Title:

Thermal glycosylation and degradation reactions occurring at reducing ends of cellulose in low temperature pyrolysis

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Abstract:

Thermal glycosylation and degradation reactions of cellulose (Avicel PH-101) were studied with or without alcohols (glycerol, mannitol, 1,2,6-hexanetriol, 3-phenoxy-1,2-propanediol and 1-tetradecanol) in N_2 at 60-280°C. The results with glycerol (heating time: 10 min) disclosed that the reducing ends are converted into glycosides with glycerol in the temperature range > 140°C without addition of any catalysts. 140°C was close to the temperature where thermal polymerization (glycosylation) of glucose is reported to start. Although the conversion was only around 20% at 140-180°C, the reactivity jumped up above 200-240°C, where thermal expansion of cellulose crystals is reported to become significant. Finally, all reducing ends were converted into the glycosides at 260°C. Such heterogeneous reactivity would arise from the lower reactivities of the reducing ends in crystalline region due to their lower accessibility for glycerol, although the reactivity in non-crystalline region is similar to that of glucose. As for the influence of chemical structure of alcohol, the glycosylation reactivity was directly related to the OH/C ratio of alcohol. Accessibility of alcohol to the reducing ends may increase with the increasing OH/C ratio. The glycosylated cellulose samples with alcohols were found to be stabilized significantly against pyrolytic coloration. From the results of neat cellulose pyrolysis as compared with those with alcohols, two competitive reactions, i.e. thermal glycosylation and degradation reactions to form dark colored substance, were suggested to occur at the reducing ends, while other glucose-units in cellulose were comparatively stable.

Keywords:

Cellulose; Pyrolysis; Reducing end; Thermal glycosylation; Thermal degradation; Coloration; Crystalline cellulose; Alcohols.

1. Introduction

One end of cellulose chain is a potential aldehyde group, and hence it is called as "reducing end". Some chemical and biochemical reactions are known to start from the reducing end. "Peeling reaction" under alkaline conditions is an example.[1] End-wise degradation proceeds from the reducing end through β-alkoxycarbonyl elimination. Some exo-cellulase-type cellobiohydrase enzymes are reported to release cellobiose from the reducing ends.[2-4]

Pyrolysis of reducing monosaccharides has been studied relating to caramelization of sugar. Thermal glycosylation is an important reaction in this caramelization process. By analyzing the reducing group content and water yield, Cerniani[5] reported that thermal polymerization (glycosylation) of glucose proceeded at 120-160°C in air. Sugisawa and Edo[6] confirmed the glycosidic bond formation by identifying the chemical structures of dimers which were obtained after heating glucose under vacuum conditions at 150°C for 2.5 h without addition of any catalysts. They identified the disaccharides, which include 1,2-, 1,3-, 1,4- and 1,6-linkages with α/β anomers, respectively. Anhydrosugars, i.e., 1,6-anhydro-β-D-glucopyranoside and its furanose isomer, are also reported from glucose at higher pyrolysis temperature and under vacuum conditions.[7,8] Although S_N1[9,10] and S_N2[7,11] mechanisms were proposed for such thermal glycosylation reaction, the mechanism is still controversial.

Formation of furanic compounds such as furfural and 5-hydroxymethylfurfural is another important pyrolysis reaction of reducing monosaccharides. Furanic compounds are believed to be the potential intermediates of colored substances in caramelization.[12] In this reaction, acyclic aldehyde or keto isomers, formed by ring-opening of reducing sugars, are considered to be the important intermediates. Kato[13] reported that yield of furfural is directly related to the reducing group content of sugar [cellulose (3.7%) < cellobiose (7.7%) < glucose (11.7%)] at 250°C. Kato and Komorita isolated 3-deoxy-D-glucosone and 3-deoxy-D-xylosone as intermediates of

furanic compounds from the pyrolyzates of glucose and xylose, respectively, at 220°C.[14] They proposed the formation mechanism of furanic compounds which includes isomerization from aldehyde to 1,2-enediol and successive ring-formation and dehydration. Mechanistic studies conducted by Shafizadeh et. al.[15], Houminer and Patai[16] and Paine et. al.[17] also support the importance of acyclic aldehyde form in furanic compound formation.

Reducing monosaccharides are known to be stabilized in their glycoside derivatives. For example, Shafizadeh[9] compared the thermal reactivity of D-xylose and phenyl-β-D-xylopyranoside with thermogravimetric (TG) analysis. Although weight loss of D-xylose occurred in two stage: 220°C (thermal polymerization) and 330°C (thermal decomposition), phenyl-β-D-xylopyranoside decomposed only in one stage at 300°C where the glycosidic bond is cleaved.

These lines of literature information suggest a hypothesis: the reducing ends of cellulose are more reactive than other glucose-units and also suffer from pyrolysis reactions such as thermal glycosylation, furanic compound formation and coloration. In spite of such potential importance of the reducing end of cellulose, there are only few papers relating to the pyrolytic reactivity of the reducing end. Essig et. al.[10] and Šimkovic et. al.[18] used $NaBH_4$-reduced cellulose samples to study the role of the reducing end on thermal weight loss behavior, and both of them reported that the weight-loss temperature moved slightly up to higher temperature region after the reduction. However, further investigations on thermal glycosylation reactivity and pyrolytic coloration at the reducing end have not been conducted yet.

In this paper, thermal glycosylation and degradation reactions of cellulose (Avicel PH-101) were studied with or without addition of various alcohols in N_2 at 60-280°C. Unlike the high temperature pyrolysis >300°C, at such low pyrolysis temperature, volatilization of cellulose is not effective, and increase in crystallinity[19], reduction in DP (degree of polymerization),[20-22] evolution of CO, CO_2 and H_2O,[21,22] formation of furanic

compound[23,24] and colored substance[19] have been reported. To study the glycosylation reactivity of cellulose reducing ends, we selected the heat treatment conditions with alcohols. Although it is difficult to detect the glycosylation products in neat pyrolysis, formation of glycosides between the reducing ends and alcohols can be evaluated by end-group analysis.

