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Influence of neutral inorganic chlorides on primary and secondary char formation from cellulose

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Abstract The influence of various alkali and alkaline earth metal chlorides (LiCl, NaCl, KCl, MgCl₂, and CaCl₂) on primary and secondary char formation from cellulose was studied at 400°C. Secondary char was formed through carbonization of the volatile products. All chlorides increased the primary char yield while decreasing the secondary char formation, and this situation was promoted in the order of alkaline earth Mg, Ca, alkali Li > alkali Na, K. Levoglucosan yield also decreased along with the secondary char yield. These results indicate that the reduced formation of volatile levoglucosan was related to the decreasing yield of secondary char. A model experiment at 250°C revealed that these chlorides, especially the two alkaline earth metals, had catalytic action on the polymerization of levoglucosan, which serves to reduce the formation of volatile levoglucosan.

Key words Cellulose · Primary char · Secondary char · Alkali metal chloride · Alkaline earth metal chloride

Introduction

Wood pyrolysis is the fundamental principle of various thermochemical processes that are performed with woody biomass, such as carbonization, gasification, and fast pyrolysis. The knowledge of the pyrolysis mechanism on a molecular basis is thus helpful in improving these conversion processes; that is, increasing the product selectivity, alleviating tar trouble in gasification, and so on. This article focuses on the effect of inorganic matter, which greatly affects the pyrolysis reactions of cellulose.

The influence of inorganic matter on cellulose pyrolysis has been studied extensively to help understand the behavior of woody biomass in thermochemical conversion processes.^{1–18} Demineralization by acid washing the samples prior to pyrolysis usually increases the levoglucosan (1,6-anhydro-β-D-glucopyranose) yield and reduces char formation.^{1–3,5} The influence of individual inorganic substances on cellulose pyrolysis has also been studied with ion-exchanged^{6–8} and impregnated^{2,9–13} samples. According to the findings, acidic substances enhance the formation of dehydration products such as levoglucosenone and furfural, while some fragmented products including glycolaldehyde and hydroxyacetone are formed more preferentially with basic substances.^{15–18} Some of these aspects are explained on the basis of the acidity or basicity involved. However, the action of neutral salts on cellulose pyrolysis is still unknown on a molecular basis.

For neutral salts, many studies have employed alkali metal halides.^{2,9–11,14} These halides are found to lower the degradation temperature slightly^{2,11} and enhance the formation of char, CO, CO₂, and H₂O^{13,14} with reduced yield of levoglucosan.^{9,13} Shafizadeh and Sekiguchi¹² reported that NaCl addition enhanced the formation of aromatic structures based on the analysis of mellitic acid. There are, however, very few articles that describe the influence of alkaline earth metal halides.^{4,11}

Attention should be paid to the situation that a considerable amount of carbonized product (defined as “secondary char” in this article) was formed from the secondary carbonization of volatile products after condensing near the outlet of the reactor with relatively low temperature. In practical terms, this type of char formation would be related to the clogging of the pyrolysis reactor. In our previous reports,^{19,20} ring-opening polymerization of levoglucosan has been proposed as a key reaction to the carbonization. This secondary carbonization is also expected to be influenced by inorganic matter through changing of product compositions. However, the influence on the secondary carbonization has not been reported yet.

In this article, the action of alkali and alkaline earth metal chlorides on primary and secondary char formation

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is described by focusing on levoglucosan as a key intermediate to secondary char formation.

Experimental

Materials

Filter paper (Kiryama Glass, oven-dried at 105°C for 24h) was used as the cellulose sample. Aqueous LiCl, NaCl, KCl, MgCl₂, or CaCl₂ solution (0.10, 0.050, or 0.010mmol in 150 μl) was added dropwise to the filter paper (37 mg). This amount of solution was completely absorbed by the filter paper. The resulting filter paper was dried in an oven at 105°C for 24h before pyrolysis. The amount of impregnation was 0.44, 0.22, and 0.044 mol/mol of the glucose-unit of cellulose. A control sample was also prepared with pure water (150 μl) in a similar fashion.

