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Pyrolysis behavior of levoglucosan as an intermediate in cellulose pyrolysis: polymerization into polysaccharide as a key reaction to carbonized product formation

Abstract Pyrolysis behavior of levoglucosan (1,6-anhydro-β-D-glucopyranose), the major anhydromonosaccharide formed during cellulose pyrolysis, was studied at 250°–400°C under nitrogen. The pyrolysis products were found to change stepwise: levoglucosan → MeOH-soluble fraction (lower-molecular-weight products and oligosaccharides) → water-soluble fraction (polysaccharides) → insoluble fraction (carbonized products). From the present experimental results, a pathway of cellulose pyrolysis via anhydromonosaccharide is proposed including polymerization to polysaccharides (a reversible reaction) as a key reaction to carbonized product formation.

Key words Pyrolysis mechanism · Cellulose · Levoglucosan · Polymerization · Carbonization

Introduction

Pyrolysis, which is defined as thermochemical conversion under a limited amount of oxygen, has a potential application for converting woody biomass into fuels and chemicals.[1–3] It is known that pyrolysis of woody biomass produces a complex mixture of gaseous, liquid, and solid products.[1–3] Although flash pyrolysis, characterized by rapid heating,[4–8]

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and vacuum pyrolysis, conducted under reduced pressure,[9] have been exploited to improve the selectivity of liquid products, these processes still produce a considerable amount of gaseous and carbonized products; and undesired carbonized products cause deterioration of the liquid's quality.[10]

Understanding the mechanism of pyrolysis of woody biomass on a molecular basis can provide useful information for improving product selectivity. Many kinetic models of cellulose pyrolysis have been proposed to predict product formation.[11,12] However, these models are somewhat oversimplified and do not describe the individual reactions that determine product composition; this is because the models are based on the weight-loss behavior of cellulose studied by thermogravimetry. Thus, the molecular basis of the pyrolysis mechanism focusing on product formation is still not clear.

During cellulose pyrolysis at temperatures above 300°C, anhydromonosaccharides including levoglucosan (1,6-anhydro-β-D-glyucopyranose) and 1,6-anhydro-β-D-glyucofuranose are known to form in substantial yields.[4,12–14] Especially a substantial amount of levoglucosan is produced: Shafizadeh et al.[15] reported a 58% levoglucosan yield from vacuum pyrolysis of cotton cellulose. Many researchers also have indicated that levoglucosan is a key initial intermediate for cellulose pyrolysis based on the experimental fact that levoglucosan and cellulose gave similar pyrolysis products.[12] Thus, the pyrolysis behavior of anhydromonosaccharides, especially levoglucosan, is important when considering product formation during cellulose pyrolysis. Levoglucosan is known to be polymerized to polysaccharide[16–19] and to be degraded to some lower-molecular-weight (LMW) products[2,14] during pyrolysis. These reactions have not yet been discussed in terms of product formation, which includes gaseous, liquid, and solid carbonized materials.

This study examined the pyrolysis behavior of levoglucosan, focusing on the formation of LMW products and solid carbonized products. A pathway that includes polymerization of anhydromonosaccharide as key to carbonized product formation is proposed.

Materials and method

High-performance liquid chromatography (HPLC) was carried out on a Shimadzu LC-10A with a STR ODS-II reverse-phase column [eluent: binary gradient 0% (v/v) to 60% (v/v) MeOH/H_2O in 15 min and then isocratically at 60% for another 5 min; flow rate 1.0 ml/min; detector UV_{220nm}] and Asahipak GS-220HQ [eluent H_2O, flow rate 1.0 ml/min, detector RID]. Gas chromatography (GC) was carried out on a Shimadzu GC-14B using a CBP-5 fused silica capillary column (25 m × 0.25 mm) [GC conditions: column temperature 210°C; injector temperature 250°C; detector (FID) temperature 250°C; carrier gas He (100 kPa)]. GC-mass spectrometry (MS) was performed on a Shimadzu GCMS-QP5000A. Proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded in $CDCl_3$ with a Bruker AC-300 FT-NMR spectrometer (300 MHz) with trimethylsilane (TMS) as an internal standard. Chemical shift is given as the δ value (ppm). Infrared (IR) spectra were obtained with a Shimadzu FTIR-8300 spectrometer uisng a KBr pellet. All chemicals other than levoglucosan were purchased from Nakarai Tesque with guaranteed grades.