2. Experimental

2.1. Materials

Avicel PH-101 (Asahi Kasei Co. Ltd.) was used as a cellulose sample after oven-drying at 105°C for 24 h. Alcohols with high boiling points (>280°C) used in this experiments are glycerol, mannitol, 1-tetradecanol (from Nacalai Tesque. Co. Ltd), 1,2,6-hexanetriol and 3-phenoxy-1,2-propanediol (from Tokyo Kasei Co.). 3-Phenoxy-1,2-propanediol was purified by column chromatography before use.

2.2. Heat treatment

Heat treatment was conducted with the apparatus shown in Figure 1. Cellulose (100 mg) and alcohol (200 mg) were mixed and placed at the bottom of a Pyrex glass tube reactor (internal diameter: 8.0 mm, thickness: 1.0 mm, length: 300 mm). After the air inside the reactor was replaced with N_2 by using aspirator connecting through a three-way tap, the reactor was inserted into a muffle furnace preheated at 60-280°C through a small hole of the top of the furnace. After heating for 3-120 min, the reactor was taken out and immediately cooled with the flowing air (30 s) and then in cold water (30 s). The treated cellulose samples were washed with 2 ml of water or ethanol (in case of 1-tetradecanol) five times and then freeze dried. Neat cellulose pyrolysis was also conducted without addition of any alcohols.

2.3. Sugar and end-group analysis

Glucose, glucitol and alcohol, which were formed from the heat treated cellulose samples after $NaBH_4$-reduction and subsequent hydrolysis, were determined by GC. Glucose is the product from repeating glucose-units and non-reducing ends, while glucitol and alcohol are from reducing ends and alcohol which is bonded to cellulose, respectively.

Reduction of the reducing ends of cellulose samples was according to the reported method.[25,26] Sodium borohydride (10 mg) was added to the suspension of cellulose sample (50 mg) in 0.1N sodium carbonate buffer (pH 10, 2 ml) and stirred at 80°C for 5 h. The pH of the reaction mixture was adjusted to 4.0 by the addition of aq. 1N HCl to terminate the reaction. After further stirring at 80°C for 30 min, one drop of saturated aq. $NaHCO_3$ solution was added to the suspension for neutralization. The $NaBH_4$-reduced cellulose sample was washed with 2 ml of aq. 0.001N HCl twice, then with 2 ml of water five times and freeze dried. These procedures were repeated twice for completing the reduction. According to the reducing group analysis data (see next section), more than 98 % of the reducing end was indicated to be reduced into glucitol moiety by this method.

To remove alcohol which is not chemically bonded to cellulose, the reduced sample was dissolved once in *N*,*N*-dimethyl acetamide (DMAc) / LiCl system with the following procedure.[27] The reduced sample (20 mg) was dispersed in DMAc (0.6 ml) and stirred at 150°C for 1 h. After cooling to 100°C, LiCl (50 mg) was dissolved into the suspension. This suspension was kept at 80°C for 2 h, at 60°C for 2h and gradually cooled down to room temperature. Resulting transparent viscous liquid was poured into water (50 ml) to regenerate cellulose sample. The obtained transparent gel was freeze dried.

Internal standards, i.e., myo-inositol (10 mg, for glucose) and meso-erythritol (0.10 mg, for glucitol and alcohol) in water (0.1 ml) was added to the cellulose sample

(10 mg) before hydrolysis and dried in a vacuum desiccator. Hydrolysis was conducted as follows. 72wt% aq. H_2SO_4 (0.1 ml) was added to the sample and heated at 30°C for 60 min. The resulting transparent liquid was diluted with water (2.8 ml) and heated in an autoclave at 121°C for 1 h. Sulfuric acid in the hydrolysate was removed with Dionex OnGuard II/A ion exchange cartridge. The hydrolysate (0.1 ml) was dried in a vacuum desiccator and trimethylsilylated with 0.1 ml of silylation reagent (BSTFA: TMCS: Pyridine = 2:1:7) at 60°C for 10 min. The GC analysis was performed on a Shimadzu GC-14B under the chromatographic conditions of column: CBP5-M25-O25, injector temperature: 250°C, detector temperature: 250°C, column temperature: 140→250°C [0→22 min], 250°C [22→25 min], carrier gas: He, flow rate: 1.5 ml/min, detector: FID.

The following indexes (1)~(4) were calculated from the obtained yields of glucose, glucitol and alcohol. Suffix [T] and [U] are used to denote "heat treated" and "untreated" cellulose samples, respectively. The indexes, Glucitol [T]/ Glucitol [U] and Glucose [T]/ Glucose [U], indicate the recovery of reducing end and other glucose-units in cellulose after heat treatment, respectively. The indexes, Alcohol [T]/ Glucitol [U] and Alcohol [T]/ (Alcohol [T] + Glucitol [T]), give some information about the glycoside formation between reducing end and alcohol. If some of the cellulose reducing ends form glycosides with alcohol, both indexes should increase. When hydrolysis and solvolysis with alcohol do not occur during heat treatment with alcohol, both indexes exhibit the same value up to 1.0 (complete conversion of the reducing ends to glycosides). In case of depolymerization proceeding, Alcohol [T]/ Glucitol [U] may exceed 1.0 due to the increasing number of reducing end or its glycoside with alocohol as compared with that of original reducing end.

$$\frac{\text{Glucitol[T]}}{\text{Glucitol[U]}} = \frac{\text{Glucitol from treated sample (mol)}}{\text{Glucitol from unteated sample (mol)}} \quad (1)$$

$$\frac{\text{Glucose[T]}}{\text{Glucose[U]}} = \frac{\text{Glucose from treated sample (mol)}}{\text{Glucose from unteated sample (mol)}} \quad (2)$$

$$\frac{\text{Alcohol[T]}}{\text{Glucitol[U]}} = \frac{\text{Alcohol from treated sample (mol)}}{\text{Glucitol from unteated sample (mol)}} \quad (3)$$

$$\frac{\text{Alcohol[T]}}{\text{Alcohol[T]+Glucitol[T]}} = \frac{\text{Alcohol from treated sample (mol)}}{\text{Alcohol + glucitol from teated sample (mol)}} \quad (4)$$