Pyrolysis and product characterization

Pyrolysis was conducted with the apparatus reported in our previous report.¹⁹ Sample was placed at the bottom of a round-shaped 30-ml flask and the flask was fitted with a cooling tube (120mm long and 14mm in diameter) and a nitrogen bag through a three-way tap. After replacing the air in the system with nitrogen, the flask was soaked in a salt bath (KNO₃/NaNO₃, 1:1, w/w) (400°C) for 10min. The flask was immediately cooled with flowing air (30s) and subsequently in cold water (3min), and the carbonized paper (defined as “primary char” in this article, Fig. 1) was taken out of the flask and weighed. The amount of the primary char was calculated by subtracting the weight of the chloride in the original paper from the weight of the carbonized paper, on the assumption that all the chloride could be included in the carbonized paper. The flask and the cooling tube were extracted with methanol (MeOH) (5.0ml) to give a MeOH-soluble fraction. The carbonized substance, which was observed near the top of the flask, is defined as secondary char in this article (Fig. 1). The secondary char that was sticking on the wall of the flask was washed with water (5.0ml) and dried before weighing. The amounts of the MeOH-soluble products and secondary char were calcu-

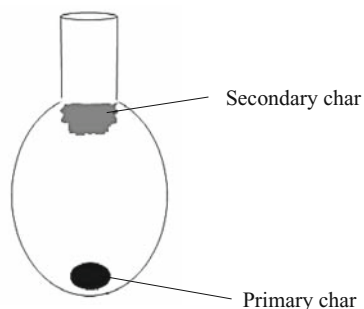


Fig. 1. Primary and secondary char formation

lated from the weight difference of the glassware before and after extraction. The MeOH-soluble fractions were analyzed by gel permeation chromatography (GPC) with a Shimadzu LC-10A (column: Asahipak GS-220 HQ; eluent: water; flow rate: 1.0ml/min; detector: refractive index; temperature: 40°C).

Influence on levoglucosan polymerization

Levoglucosan (8.1 mg, 0.050mmol) was taken into a round-shaped flask (30 ml) and dissolved in a chloride aqueous solution (0.0050mmol in 0.10ml). The resulting solution was evaporated in vacuo to form a thin film at the bottom of the flask. Heat treatment was conducted in N₂ with an apparatus similar to that described above. To avoid the formation of carbonization products, which make investigation of polymerization reactivity difficult, 250°C was chosen as the heating temperature. After 1 min of heating at 250°C, the reaction was quenched by cooling with flowing air (30s) and in cold water (3min). The reaction mixture was extracted with water (0.5 ml) and analyzed with GPC under the chromatographic conditions described above.

Results and discussion

Figure 2 summarizes the primary and secondary char yields at various chloride addition levels. The hashed line in Fig. 2 shows the total char yield [23%, primary (7%) + secondary (16%)] in pure cellulose (neat). With addition of chloride, the primary char yield increased to 16%–54% (excluding the amount of chloride) and the secondary char yield decreased (0%–16%). This situation was promoted with the increased level of chloride.

Alkaline earth metals (MgCl₂, CaCl₂) exhibited much greater influences than alkali metals (NaCl, KCl) except for LiCl. The influence of LiCl was rather similar to those of the alkaline earth metals. The addition of Mg (0.22, 0.44 mol), Ca (0.22, 0.44 mol), and Li (0.44 mol) reduced the secondary char yields to undetectable levels, while the primary char yields increased by 3.6 to 7.3 times as compared with pure cellulose. Consequently, the total char yields increased substantially (1.5 to 2.3 times). Contrary to this, the total char yields from the NaCl- and KCl-impregnated samples were not greatly affected (increased by 1.2 to 1.5 times).

Gel permeation chromatograms of the MeOH-soluble fractions at 0.44 mol/mol of glucose-unit are shown in Fig. 3. The peak areas in the chromatogram decreased in the order of neat > Na, K > Li, Mg, Ca, and this order was quite similar to that observed for secondary char formation. The peak areas at 10min, which correspond to the yield of levoglucosan, were reduced by Na, K, and Ca impregnation, and levoglucosan was not detected from the Li- and Mg-impregnated samples. Figure 4 summarizes the primary, secondary, and total char yields as plotted against the levoglucosan yields. Some positive correlation existed between the secondary char and levoglucosan yields, while the