Pyrolysis of levoglucosan was conducted in a round flask (30 ml) with a glass tube (120 mm long, 14 mm diameter) for trapping the volatile products attached with a nitrogen bag through a three-way tap, as shown in Fig. 1.

Levoglucosan (50 mg) obtained by pyrolysis of filter paper was placed at the bottom of the flask by evaporating the solution in MeOH (2.0 ml) in vacuo. The flask, attached to the other apparatus, was heated in a salt bath (KNO_3/$NaNO_3$ 1:1, w/w) at 250°, 300°, and 400°C after replacing the air in the reaction system with nitrogen. After the reaction was quenched by immediate cooling with airflow for 30 s and subsequently in cold water for 3 min, the reaction system was opened to release the gaseous product. The flask and cooling tube were extracted with MeOH (2.0 ml) and water (2.0 ml) successively to give MeOH-soluble and water-soluble fractions, respectively. The amounts of the
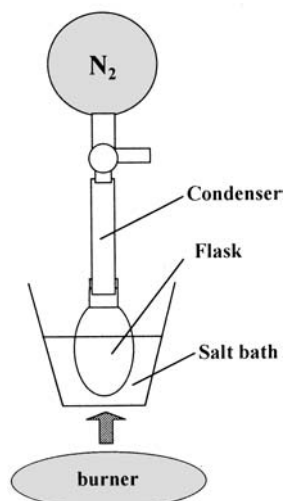
fractions were determined by subtracting the weight of the glassware from that before opening or extractions. HPLC analysis of the MeOH-soluble fraction was conducted without evaporating the solvent to retain the volatile products. ^{1}H-NMR spectra of the water-soluble fractions were obtained after acetylation with acetic anhydride (1.0 ml) and pyridine (1.0 ml) at room temperature overnight. Unreacted levoglucosan was determined in the MeOH-soluble fraction with GC after acetylation using inositol hexaacetate as an internal standard.

Results and discussion

Change in product composition during pyrolysis of levoglucosan

Pyrolysis of levoglucosan was conducted at 250°, 300°, and 400°C under nitrogen at atmospheric pressure for 0.5–5.0 min, and the reaction mixture was fractionated into gaseous, MeOH-soluble, water-soluble, and insoluble fractions by successive extraction with MeOH and water. Methanol-soluble and water-soluble fractions were obtained as yellow oil and a colorless to brown solid, respectively. Insoluble fractions were obtained as black solids. Formation of the gaseous fraction was not significant under the present experimental conditions.

The change in the product composition of the reaction mixture is shown in Fig. 2. Although unreacted levoglucosan was recovered in the MeOH-soluble fraction, this fraction in Fig. 2 does not include levoglucosan. A stepwise change in product composition is clearly observed at 250° and 300°C during pyrolysis. At 250°C, the MeOH-soluble fraction (excluding the unreacted levoglucosan) is formed with a decrease in the amount of levoglucosan, whereas other fractions are barely formed until after 2 min of pyrolysis. Under more drastic conditions (300°C), the MeOH-soluble fraction is formed initially (as observed at 250°C) with a maximum yield of 50% at 0.5 min, followed by production of the water-soluble fraction and decreasing amounts of the MeOH-soluble fraction. Furthermore, transformation from water-soluble to insoluble fractions is clearly observed, although the MeOH-soluble fraction tends to level off at a longer reaction time. These observations indicate that change in the product composition (levoglucosan → MeOH-soluble → water-soluble → insoluble fractions) occurs during levoglucosan pyrolysis. When the pyrolysis temperature is raised to 400°C, the stepwise formation of the products observed at 250° and 300°C is not seen, and all fractions are formed beginning at the initial stage of the pyrolysis. This observation is probably due to the drastic conditions (e.g., 400°C), which make the stepwise transformation ambiguous.