Number-average degree of polymerization ($\overline{\text{DP}}_\text{n}$) of cellulose sample was evaluated according to the Eq. (5). The $\overline{\text{DP}}_\text{n}$ of original cellulose was 192±5.

$$\overline{\text{DP}}_\text{n}(\text{End-group analysis}) = \frac{\text{Glucose + glucitol from sample (mol)}}{\text{Glucitol + alcohol from sample (mol)}} \quad (5)$$

2.4. Reducing group determination by the BCA method

The BCA method was conducted according to the procedure reported by Zhang et. al.[28] Solution A (97.1 mg of sodium bicinchoninate, 2.71 g of $NaCO_3$ and 1.21 g of $NaHCO_3$ in 50 ml of water) and solution B (39.9 mg of anhydrous $CuSO_4$ and 63.1 mg of L-serin in 50 ml of water) were prepared. A mixture of solution A (0.5 ml) and B (0.5 ml) was added to a suspension of cellulose sample (2.0 mg) in water (1.0 ml) and the suspension was heated at 75°C for 30 min. After removal of residue by filtration, absorvance at 560 nm was measured with a Shimadzu UV-2400 spectrometer. Calibration curve was obtained with glucose (a standard compound), and hence, the data reported in this paper are as glucose equivalent values. With this measurement, content of reducing group in original cellulose was 28.4±0.8 mmol/g (glucose equivalent). The $\overline{\text{DP}}_\text{n}$ of original cellulose calculated from this value was 218±6, which is coincide with the value (192±5) which was obtained from the end-group analysis data (see above). The reducing group content in heat-treated cellulose is shown as percentage against that of original cellulose [Eq. (6)].

$$\text{Reducing group content(BCA)}(\%) = \frac{\text{Reducing group in treated sample (mol)}}{\text{Reducing group in unteated sample (mol)}} \times 100 \quad (6)$$

2.5. Gel permeation chromatography (GPC)

Molecular weight (MW) distribution was evaluated as phenyl isocarbamate derivatives. Sample (5 mg) and phenyl isocyanate (0.2 ml) were added to pyridine (2 ml) and the mixture was stirred at 80°C. After 24h, the reaction mixture became yellow transparent solution. Methanol (0.5 ml) was added to the solution to terminate the reaction, and then solvent was removed by evaporation *in vacuo* to give dark-yellow syrup or light-yellow crystalline substances. The phenyl isocarbamate derivatives were dissolved in tetrahydrofuran (THF) and analyzed by GPC. The GPC analysis was performed with a Shimadzu LC-10A under the chromatographic conditions of column: Shodex LF-804, column temperature: 40°C, eluent: THF, flow rate: 0.6 ml/min, detector: UV_{254nm}.

2.6. X-ray diffraction

X-ray diffraction diagrams of cellulose samples were recorded with a Rigaku RINT 2000 V (Cu Kα, λ=1.542, 40 kV, 30 mA). Crystallinity was evaluated according to the Eq. (7) reported by Segal et. al.:[29]

$$\text{CrI} = \left[\frac{I_{002} - I_{\text{am}}}{I_{002}}\right] \times 100 \quad (7)$$

where CrI expresses the relative degree of crystallinity, I_{002} is the maximum intensity of the 002 lattice diffraction at 2θ = 22.8° and I_{am} is the intensity of diffraction at 2θ = 18°. Crystallinity of the original cellulose was 82.7±0.4.

3. Results and discussion

3.1. Thermal glycosylation reactivity of cellulose with alcohols

Thermal glycosylation reactivity of cellulose (Avicel PH-101) was studied first in presence of glycerol under the heating conditions of N_2/ 60-280°C/ 10 min. Figure 2 shows the temperature-dependency of various indexes which were obtained from the data of sugar and end-group analysis. The Glucose [T]/ Glucose [U] ratios, which show the recovery of the glucose-units other than reducing ends, are alwasy close to 1.0 in 60-280°C, and this indicates that the glucose-units in cellulose are fairly stable against thermal decomposition under these heating conditions. Contrary to this, the Glucitol [T]/ Glucitol [U] ratio, which shows the recovery of the reducing ends, starts to decrease at 140°C, and the reduction rate becomes significant at higher temperatures. Finally, this ratio became almost zero at 260 and 280°C. These results clearly indicate that the reducing end-groups react selectively before other glucose-units decompose. Content of reducing group, which was evaluated by the BCA method based on the reduction of Cu^{2+} to Cu^{+}, is also reduced synchronously with the decreasing Glucitol [T]/ Glucitol [U] ratio. Accordingly, the reducing ends of cellulose are converted into non-reducing structures by this conversion.

With the decrease in the number of the reducing ends (Glucitol [T]/ Glucitol [U]), uptake of glycerol by cellulose increased inversely, which is shown by the Glycerol [T]/ Glucitol [U] and Glycerol [T]/ (Glycerol [T] + Glucitol [T]) ratios. These results suggest thermal glycosylation reaction proceeding between the reducing ends and glycerol. The Glycerol [T]/ Glucitol [U] ratios exceeded 1.0 at 260 (1.5) and 280°C (1.6), and these were much larger than the Glycerol [T]/ (Glycerol [T] + Glucitol [T]) ratios (1.0 and 1.0, respectively), although deviation between these two types of ratios were quite small at the temperatures < 240°C. Such deviation is understandable with depolymerization of cellulose by solvolysis reaction. The MW reduction of the glycerol-treated cellulose at 260 and 280°C were confirmed by GPC analysis. Some

examples of the GPC data are illustrated in Fig. 3. Solvolysis of cellulose by ethyrene glycol has been reported at higher temperature (320-350°C) and higher pressure (4-7 MPa).[30]