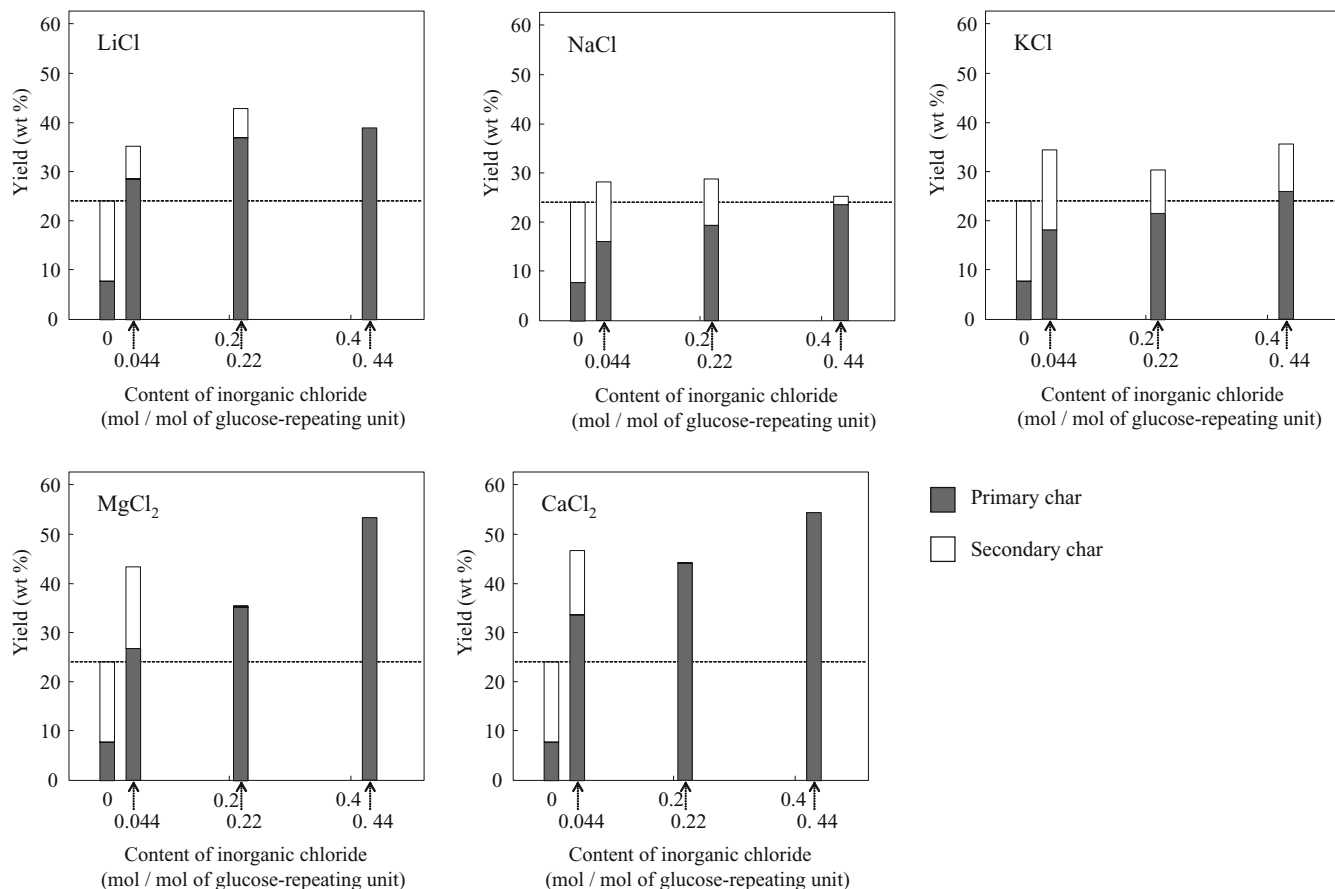
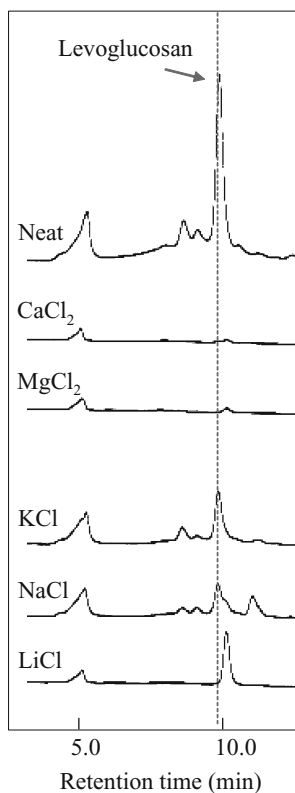


