelluloses and cellulose, respectively.

In this present study, we aimed to evaluate quantitatively decomposition behaviors of various crystalline celluloses as treated by semi-flow HCW. The obtained residues of celluloses and water-soluble (WS) portions after their treatments were, therefore, investigated in order to understand how different crystalline forms of celluloses are decomposed.

Materials and Methods

Preparation of various types of crystalline cellulose samples

Various types of crystalline celluloses were prepared from cotton linter (Buckeye 1AY-500). Cotton linter in its native form is cellulose I (Cell I). Mercerized cellulose with crystalline form of cellulose II (Cell II) was prepared from Cell I by soaking it into 20.0% of aqueous NaOH solution for 24h at ambient temperature, followed by washing thoroughly with water and freeze-drying (Isogai et al. 1998). Samples with the crystalline forms of celluloses III_I (Cell III_I) and III_{II} (Cell III_{II}) were prepared from Cell I and Cell II, respectively, by soaking them in 100% ethylenediamine (EDA) for 24h at ambient temperature, washed with dried methanol and kept under vacuum.

The prepared Cell III_I and Cell III_{II} were further used for the preparation of celluloses IV_I (Cell IV_I) and IV_{II} (Cell IV_{II}). They were firstly soaked in glycerol for 3 days at ambient temperature and then heated in a reaction vessel at 260˚C/0.6MPa for 30 min (Isogai et al. 1989). After cooling down to ambient temperature, the product was washed with water and acetone successively and dried in vacuum. To simplify, the cotton linter (Cell I) was converted into group I (CelI I, III_I and IV_I) and group II (Cell II, III_{II} and IV_{II}) celluloses. The chemical compositions of these celluloses were also analyzed and all the cellulose samples were found to contain similar components of about 99.9wt% glucose and 0.1wt% xylose.

To evaluate decomposition behaviors for various types of crystalline celluloses by semi-flow HCW treatment, cellulose samples with the similar degree of polymerization (DP) are appropriate for their comparison. Consequently, these celluloses were adjusted by trial and error for their DPs by changing the treatment condition mentioned above for converting Cell I to various forms of celluloses.

Determination of the degree of polymerization (DP) and crystallinity of the celluloses

The degree of polymerization (DP) is an important parameter to be considered in order to study the decomposition behaviors. The viscosities of the celluloses were, therefore, measured by using 0.5M cupriethethylenediamine (Cuen) (TAPPI, 1982) in a Cannon Fenske capillary viscometer. The viscosity average DP of the cellulose samples was calculated from the intrinsic viscosity $[\eta]$ according to the Eq. (1) (Sihtola et al. 1963):

$$DP^{0.905} = 0.75[\eta] \qquad \text{Eq. (1)}$$

Apart from the DP, the crystallinity of the celluloses is another essential parameter. The XRD patterns of these celluloses were recorded by X-ray diffractometer Rigaku RINT 2200 equipped with monochrometer. About 20mg of cellulose was placed on the glass sample holder and flattened carefully, then mounted on the sample holder. X-ray diffraction (XRD) was conducted on reflectance modes through a 2θ range between 7.5˚ and 32.5˚ by Cu-K_α radiation (λ=0.1542nm), operated at 40kV and 30mA at ambient temperature.

Gaussian functions were used to deconvulate the XRD patterns of various crystalline celluloses, and the crystallinity was calculated from the ratio of the area of all crystalline peaks with less background to the total area (Park et al. 2010).

The diffraction angles of each XRD pattern and their assignment diffraction planes are summarized based on a newly proposed conventional indexing for various unit cells of cellulose (French 2013). Here, the unit cells were mainly referenced to the orientation along c-axis, whereby various data from literatures and experimental approaches were used, thus some variations may be occurred (Gardiner et al. 1985; Isogai 1994; Langan et al. 2001; Nishiyama et al. 2002; 2003; Wada et al. 2004).

Fourier transform-infrared (FT-IR) analysis of residual celluloses

The FT-IR analysis was carried out for the residues of the celluloses obtained after HCW treatments. The spectra of the dried sample pellets in KBr were recorded using a Shimadzu IR-8000 spectrophotometer. All the spectra were recorded with an accumulation of 64 scans, revolution of 4 cm^{-1}, in a range from 4000 to 400 cm^{-1}.

Treatment of various crystalline celluloses by semi-flow HCW

The prepared celluloses (about 0.4g) as starting materials were treated individually within a 5ml reaction vessel in a semi-flow HCW system at temperatures of 230˚C, 250˚C and 270˚C under 10MPa for 2min to 15min. The semi-flow HCW conversion system and its operational procedures as explained elsewhere were adapted for this study (Lu et al. 2009; Phaiboonsilpa et al. 2010; 2011). Briefly, the ambient distilled water from a water tank was flown through the reaction vessel by a pump in order to pressurize the system at 10MPa controlled by a back-pressure regulator. To raise the temperature, the preheating unit monitored by thermocouples was used to reach at the designated temperature for about 20min under 10MPa. In addition, another heating unit was installed at the reaction vessel to maintain the designated temperature in the reaction vessel, into which the HCW was passed through at the flow-rate of 10ml/min.

These treatments yielded residues of celluloses and WS portions. After the HCW passing through reaction vessel, the WS portions were cooled down immediately by the cooling system to terminate all reactions. The WS portions collected every 5min were allowed to settle in ambient temperature and pressure for a minimum of 12h, before filtering them by 0.45μm membranes prior to subsequent analysis. The residues of celluloses left in the reaction vessel were, on the other hand, collected, dried unless otherwise mentioned and evaluated for its DP and crystallinity, again (Ehara et al. 2002; Kumar et al. 2010). The experimental process for the study is illustrated in Fig. 1.

The WS portions were, then, characterized and analyzed by using high-performance anion-exchange chromatography (HPAEC), high-performance liquid chromatography (HPLC) and capillary electrophoresis (CE) as described previously (Lu et al. 2009; Phaiboonsilpa et al. 2010; 2011). The product percentages, presented on oven-dried weight basis of the initial material, are based on the chromatogram peak areas of the HPAEC, HPLC and CE.

Results and Discussion

To evaluate decomposition behaviors for various types of crystalline celluloses by semi-flow HCW treatment, the celluloses must be the same in their DPs as the starting materials. Therefore, as shown in Table 1, the DP of those celluloses was adjusted by trial and error to be similar. Thus, they can be directly compared as they are decomposed. The XRD patterns of these starting celluloses are shown in Fig. 2. The diffraction angles of each XRD pattern and their assignment diffraction planes are summarized in Table 2. For the celluloses in Table 1 and Fig. 2, the semi-flow HCW treatments were carried out at temperatures of 230˚C, 250˚C and 270˚C under 10MPa for 2 min to 15min (230-270˚C/10MPa/2-15min).