Uptake of glycerol by cellulose started from 140°C. This temperature is close to the temperature where thermal glycosylation (polymerization) of glucose is reported to start.[6] However, uptake of glycerol does not show direct relationship with heating temperature. The Glycerol [T]/ Glucitol [U] ratios are around 0.2 at 140-180°C, while this ratio jumped up at 200-240°C. Finally, glucitol from the reducing ends disappeared at 260 and 280°C, where all reducing ends are suggested to be converted into glycosides with glycerol. Figure 4 shows the results of prolonged heating experiments up to 120 min at some selected temperatures (160, 200 and 240°C). The data at 160°C clearly shows the heterogeneous reactivities, which are observed at < 10 min and > 10 min, respectively. The thermal glycosylation reaction at 160°C became slow at the level (Glycerol [T]/ Glucitol [U] ratio: 0.2) where 20% of the reducing ends are converted into glycosides.

Such heterogeneous reactivity may arise from the crystalline nature of cellulose. The fraction 0.2 with higher thermal glycosylation reactivity coincides with that of non-crystalline (paracrystalline) region of cellulose (crystallinity: 82.7±0.4). The reducing ends in non-crystalline region would react more effectively with glycerol, since these sites would be accessed by glycerol more easily than those in the crystalline region. It is expected that the reducing ends in the crystalline region become reactive at higher temperature than 200-240°C, due to the increasing mobility of cellulose crystals.

Thermal expansion and increasing deuteration reactivity in this temperature range have been reported. Wada[31] obtained *in situ* X-ray diffraction data for tunicate (*Halocynthia*) cellulose during heat treatment and he reported that thermal expansion of the *a* axis of cellulose became significant at > 220-230°C. Horikawa and

Sugiyama[32] reported the deuteration rate of cellulose which increased significantly at 230°C. These are similar to the temperature where thermal glycosylation reactivity increased significantly in this study.

From the deviation between Alcohol [T]/ (Alcohol [T] + Glucitol [T]) ratio and Alcohol [T]/ Glucitol [U] ratio in Fig. 4, solvolysis reaction is suggested to occur also at 200 and 240°C in prolonged heating, although this is still not effective at 160°C. Decrease in the MW of cellulose at 200 and 240°C was confirmed with their GPC data (not shown). Interestingly, depolymerization tends to level-off at around $\overline{DP}_n$ 120 (Glycerol [T]/ Glucitol [U] ratio: around 1.6). Although the mechanism is unknown presently, similar leveling-off DP has been reported in solvolysis of cellulose with ethyrene glycol[30].

Table 1 summarizes the results of various alcohols. Thermal glycosylation reactivity was evaluated with the Alcohol [T]/ (Alcohol [T] + Glucitol [T]) ratio. Deviation between this ratio and the Alcohol [T]/ Glucitol [U] ratio are explainable with the solvolysis depolymerization as discussed above. The GPC data of mannitol- and 1,2,6-hexanetriol-treated cellulose samples are illustrated in Fig. 5. Glycerol, mannitol and 1,2,6-hexanetriol were effective for thermal glycosylation of cellulose, and these reactions were almost completed at 280°C in 10 min heating. In contrast, 3-phenoxy-1,2-propanediol and 1-tetradecanol did not react to cellulose at all. Some relationships are observed between thermal glycosylation reactivity and the OH/C ratio of alcohol: relative reactivity: glycerol (1.0), mannitol (1.0) > 1,2,6-hexanetriol (0.5) >> 3-phenoxy-1,2-propanediol (0.22), 1-tetradecanol (0.07) (value in parenthesis: OH/C). Thus, hydrophilic nature of alcohol is a critical factor in thermal glycosylation of cellulose. Less hydrophilic alcohols would have lower accessibility to the reducing ends even in the non-crystalline region.

The GPC data (Figs. 3 and 5) indicate that the solvolysis efficiency is also dependent on chemical structure of alcohol: mannitol > glycerol > 1,2,6-hexanetriol.

Interestingly, change in the MW distribution of 1,2,6-hexanetriol-treated cellulose (280°C/ 10 min) was quite small, although thermal glycosylation at the reducing ends was already completed (Table 1).

3.2. Thermal glycosylation and degradation reactions of cellulose

Figure 6 summarizes the Glucitol [T]/ Glucitol [U] ratios and Glucose [T]/ Glucose [U] ratios as indicators of the recovery of reducing end and other glucose-units in cellulose, respectively. As for the alcohol-treated cellulose samples, Alcohol [T]/ (Alcohol [T] + Glucitol [T]) ratio is also shown as an indicator of uptake of alcohol by cellulose. Some of the data are already shown in Fig. 2 and Table 1.

In case of glycerol, mannitol and 1,2,6-hexanetrol, which were effective for thermal glycosylation, the Glucitol [T]/ Glucitol [U] ratio decreased significantly, and these results are explainable with the thermal glycosylation reaction between alcohol and the reducing end as discussed earlier. Interestingly, the Glucitol [T]/ Glucitol [U] ratio also decreased down to the similar levels with the inactive alcohols (3-phenoxy-1,2-propanediol and 1-tetradecanol) and even under neat pyrolysis condition without addition of any additives (control). On the other hand, the Glucose [T]/ Glucose [U] ratios were always showed higher values (0.85-0.97), which are rather close to 1.0 (complete recovery), under all heating conditions. These results suggest that the reducing end of cellulose is also reactive without addition of reactive alcohols.