Fig. 2. Influence of the inorganic chlorides on primary and secondary char formation from cellulose ($N_2/400^\circ C/10\text{ min}$)

Fig. 3. Gel permeation chromatograms (GPCs) of the methanol-soluble fractions obtained from the chloride-impregnated cellulose samples ($N_2/400^\circ C/10\text{ min}$). *Neat*, neat cellulose



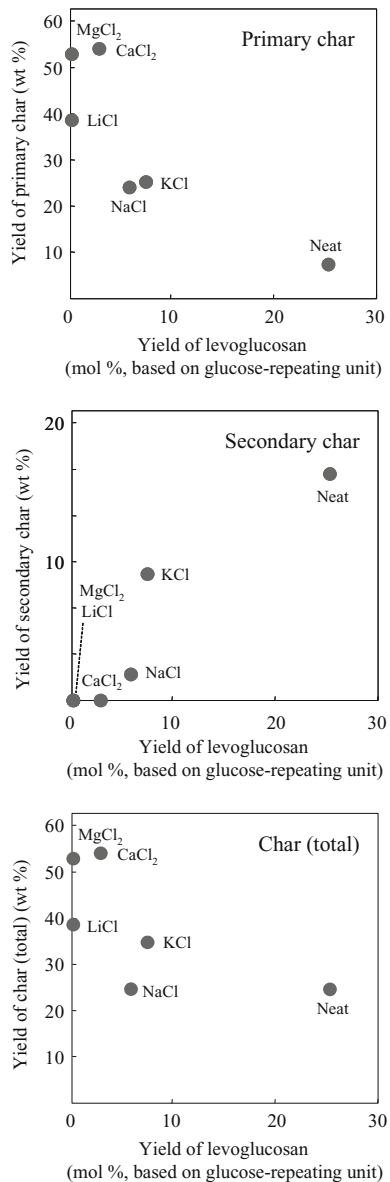
primary char yield was negatively correlated with the levoglucosan yield. Due to these opposite relationships between primary and secondary char yields, the total char yields from the neat and Na- and K-impregnated samples were almost independent of the levoglucosan yield.

Influence of the chlorides on the polymerization of levoglucosan is shown in the GPC chromatograms for the heat-treated mixtures of levoglucosan and chlorides (1:0.1, mol/mol, N_2 atmosphere, $250^\circ C$, 1 min) in Fig. 5. Intensity of the peak area observed in the region of molecular weight higher than levoglucosan increased with addition of chloride. Polymerization reactivity was evaluated by introducing the “polymerization index”, which is defined as: peak area (region of molecular weight higher than levoglucosan)/peak area (levoglucosan).

The larger the polymerization index becomes, the greater is the catalytic activity. The obtained polymerization indexes are summarized in Fig. 6. All these chlorides had catalytic action on the polymerization of levoglucosan. The alkaline earth metals, which substantially increased the primary and total char yields, had especially high catalytic activities. The catalytic activity of LiCl was weak like other alkali metals, although the enhancing effect on the primary char formation was much greater than NaCl and KCl.

Based on these lines of evidence, the influence of alkali and alkaline earth metal chlorides on primary and second-

Fig. 4. Relationships between the primary, secondary, and total char yields with the levoglucosan yield



ary char formation from cellulose can be discussed in terms of the formation of volatile levoglucosan. In pure cellulose, a substantial amount of levoglucosan vaporizes and condenses on areas of the reactor wall with lower temperature, where levoglucosan is subject to secondary carbonization (Fig. 7). Consequently, secondary char yield depends on the amount of volatile levoglucosan. Kawamoto et al.^{19,20} have reported that the ring-opening polymerization of levoglucosan is a key reaction for carbonization. Reduction of the amount of volatile levoglucosan induced by alkali and alkaline earth metal chlorides would be related to the inhibition of secondary char formation.