Evaluation of the residues of celluloses

The XRD patterns recorded for the residues of celluloses in group I and group II after XRD analysis are shown in Figs. 3 and 4, respectively. In Fig. 3, the XRD patterns of the residues from Cell I are observed to remain the same as in the starting Cell I, in contrast with the XRD patterns of residues from Cell III_I and Cell IV_I. Two equatorial reflections of Cell III_I at $2\theta \approx 11.7$ and 20.8˚ indexed as 010 and $1\bar{1}0$, respectively, can be observed at the starting of Cell III_I. After the HCW treatments at 230-270˚C/10MPa/15min, the peak at $2\theta \approx 11.7$˚, for all residues from Cell III_I was totally disappeared, whereas a peak at $2\theta \approx 20.8$˚ was noticeably becoming smaller at elevated temperatures. In addition, the XRD peaks at $2\theta \approx 14.4$, 16.3 and 22.5˚ were intensively appeared. These peaks were similar to those of Cell I, indexed as $\bar{1}10$, 110 and 200, respectively. Here, therefore, all residues from Cell III_I were observed to be totally converted to Cell I. A similar result is reported for Cell III_I treated in ethylenediamine (EDA) to be reversed and converted into Cell I by treatment in warm water, whereas Cell III_I treated with liquid ammonia (140˚C,12kPa) was found to be stable to boiling water for a few hours (Sueoka et al. 1973; Roche et al. 1981; Yatsu et al. 1986; Wada 2001; Wada et al. 2008).

Whereas for Cell IV_I, the peak at $2\theta \approx 15.4$˚ (indexed as $1\bar{1}0$) was shown to emerge into two peaks as it was treated in the elevated temperatures. Although the changes were not seen for residue from Cell IV_I at 230˚C, this corresponding peak started to be transformed at 250˚C and 270˚C, which was found to be corresponded to that of Cell I; indexed as $\bar{1}10$ and 110.

As for the residues from group II shown in Fig. 4, the XRD patterns of residues from Cell II and Cell IV_{II} remained the same. In contrast, the residues from Cell III_{II} were observed to be transformed to other crystalline form. The peak at $2\theta \approx 12.1$˚ (indexed as 010) for all residues from Cell III_{II} was shown to have no changes compared with the control Cell III_{II}. However, a peak at $2\theta \approx 20.4$˚ was completely emerged into two peaks at $2\theta \approx 19.7$ and 22.0˚, as can be seen with residues from Cell III_{II}. These peaks corresponded, respectively, to crystalline peaks at 110 and 020 of Cell II. Moreover, a small peak at $2\theta \approx 15.1$˚ was noticed and became more prominent at 270˚C, which also matched up with crystalline peak of Cell IV_{II} that indexed as $1\bar{1}0$.

Thus, these outcomes of residues from Cell III_{II} after HCW treatments comprised a mixture of Cell II and Cell IV_{II}.

All XRD patterns on residues from celluloses in Figs. 3 and 4 were recorded and compared for the dried residual samples. Therefore, they were also examined under the wet conditions by X-ray diffractometry for the residues from celluloses of Cell III_I, Cell IV_I and Cell III_{II}. Figure 5 shows the obtained XRD patterns of residues from Cell III_I as treated by semi-flow HCW at lower temperature (230˚C/10MPa/2-15min). It seems apparent that Cell III_I has started to be converted to Cell I at an early stage of the HCW treatment. The peaks for $1\bar{1}0$ of Cell III_I were disappearing even after 2 min treatment. Similar observations were recorded for Cell III_I treated at the higher temperature (250-270˚C/10MPa/2-10min). In the same way, the wet residues of celluloses were also examined and found that they had already been converted as well.

The same was performed for Cell IV_I and Cell III_{II}, at 230-270˚C/10MPa/2-10min and they were found to behave in a similar manner. Cell IV_I has started to be converted to Cell I at 10 min treatments under 250-270˚C/10MPa, whereas for Cell III_{II}, the conversion has occurred even at 2 min treatment under 230˚C/10MPa to Cell II mainly and to Cell IV_{II} to some extent. All these results showed that they have already been converted at the early stage of the HCW treatment at 230-270˚C/10MPa. Since Cell III_{II} was observed to be converted to Cell II and Cell IV_{II}, further treatments for Cell II were also performed at 270˚C/10MPa/2-10min in order to check whether it would be converted to Cell IV_{II}. However, no significant crystallographic changes was observed, thus it remained as Cell II at 270˚C/10MPa/2-10min.

In relation to the residues from Cell III_I, Cell IV_I and Cell III_{II} in Figs. 3-5, the FT-IR measurements were performed to compare with the XRD results. For the FT-IR spectra, they were focused only on the OH stretching regions before and after the HCW treatments as shown in Fig. 6. The extensively discussed bands in literatures at 3,480, 3,300 and 3150 cm^{-1} were found in the spectra of Cell III_I, whereas the residues of celluloses were found to be similar as those of halocynthia and ramie which are Cell I (Cell I_β type) (Wada, 2001; Kokot et al. 2002; Zugenmaier, 2008). The bands at 3,720 cm^{-1} was clearly observed showing that Cell III_I has been converted to Cell I.

In contrast, neither Cell IV_I nor Cell III_{II} was regularly discussed in literatures. The residues from Cell IV_I that consisted of a mixture of Cell I and Cell IV_I, usually has higher proportion of Cell IV_I (Marrinan et al. 1956; Zugenmaier, 2008). Despite the presence of a high proportion of Cell IV_I, there seems to be no distinctive absorption which could be attributed to Cell IV_I. It is, therefore, assumed that the spectra of the residues from Cell IV_I resemble that from Cell I.

The Cell III_{II} spectrum has close resemblance with that of Cell II as suggested by Marrinan et al. (1956) that the distance of the hydrogen bonding must be very similar in the two forms. Similarly, the general appearance of Cell IV_{II} spectrum resembles that of Cell II. The FT-IR spectra of the residues from Cell III_{II} at 230-270˚C agreed with the corresponding XRD patterns in Fig. 4 that consisted of a mixture of Cell II and Cell IV_{II}.

All the observations above showed that the interconversion of various crystalline celluloses of Cell III_I, Cell IV_I and Cell III_{II} has occurred at either early or later stage of the HCW treatments. From these results, a possible interconversion for the preparation process and transformation of celluloses by HCW treatments can be summarized as in Fig. 7.

In spite of the crystallographic changes occurred for the residues from Cell III_I, IV_I and III_{II}, the changes in crystallinity and DP for residues of celluloses after HCW treatments were demonstrated in Fig. 8. The crystallinity for residues from Cell III_I, IV_I and III_{II} was evaluated from the obtained XRD patterns as treated by the corresponding temperatures. The overall results were found out to be increased slightly and remained almost constant approximately at 90%. The slight increase could be due to the combined effects of an aqueous environment that removed the paracrystalline portions of celluloses during hydrolysis (Weimer et al. 1995) and annealing that could take place on the cellulose at temperature between 220˚C and 280˚C (Yamamoto et al. 1993). This observation was also in agreement with previous studies, that even at a severe treatment temperature 270˚C, the crystallinity was observed to remain almost unchanged (Sasaki et al. 2004; Jollet et al. 2009; Kumar et al. 2010, Tolonen et al. 2011). One study emphasized that (i) crystallinity and (ii) changes in the crystalline form of a cellulose; as the two of the main determining factors efficacy of hydrolysis of biomass (Cetinkol et al. 2010). However, it is generally thought that drying could lead to the formation of new hydrogen bonds and recrystallization, which would increase the crystallinity rather than reducing it (Tolonen et al. 2011).

Contrary to the crystallinity results, the DP for all residues of celluloses was seen to decrease slightly with increase in temperature (Tolonen et al. 2011). The expectation that the lower DP celluloses such as Cell IV_{II} would be easier to decompose due to their shorter average lengths of molecules, however, was not observed in Fig. 8. The DP was decreased and leveling off to about 70 even after the treatment at 270˚C/10MPa/15min. The present interpretations suggested that the crystalline structure of various types of celluloses were still rigid, but only broken down into shorter-chain of cellulose molecules. As temperature increases, the DP decreases which would raise the solubility of cellulose in water and conversion of cellulose to the hydrolyzed and degraded products (Sasaki et al. 2004; Yu et al. 2009). In Fig. 8, the DP of group I celluloses was observed to be generally higher than that of group II. This shows that group II is easier to be decomposed as compared with group I. Also, based on visual examination, the fibers as the starting materials have been changed into powder-liked residues after the HCW treatment.