Figure 7 shows the GPC chromatogram of cellulose after heat treatment in N_2 at 240°C for 10 min. The chromatogram obtained after reheating of the glycerol-treated cellulose (240°C/ 30 min) under the similar conditions (240°C/ 10 min) is also included for comparison. The MW distribution of cellulose moved slightly to higher MW region after heating, although such change was not significant in reheating of the glycerol-treated cellulose with much less reducing end remaining. Formation of

higher MW products can be seen more easily in the curve a)-b) (Fig. 7). From these results, thermal glycosylation at the reducing end is also suggested to occur even in neat pyrolysis of cellulose. The reducing ends in non-crystalline region may react with adjacent cellulose molecule. However, this reactivity would be much lower than those in presence of reactive alcohols, since the fraction of cellulose which move to higher MW region is not large. Restricted mobility of cellulose molecule may be a reason for such lower thermal glycosylation reactivity.

Pictures of the glycerol-, mannitol- and 1,2,6-hexanetriol-treated cellulose samples (280°C/ 10 min) are illustrated in Fig. 8 as compared with the control sample obtained without addition of any additives. Contents of reducing group as determined by the BCA method are also included in parentheses. Cellulose was severely colored in neat pyrolysis, while the alcohol-treated cellulose samples were almost colorless. These results suggest that the thermal glycosylation in presence of these reactive alcohols stabilize cellulose against pyrolytic coloration. This is also supported by the results (Fig. 9) of reheating experiments of these alcohol-treated cellulose samples in N_2 at 240 and 280°C for 10 min. At both temperatures, coloration was substantially inhibited in the alcohol-treated cellulose samples, in which most of their reducing ends were converted into non-reducing glycosides (Table 1). These results also indicate the importance of cellulose reducing ends in this coloration.

The content of reducing group (142.3% against original cellulose) of the control sample was much higher than those (3.6-12.8%) of the alcohol-treated cellulose samples. Since the recovery of reducing end (Glucitol [T]/ Glucitol [U]) in the control sample was quite small (0.07) (Fig. 6), most of these reducing groups arise from the pyrolysis products. This reducing group formation may be related to the coloration, although detailed mechanisms are unknown presently. Formation of furanic compounds such as furfural and 5-hydroxymethylfurfural may be a candidate.

From the present results, two competitive pyrolysis pathways are proposed for

relatively low temperature (<280°C) pyrolysis of cellulose (Fig. 10). One is thermal glycosylation and the other is thermal degradation into colored substances, both of which start from the reducing end-groups. With reactive small alcohol such as glycerol, mannitol and 1,2,6-hexanetriol, thermal glycosylation proceeds predominantly due to their easy access to the reducing ends (R: alcohol). In neat pyrolysis (R: cellulose molecule), these two pathways become more competitive, since the glycosylation reactivity is lowered through restricted mobility of cellulose molecules. Thus, pyrolytic coloration proceeds in neat pyrolysis, while the color formation is inhibited in presence of reactive alcohol through converting the reducing ends into more stable glycosides.

4. Conclusions

The reducing ends of cellulose were found to be converted into glycosides at relatively low temperature (< 280°C) pyrolysis of cellulose in presence of alcohol with high OH/C ratio. Hydrophilicity of alcohol was a critical factor for this reaction. This glycosylation reactivity was influenced by the crystalline structure of cellulose. The reducing ends in the non-crystalline region were suggested to be more reactive than those in the crystalline region. The reactivity in the crystalline region increased at > 200-240°C where thermal expansion of cellulose crystals becomes significant. In neat cellulose pyrolysis, two competitive pathways, i.e., thermal glycosylation and pyrolytic coloration, have been proposed, both of which occur at the reducing ends. The latter pyrolytic coloration pathway was effectively inhibited in presence of reactive alcohol, since thermal glycosylation, which converts the reducing ends into more stable glycosides, occurred predominantly before pyrolytic coloration occurred.

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Figure 1. Apparatus used for heat-treatment experiments.

Figure 2. Influence of heat-treatment temperature on reducing group content measured by the BCA method and recovery of glucitol (from reducing-ends), glucose (from other glucose-units) and glycerol (from glycosides) after $NaBH_4$-reduction and subsequent hydrolysis of heat-treated cellulose with glycerol (N_2 / 10 min).

Figure 3. GPC chromatograms of glycerol-treated cellulose samples (N_2 / 10 min / after triphenylcarbanilation).

Figure 4. Influence of heat-treatment time on reducing group content measured by the BCA method and recovery of glucitol (from reducing-ends), glucose (from other glucose-units) and glycerol (from glycosides) after $NaBH_4$-reduction and subsequent hydrolysis of heat-treated cellulose with glycerol in N_2 .

Figure 5. GPC chromatograms of mannitol- and 1,2,6-hexanetriol-treated cellulose samples (N_2 / 10 min / after triphenylcarbanilation).

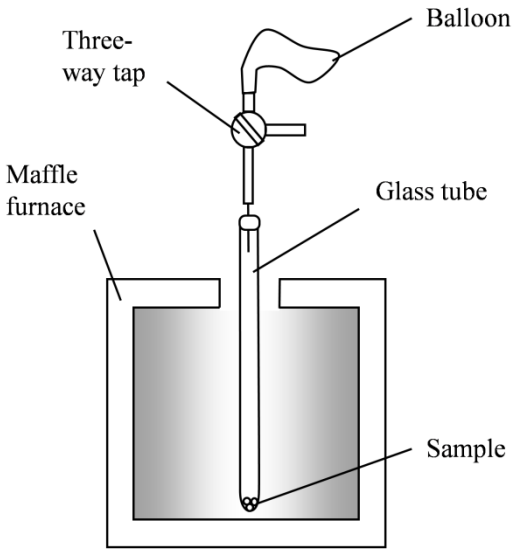
Figure 6. Recovery of glucitol (from reducing-ends), glucose (from other repeating glucose-units) and alcohol (from glycosides) after $NaBH_4$-reduction and subsequent hydrolysis of heat-treated cellulose with additives (N_2 / 10 min).

Figure 7. GPC chromatograms of untreated and glycerol-treated cellulose samples after heating (N_2 / 10 min / after triphenylcarbanilation).

Figure 8. Photographs of the heat-treated cellulose samples with various alcohols (N_2 / 280°C / 10 min).