The catalytic action of these chlorides on the polymerization of levoglucosan would reduce the amount of volatile levoglucosan, although they probably have complex action on cellulose pyrolysis. Indeed, the action of MgCl₂ and CaCl₂ as Lewis acids to promote solid-state hydrolysis has

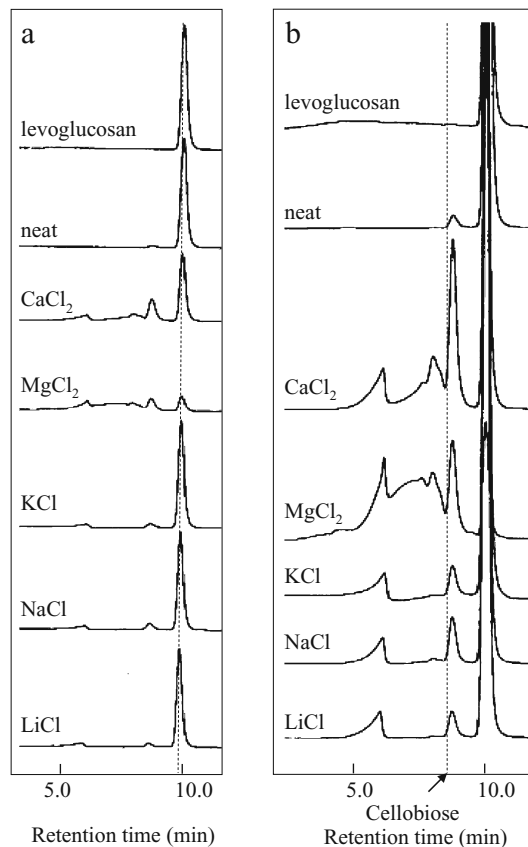


Fig. 5. **a** Gel permeation chromatograms of the heat-treated mixtures of levoglucosan and chlorides (levoglucosan : chloride = 1 : 0.1 mol/mol, N₂/250°C/1 min). **b** Enlarged chromatograms

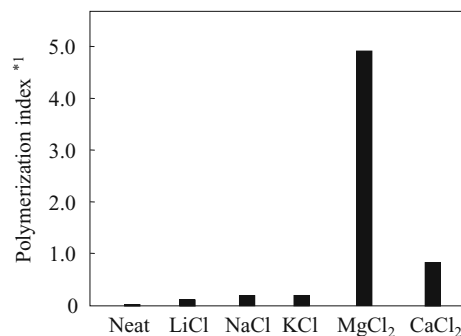


Fig. 6. Catalytic activities of the inorganic chlorides on the polymerization of levoglucosan (levoglucosan : chloride = 1 : 0.1 mol/mol, N₂/250°C/1 min). Polymerization index = peak area (products of higher molecular weight than levoglucosan)/peak area (levoglucosan) in GPC

been found at elevated temperature.²¹ The affinity of Mg²⁺ or Ca²⁺ for the ring oxygen of levoglucosan has been used to explain the catalytic activity. Relatively strong influence of LiCl on cellulose carbonization, which has low catalytic activity, suggests that other mechanisms also play important roles, although further study is necessary to clarify the mechanism.

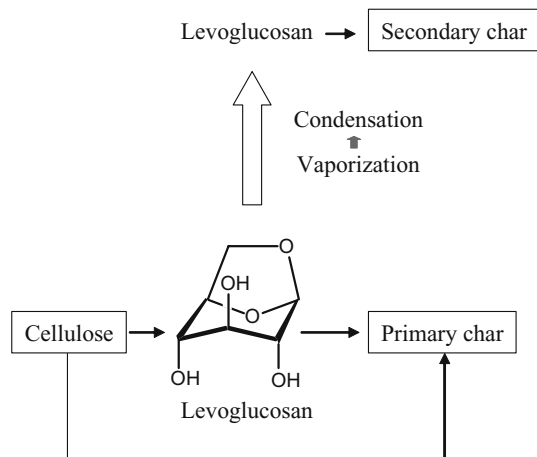


Fig. 7. Levoglucosan as a key intermediate for secondary char formation in cellulose pyrolysis

Conclusions

Alkali and alkaline earth metal chlorides increased the primary char yield while inhibiting secondary char formation. The yield of levoglucosan, the important intermediate in cellulose pyrolysis, was also substantially reduced with these salts. Especially strong actions were observed for the alkaline earth metal chlorides, and these chlorides had strong catalytic activities on the polymerization of levoglucosan. Based on these results, inhibition of secondary char formation appears to be related to the reduced formation of volatile levoglucosan in the presence of these salts.