Figure 9 illustrates the relationship of DP and residues of celluloses after HCW treatments. Both are seen to decrease as the treatment temperatures were increased. It has also been reported in previous studies that the DP of residues gradually decreased with increasing cellulose decomposition (Sasaki et al. 2004; Tolonen et al. 2011).

The overall yield of the residues after semi-flow HCW treatment for various types of celluloses is shown in Fig. 10. These residues notably decreased with the increase in temperatures. The residues of various types of celluloses obtained particularly at treatment condition of 230˚C/10MPa/15min were still quite high in yield, in the range of 70-90wt%. This is agreeable as the condition was known not to hydrolyze the crystalline cellulose in wood (Lu et al. 2009; Phaiboonsilpa et al. 2010; 2011).

Since in the present study, the starting DP was adjusted to be the same for all celluloses, a direct comparison can be made for decomposition behaviors of celluloses. As DP in the residues of celluloses is a function of cellulose decomposition, the observed changes on residues were only due to the different crystalline structures of celluloses as starting materials. The various crystalline celluloses prepared as the starting materials have assisted the decomposition process in HCW treatments even though the interconversion of some celluloses have occurred.

Cell I yielded the highest residue among various types of celluloses used in this study followed by Cell III_I and IV_I, as in Fig. 10. At 230 and 250˚C, both Cell III_I and IV_I behaved very similarly, however, Cell IV_I was decomposed more at 270˚C as compared with Cell III_I. This trend was later followed by Cell II, III_{II} and IV_{II}. Both Cell III_{II} and IV_{II} behaved in a similar way, nevertheless, Cell IV_{II} was decomposed more at 270˚C as compared with Cell III_{II}. Cell II was observed to have no residues left at 270˚C. Therefore, no crystallinity and DP values were recorded in Fig.8.

As a conclusion, Cell I in native crystalline form was found to be the most resistant against decomposition, while Cell II, III_{II} and IV_{II} were decomposed the most as compared with the other types of celluloses such as Cell III_I and IV_I. This could be an indication of the easiness for decomposition of the various crystalline cellulose samples and it seemed likely that group I celluloses (Cell I, III_I and IV_I) had higher resistance to be decomposed as compared with group II celluloses (Cell II, III_{II} and IV_{II}).

Evaluation of the water-soluble (WS) portions

For the temperature ranges under high pressure, ionic products of water increases, thus, hydrolysis reaction would be proceeded without any catalysts (Franck 1987; Dinjus et al. 2004; Kruse et al. 2007; Lu et al. 2009, Phaiboonsilpa et al. 2010). If such a reaction is prolonged, hydrolyzed products would be degraded due to high temperature treatment. A reaction scheme showing how cellulose I is decomposed as treated by semi-flow HCW is shown in Fig. 11 (Phaiboonsilpa et al. 2010). The products resulted from cellulose decomposition in the treatment can be categorized into hydrolyzed and degraded products.

Under these treatment conditions, the glucosidic lingkages of cellulose are cleaved and cellulose starts to be hydrolyzed into cello-oligosaccharides, subsequently, hydrolyzed to monosaccharide such as glucose (Antal et al. 1990a; Ehara et al. 2002; Kruse et al. 2003; Phaiboonsilpa et al. 2010). Fructose and mannose are also obtained during the process as a result of isomerization of glucose. Monosaccharides are unstable at high temperature and thus some parts of them are further converted into their degraded products such as furfural, 5-hydroxymethyl furfural (5HMF), levoglucosan through dehydration, and erythrose, glycolaldehyde, methylglyoxal through fragmentation (Antal et al. 1990b). A prolonged treatment allows further degradation to take place, generating other products such as organic acids. It is important to know the decomposition pathway of cellulose as the degraded products could inhibit the fermentation process for ethanol production (Palmqvist et al. 2000). The WS portions for various crystalline celluloses obtained from each treatment were found to follow similar decomposition pathway as in Fig. 11.

To observe the decomposition behavior of various crystalline celluloses, the yields of the hydrolyzed and degraded products were investigated. However, the latter is a result of the degradation of the former. Thus, the total yields reflect the easiness of the hydrolysis decomposition behavior. Figure 12 shows one example of the results on such yields. It can be seen that for both groups, more than 50wt% of the products consisted of hydrolyzed products and that higher portion of them are obtained as compared with degraded products. According to Fig.11, the hydrolyzed yields produced were still at the upper paths of cellulose decomposition pathway. This could be an indication that the cellulose samples have resistance against decomposition. From Fig. 12, it is apparent that the group II is easier than group I for hydrolysis reactions. These results from WS portions are in good agreement with those from residues of celluloses.

Concluding Remarks

The decomposition behaviors on various types of crystalline celluloses were investigated at 230-270˚C/10MPa/2-15min. To compare directly the effect of the treatment, the DP of the celluloses was adjusted by trial and error to be similar prior to the treatment. Based on the results of the residues, crystallographic changes were found to be occurred during the HCW treatment for Cell III_I, Cell IV_I and Cell III_{II}. In general, group I celluloses (Cell I, III_I, Cell IV_I) have been converted to Cell I and group II (Cell II, III_{II}, IV_{II}) to Cell II. Despite of these changes, the overall results of residues showed that group I has higher resistance to be decomposed than group II. In the meantime, for the WS portions, celluloses in group II were decomposed more to be the hydrolyzed and degraded products as compared with those in group I. The results on the WS portion revealed that the degree of difficulty for decomposition is greater in group I than group II. Based on these findings, it can be concluded that group I has more resistance to be decomposed than group II.

Based on the obtained results, it was clear that the decomposition behaviors were due to their different crystalline forms of celluloses. For that reason, it is recommended to transform one type crystalline allomorph of cellulose to the other for a better hydrolysis reaction. All these data are, therefore, useful in order to understand the behaviors of different types of crystalline celluloses that provide information for efficient use of lignocellulose.

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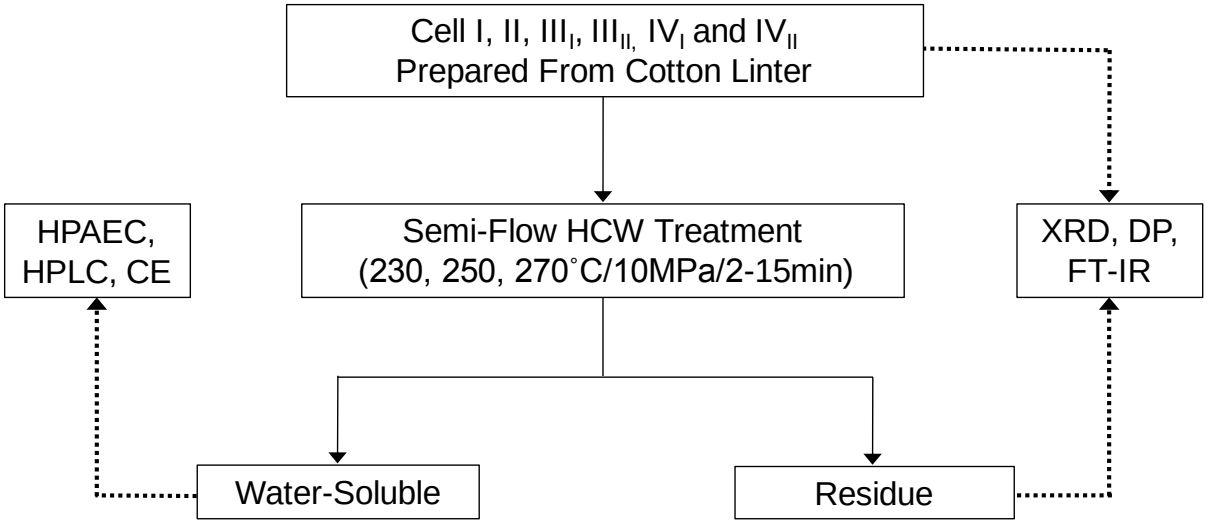
Fig.12 The yields on the water-soluble portions from various types of crystalline celluloses as treated by semi-flow HCW at 270˚C/10MPa/15min.