Figure 9. Pyrolytic coloration behavior of the alcohol-treated cellulose samples (N_2 / 280°C / 10 min) during reheating in N_2 at 240 and 280°C for 10 min.

Figure 10. Thermal glycosylation and degradation reactions to form colored substances, which are proposed as competitive reactions preferably occurring at the reducing ends in low temperature pyrolysis of cellulose.



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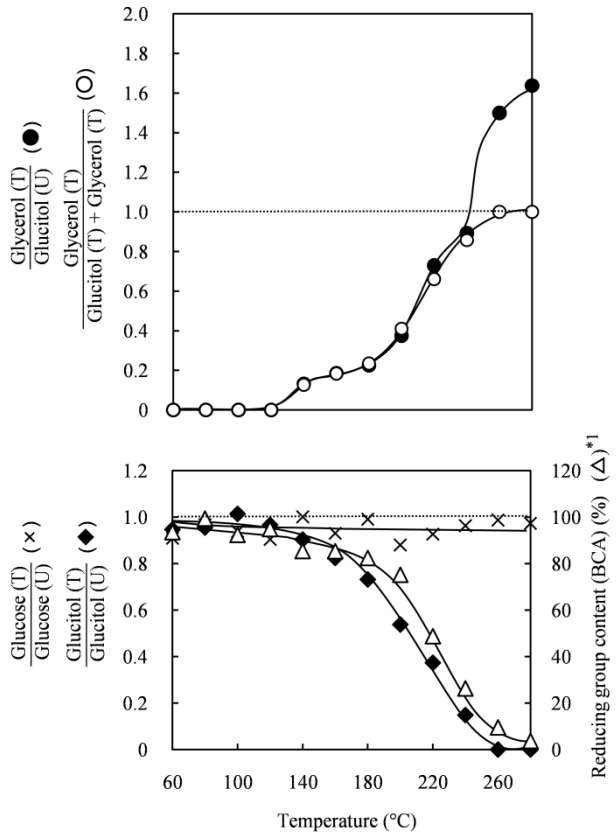

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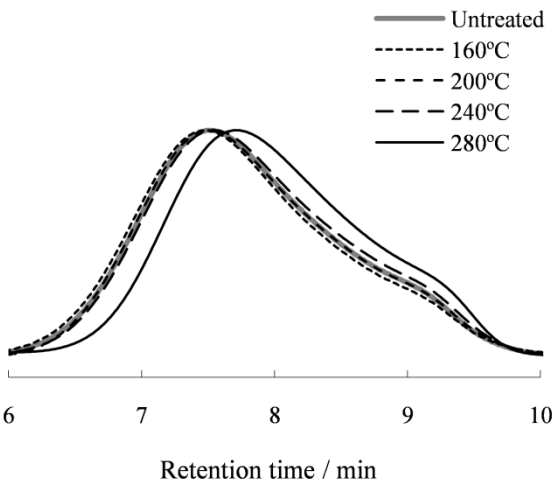
U:untreated cellulose, T: heat-treated cellulose.

*1 Normalized to untreated cellulose (100%).



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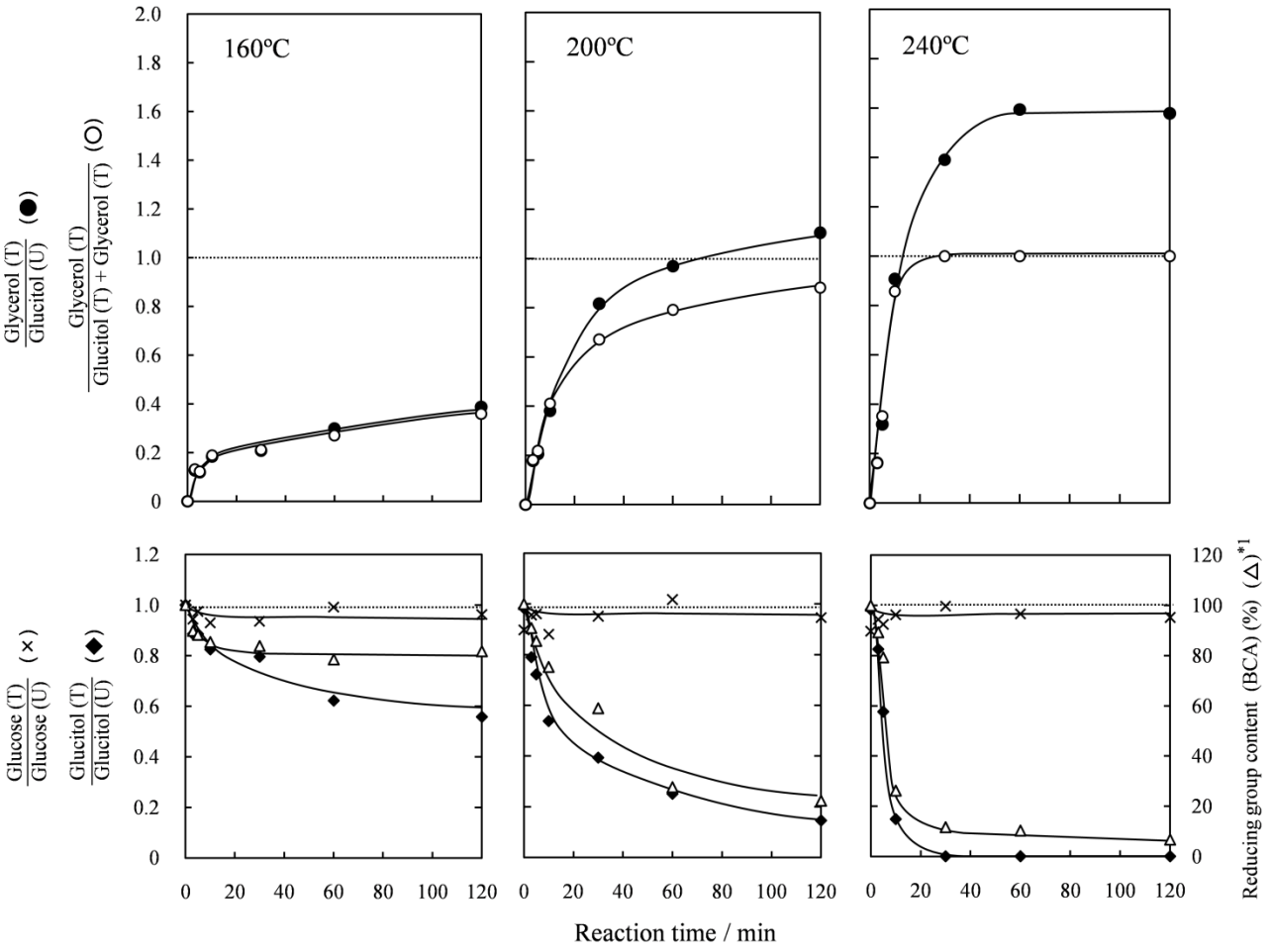