References

- Hosoya T, Kawamoto H, Saka S (2007) Influence of inorganic matter on wood pyrolysis at gasification temperature. *J Wood Sci* 53:351–357
- Jensen A, Dam-Johansen K (1998) TG-FTIR study of the influence of potassium chloride on wheat straw pyrolysis. *Energy Fuel* 12:929–938
- Shafizadeh F, Furneaux RH, Cochran TG, Scholl JP, Sakai Y (1979) Production of levoglucosan and glucose from pyrolysis of cellulose materials. *J Appl Polym Sci* 23:3525–3539
- Müller-Hagedorn M, Bockhorn H, Krebs L, Müller U (2003) A comparative kinetics study on the pyrolysis of three different wood species. *J Anal Appl Pyrol* 68,69:231–249
- Piskorz J, Radlein DStAG, Scott DS (1989) Pretreatment of wood and cellulose for production of sugars by fast pyrolysis. *J Anal Appl Pyrol* 16:127–142
- DeGroot WF, Shafizadeh F (1984) The influence of exchangeable cations on the carbonization of biomass. *J Anal Appl Pyrol* 6:217–232
- Pan W, Richards GN (1989) Influence of metal ions on volatile products of pyrolysis of wood. *J Anal Appl Pyrol* 16:117–126
- Richards GN, Zheng G (1991) Influence of metal ions and of salts on products from pyrolysis of wood: applications to thermochemical processing of newsprint and biomass. *J Anal Appl Pyrol* 21:133–146
- Tsuchiya Y, Sumi K (1970) Thermal decomposition products of cellulose. *J Appl Polym Sci* 14:2003–2013
- Fung DPC, Tsuchiya Y, Sumi K (1972) Thermal degradation of cellulose and levoglucosan – the effect of inorganic salts. *Wood Sci* 5:38–43
- Varhegyi G, Antal MJ Jr, Szekely T, Jakab E (1988) Simultaneous thermogravimetric-mass spectrometric studies of the thermal decomposition of biopolymers. 1. Avicel cellulose in the presence and absence of catalysts. *Energy Fuel* 2:267–272
- Shafizadeh F, Sekiguchi Y (1983) Development of aromaticity in cellulosic chars. *Carbon* 21:511–516
- Halpern Y, Patai S (1969) Pyrolytic reactions of carbohydrates. Part VI. Isothermal decomposition of cellulose in vacuo, in the presence of additives. *Isr J Chem* 7:685–690
- Madorsky SL, Hart VE, Straus S (1956) Pyrolysis of cellulose in a vacuum. *J Res Natl Bur Stand* 56:343–354
- Tsuchiya Y, Sumi K (1970) Thermal decomposition products of cellulose. *J Appl Polym Sci* 14:2003–2013
- Halpern Y, Riffer R, Broido A (1973) Levoglucosone (1,6-anhydro-3,4-dideoxy- Δ^3 - β -D-pyranosen-2-one). Major product of the acid-catalyzed pyrolysis of cellulose and related carbohydrates. *J Org Chem* 38:204–209
- Dobe G, Rossinskaja G, Telysheva G, Meier D, Faix O (1999) Cellulose dehydration and depolymerization reactions during pyrolysis in the presence of phosphoric acid. *J Anal Appl Pyrol* 49:307–317
- DeGroot WF, Shafizadeh F (1984) The influence of exchangeable cations on the carbonization of biomass. *J Anal Appl Pyrol* 6:217–232
- Kawamoto H, Murayama M, Saka S (2003) Pyrolysis behavior of levoglucosan as an intermediate in cellulose pyrolysis: polymerization into polysaccharide as a key reaction to carbonized product formation. *J Wood Sci* 49:469–473
- Kawamoto H, Hatanaka W, Saka S (2003) Thermochemical conversion of cellulose in polar solvent (sulfolane) into levoglucosan and other low molecular-weight substances. *J Anal Appl Pyrol* 70:303–313
- Shimada N, Kawamoto H, Saka S (2007) Solid-state hydrolysis of cellulose and methyl α - and β -D-glucopyranosides in presence of magnesium chloride. *Carbohydr Res* 342:1373–1377