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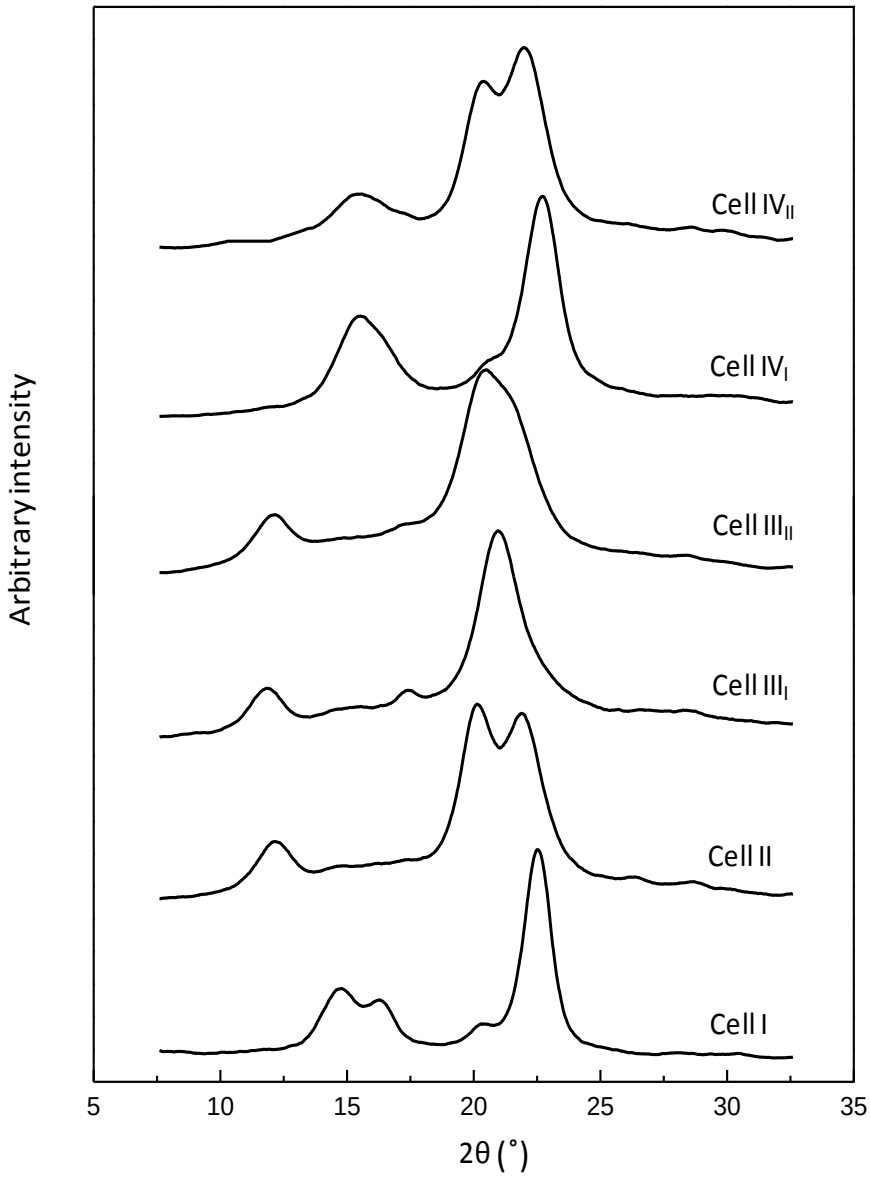


Fig.2 The XRD patterns for various types of crystalline celluloses prepared in this study

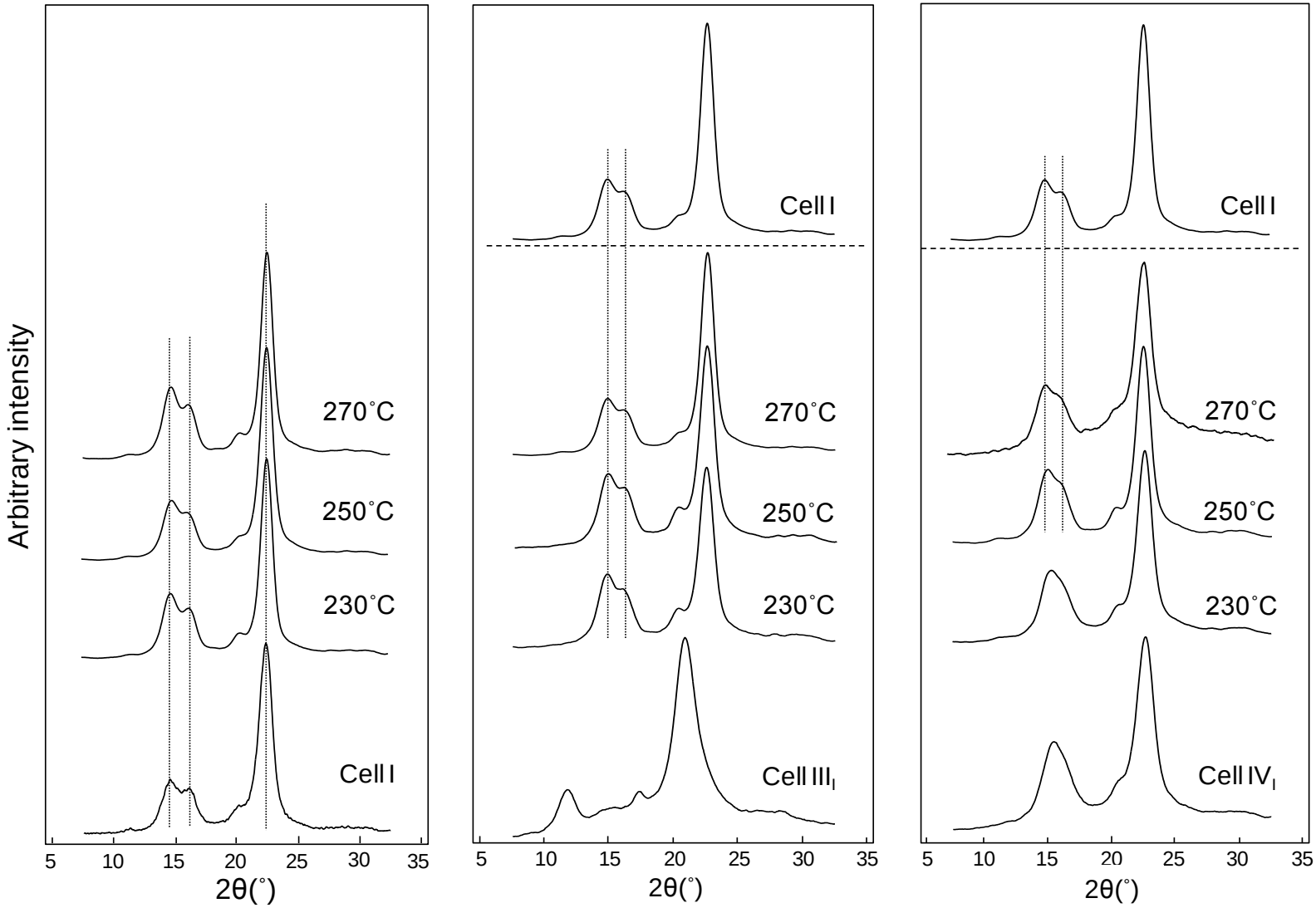


Fig. 3 The XRD patterns for the residues from Cell I, Cell III_I and Cell IV_I (from left to right) as treated by semi-flow HCW at 230-270˚C/10MPa/15min