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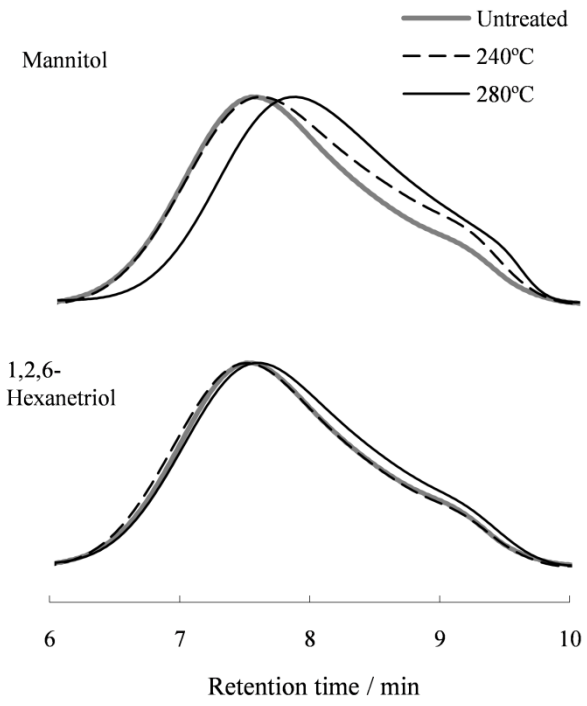
U: untreated cellulose, T: heat-treated cellulose.

*1 Normalized to untreated cellulose (100%).



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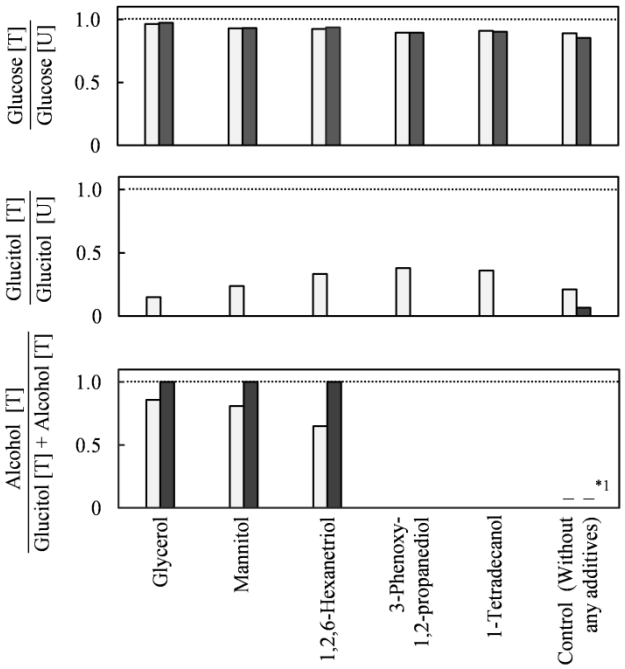


Figure 6. Recovery of glucitol (from reducing-ends), glucose (from other repeating glucose-units) and alcohol (from glycosides) after $NaBH_4$-reduction and subsequent hydrolysis of heat-treated cellulose with additives (N_2 / 10 min).
□ : 240°C, ■ : 280°C, U: untreated cellulose, T: heat-treated cellulose.
*1 Not measured.

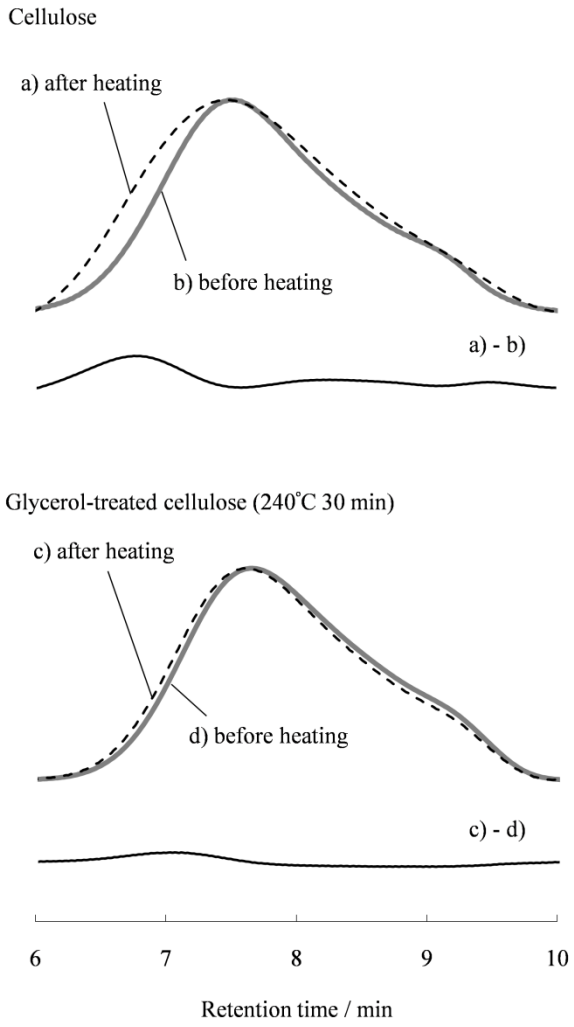


Figure 7. Change in the GPC chromatograms (triphenylcarbanilated derivatives) in heat-treatment of Avicel PH-101 and its glycerol-treated sample (240°C / 30 min) in N_2 for 10 min.