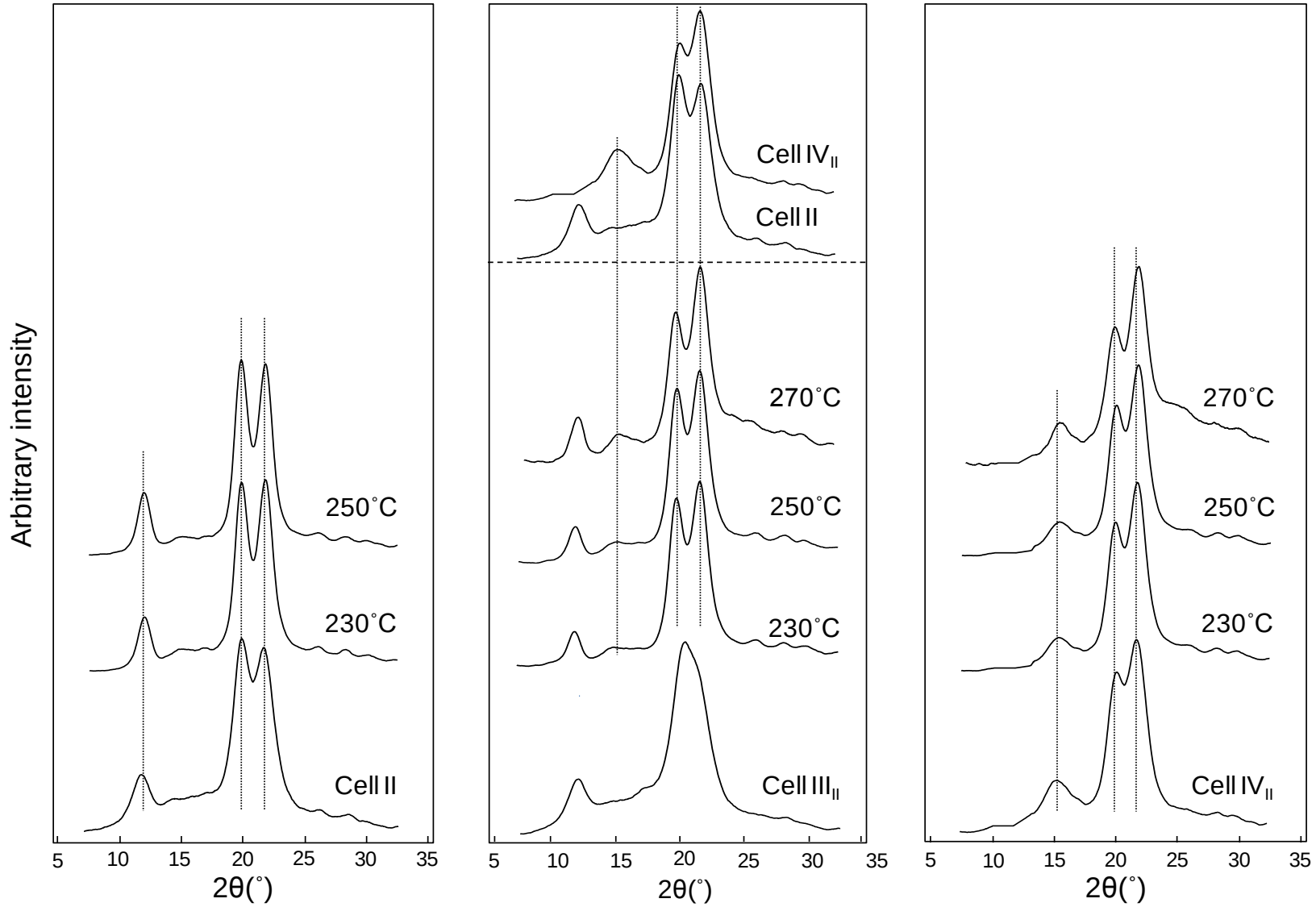


Fig. 4 The XRD patterns for the residues from Cell II, Cell III_{II} and Cell IV_{II} (from left to right) as treated by semi-flow HCW at 230-270˚C/10MPa/15min

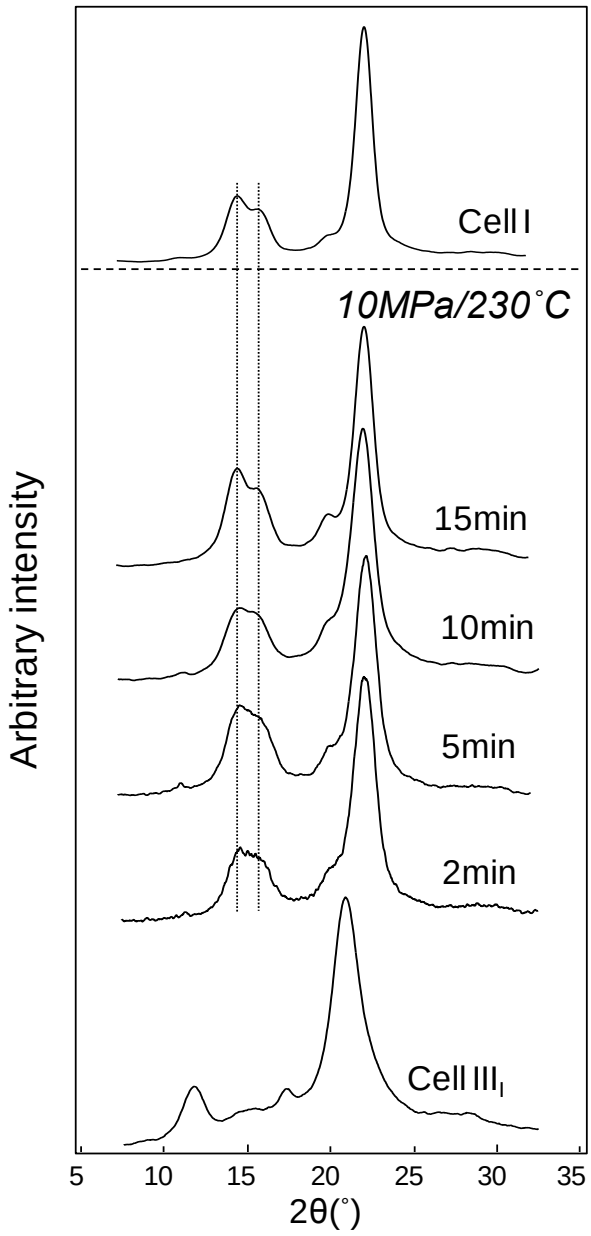


Fig. 5 The XRD patterns for the residues from Cell III_I as treated by semi-flow HCW at 230˚C/10MPa for different treatment times

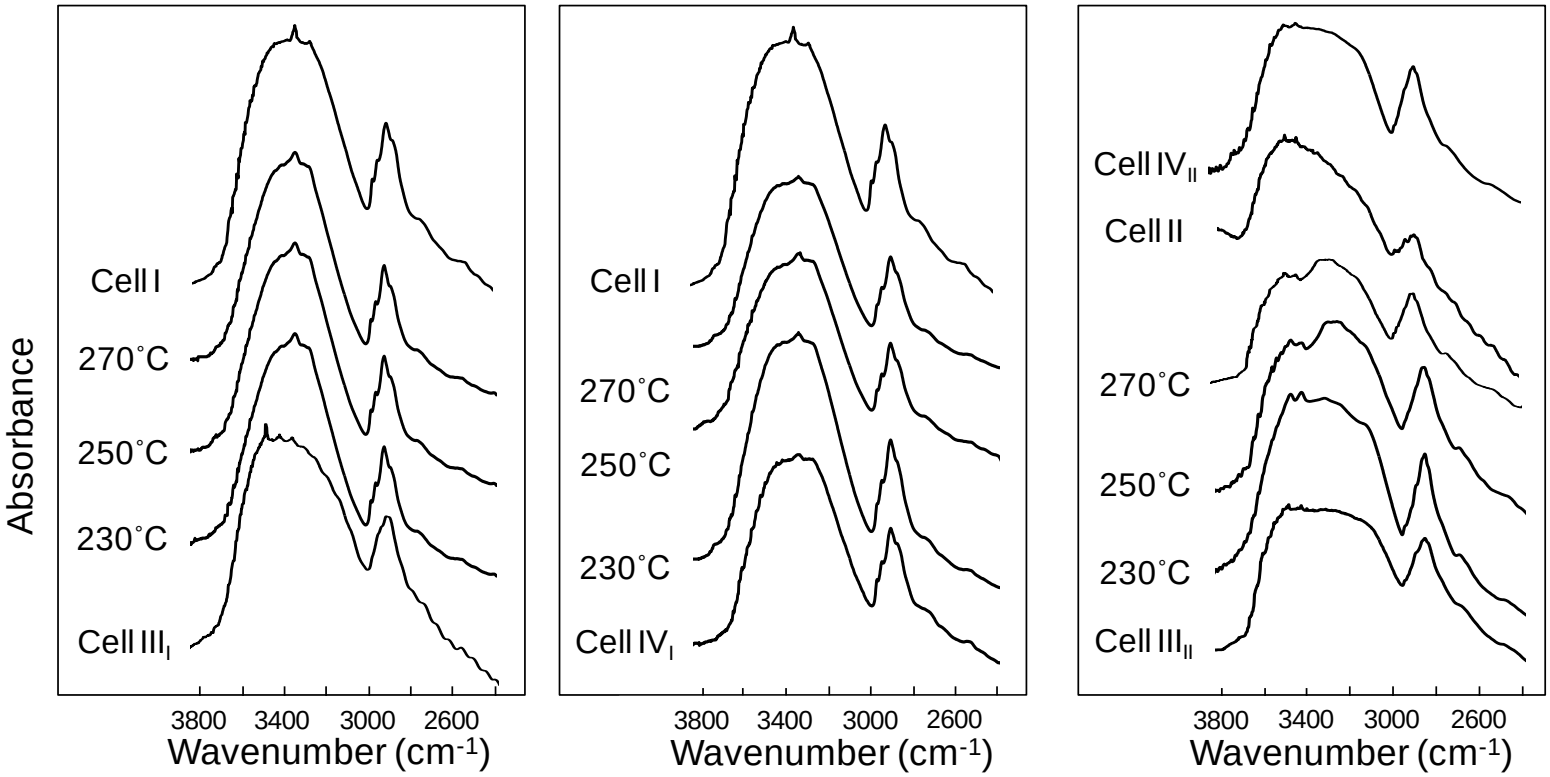


Fig. 6 The FT-IR spectra for the residues from Cell III_I, Cell IV_I and Cell III_{II} (from left to right) as treated by semi-flow HCW at 230-270˚C/10MPa/15min

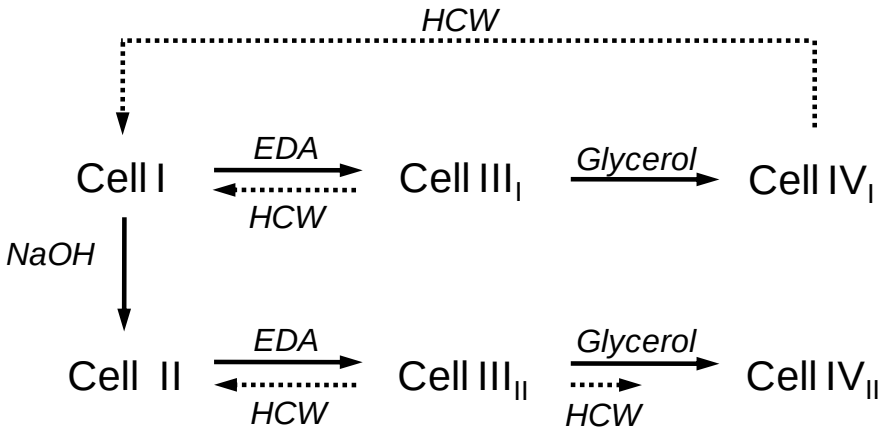


Fig. 7 The possible interconversion pathways for various types of crystalline celluloses