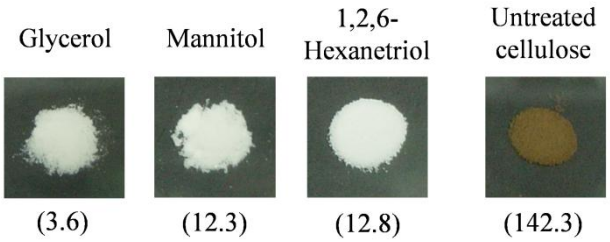
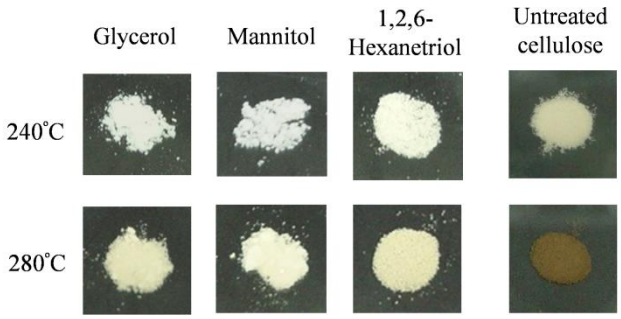


Figure 8. Photographs of the heat-treated cellulose samples with various alcohols (N_2 / 280°C / 10 min). Number in parenthesis: reducing group content (%, BCA method) normalized to untreated cellulose (100%).



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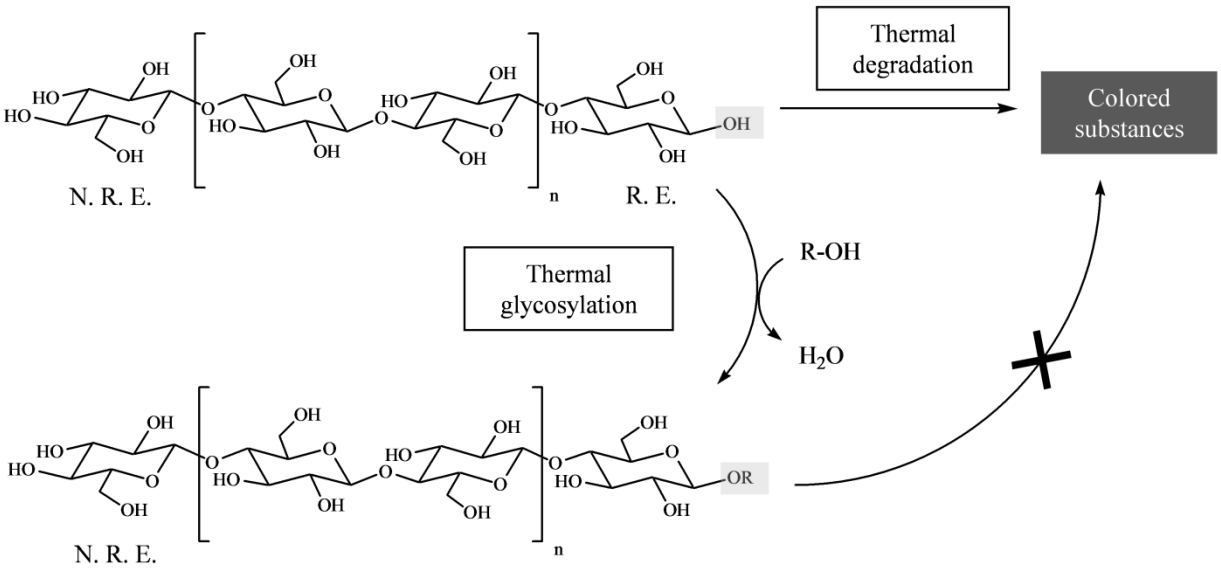

Figure 10. Thermal glycosylation and degradation reactions to form colored substances, which are proposed as competitive reactions preferably occurring at the reducing ends in low temperature pyrolysis of cellulose.
R. E.: reducing end, N. R. E.: non-reducing end.

Legends of table

Table 1 Reactivity of various alcohols for thermal glycosylation at the reducing ends of cellulose as indicated by the recovery of alcohol (from glycosides) and glucitol (from unreacted reducing ends) after $NaBH_4$-reduction and subsequent hydrolysis of heat-treated cellulose with alcohols (N_2 / 10 min).

Table 1 Reactivity of various alcohols for thermal glycosylation at the reducing ends of cellulose as indicated by the recovery of alcohol (from glycosides) and glucitol (from unreacted reducing ends) after $NaBH_4$-reduction and subsequent hydrolysis of heat-treated cellulose with alcohols (N_2 / 10 min).

	OH/C	$\frac{\text{Alcohol (T)}}{\text{Glucitol (U)}}$		$\frac{\text{Alcohol (T)}}{\text{Glucitol (T) +Alcohol (T)}}$	
		240°C	280°C	240°C	280°C
Glycerol	1	0.89	1.64	0.86	1.00
Mannitol	1	1.00	1.71	0.81	1.00
1,2,6-Hexanetriol	0.5	0.62	0.93	0.65	1.00
3-Phenoxy-1,2-propanediol	0.22	0	0	0	-[*1]
1-Tetradecanol	0.07	0	0	0	-[*1]

U: untreated cellulose, T: heat-treated cellulose.

OH/C: number of OH / number of C in alcohol.

[*1] Both glucitol and alcohol were not detected.