Solid line: Preparation process; Dotted line: Transformation by HCW

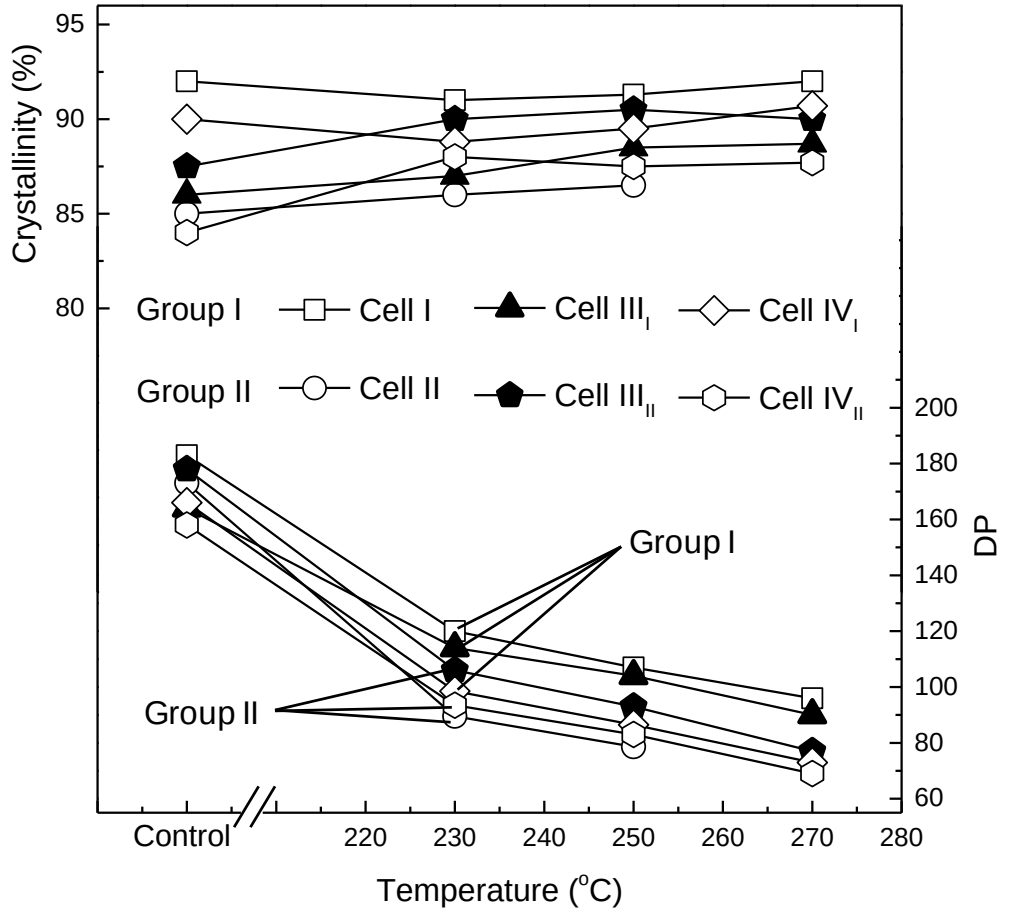
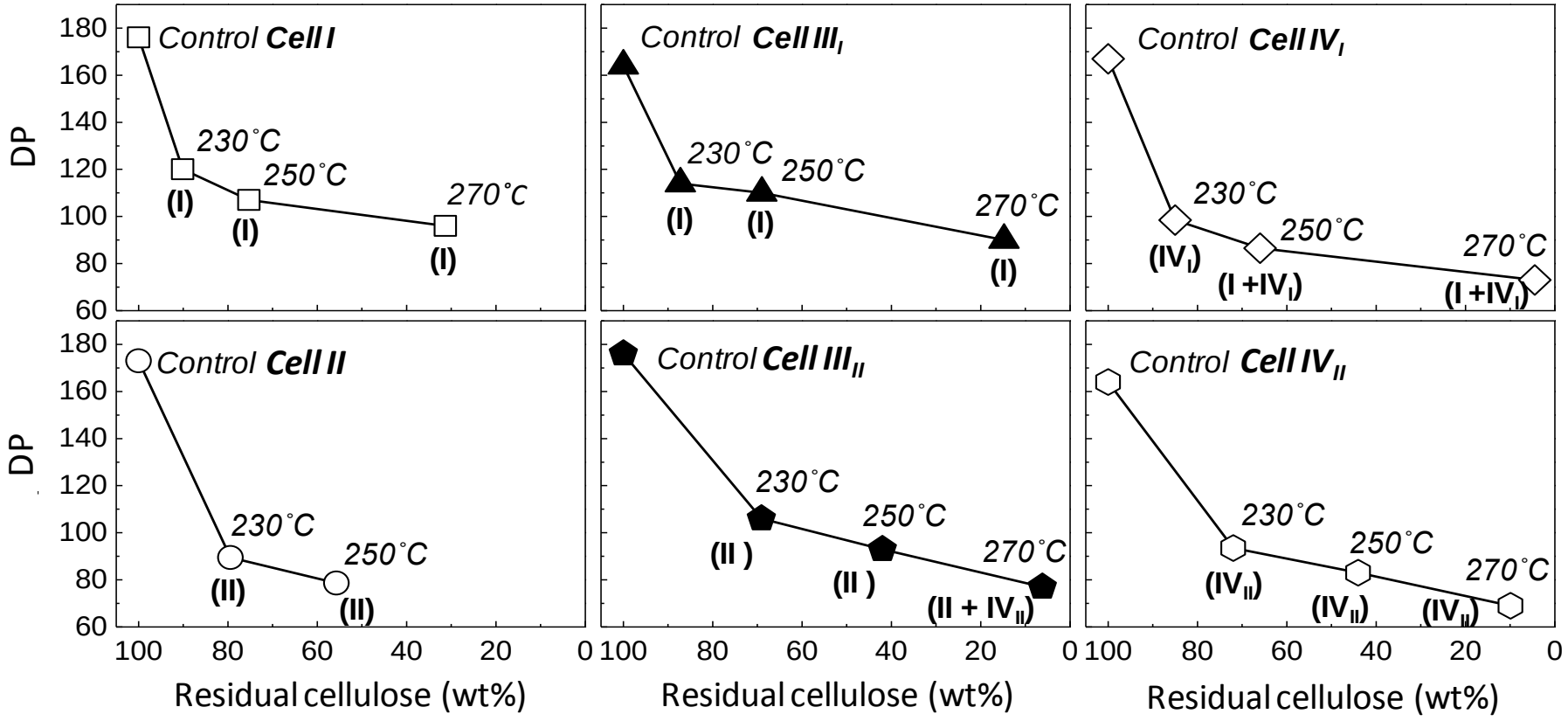


Fig. 8 The changes on crystallinity and DP for the residues from various crystalline celluloses as treated at different temperatures under 10MPa for 15 min (230-270˚C/10MPa/15min) by semi-flow HCW



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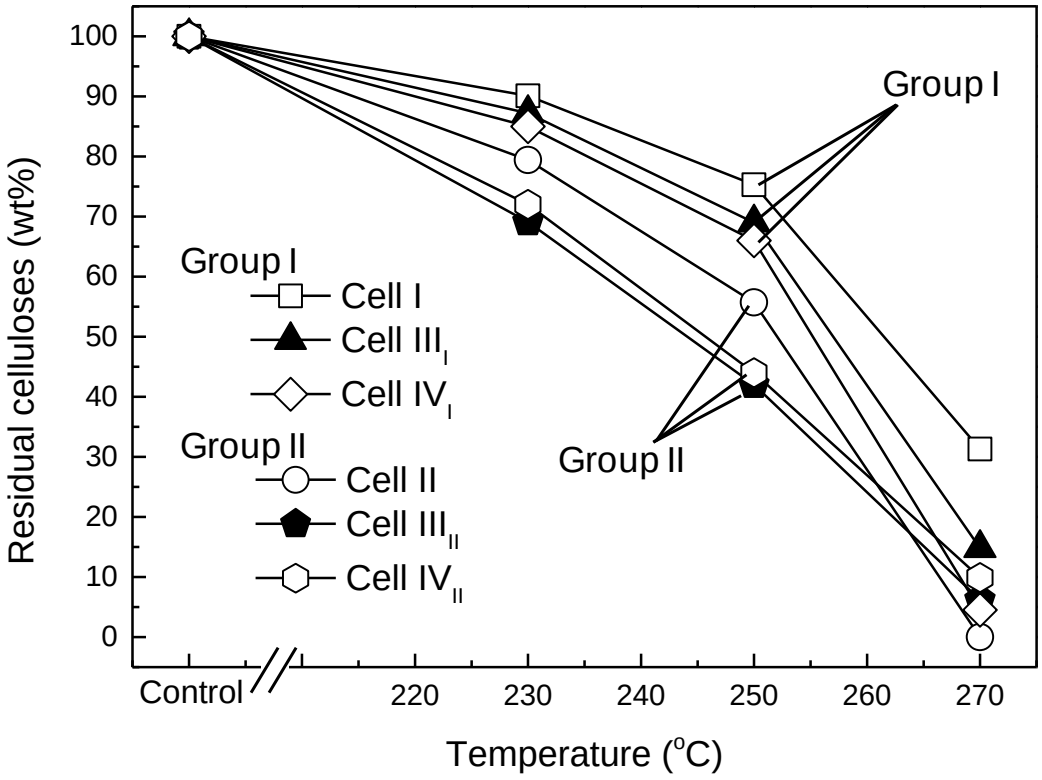
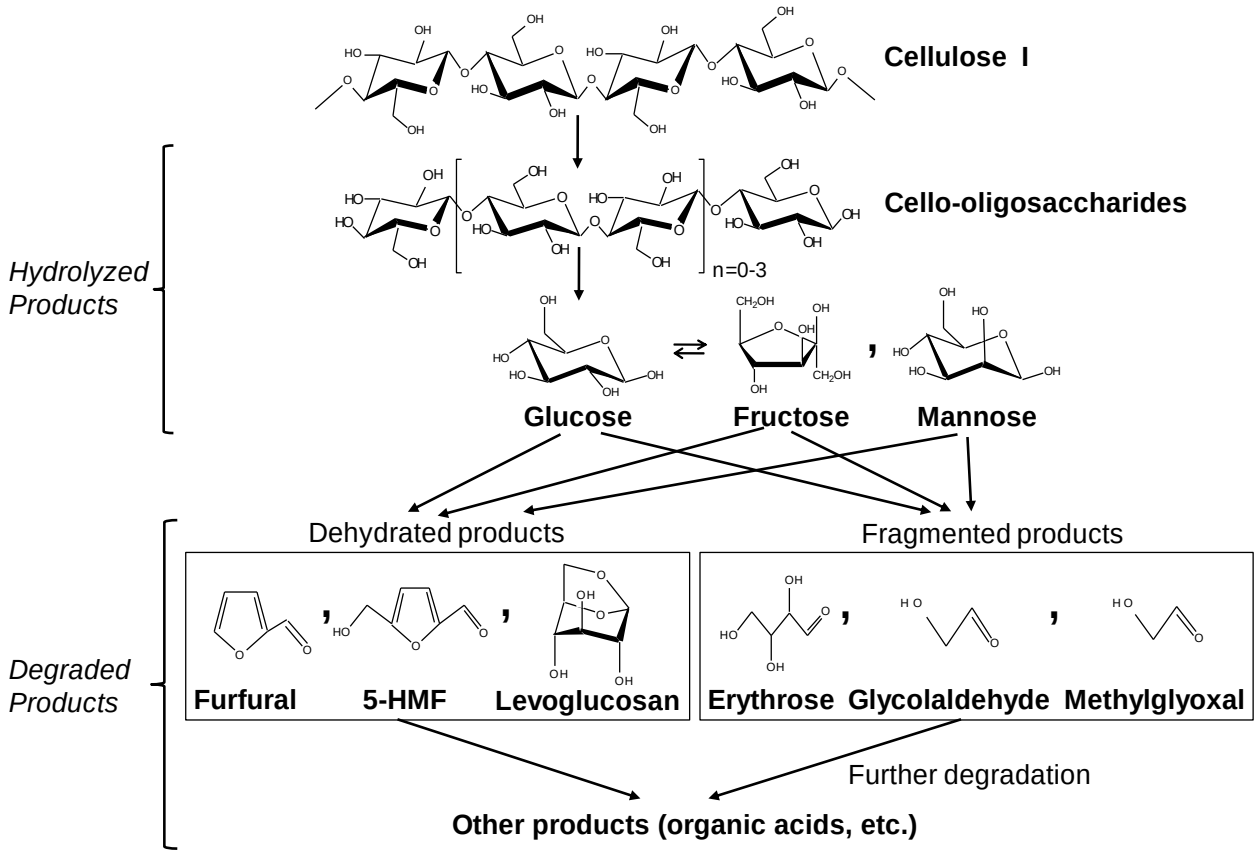


Fig. 10 The changes on the residues from various types of crystalline celluloses as treated at different temperatures under 10MPa for 15min (230-270˚C/10MPa/15min) by semi-flow HCW



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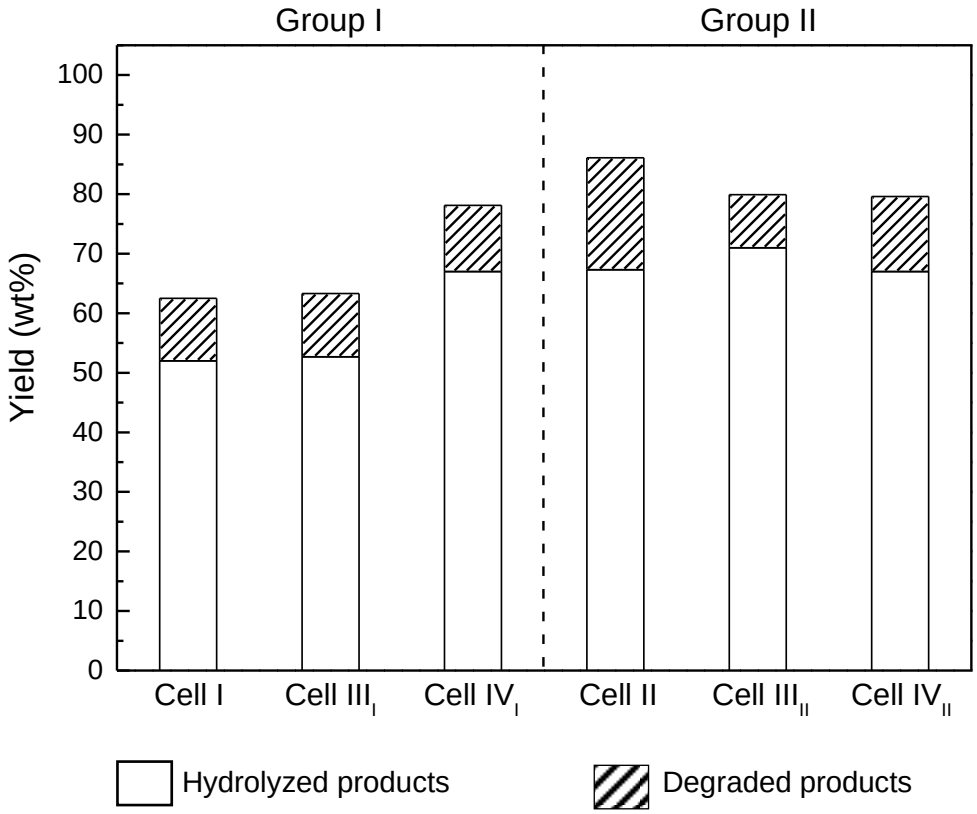

Fig. 12 The yields on the water-soluble portions from various types of crystalline celluloses as treated by semi-flow HCW at 270˚C/10MPa/15min.

Table 1 The DP and crystallinity for various types of crystalline celluloses prepared in this study

Cell	DP	Crystallinity (%)
I	176	92
II	173	85
III_I	164	86
III_{II}	176	87
IV_I	167	90
IV_{II}	164	85

Table 2 The diffraction planes and angles in XRD patterns of various crystalline celluloses

Cell	Diffraction planes / Diffraction angles, 2θ (˚)		
I	$\bar{1}10$ / 14.4	110 / 16.3	200 / 22.5
II	$\bar{1}10$ / 12.1	110 / 19.7	020 / 22.0
III_I	010 / 11.7	100 / 20.8	$1\bar{1}0$ / 20.8
III_{II}	010 / 12.1	100 / 20.4	$1\bar{1}0$ / 20.4
IV_I	$1\bar{1}0$ / 15.4	020 / 21.8	200 / 22.2
IV_{II}	$1\bar{1}0$ / 15.1	012 / 20.6	200 / 22.5

I, II and III_I according to French (2013)