Characterization of the products

Figure 3 shows the chromatograms of the MeOH-soluble fractions. The chromatogram obtained after evaporation
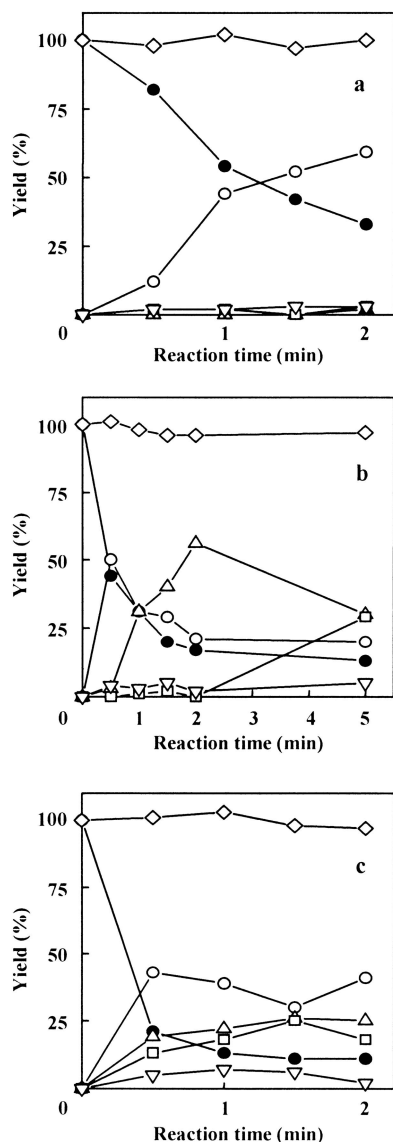

Fig. 1. Experimental apparatus

Fig. 2. Change in product composition during pyrolysis of levoglucosan. **a** 250°C. **b** 300°C. **c** 400°C. *Solid circles*, levoglucosan; *open circles*, MeOH-soluble fraction (excluding unreacted levoglucosan); *triangles*, water-soluble fraction; *squares*, insoluble fraction; *open inverted triangles*, gaseous fraction; *diamonds*, total
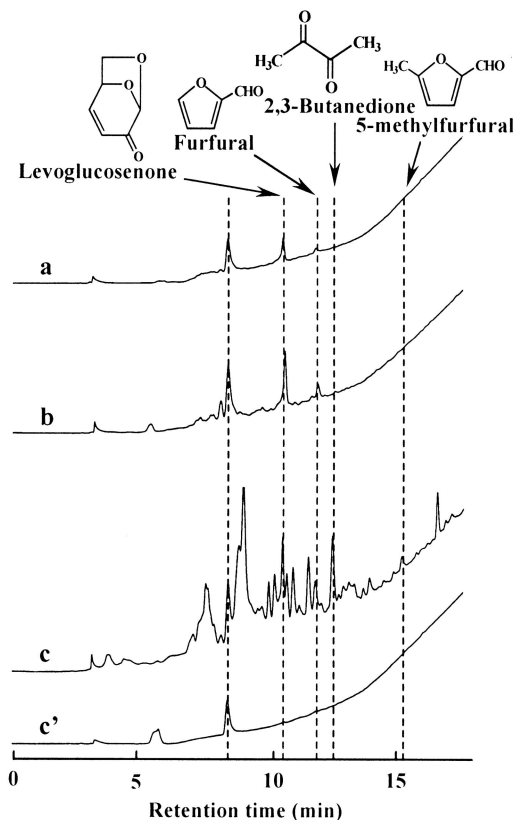

Fig. 3. High-performance liquid chromatography (HPLC) of the MeOH-soluble fractions obtained from pyrolysis of levoglucosan. **a** 250°C/2 min. **b** 300°C/2 min. **c** 400°C/2 min. **c′** 400°C/2 min/after evaporation under reduced pressure (2 mmHg) at 130°C for 30 min

under reduced pressure (2 mmHg) at 130°C for 30 min is included. By comparing these patterns with those of authentic compounds, the products observed at 11.0, 12.3, 12.9, and 15.6 min were identified as levoglucosenone, furfural, 2,3-butanedione, and 5-methylfurfural, respectively, which are formed by dehydration or fragmentation (or both) of levoglucosan. These structures were also confirmed with GC-MS. Some products, including levoglucosenone and furfural, were observed as major peaks in the chromatograms at 250°C and 300°C, respectively (Fig. 3, *a, b*). At 400°C (Fig. 3, *c*) the products observed as minor peaks in the chromatograms *a* and *b* are also observed as major peaks. Based on a comparison of chromatograms *c* and *c′*, almost all the products observed in chromatogram *c* are volatile. These chromatographic analyses indicate that the

MeOH-soluble fraction includes volatile LMW substances formed by dehydration and fragmentation.

Some results of gel permeation chromatography (GPC) analysis are shown in Fig. 4. In the chromatogram of the MeOH-soluble fraction (300°C/2 min), two small peaks at 8.2 and 9.1 min are observed, with a peak at 10.0 min that corresponds to unreacted levoglucosan. In contrast, the chromatogram of the water-soluble fraction (300°C/2 min) has broad peaks at a much shorter retention time, with shoulders similarly observed at 8.2 and 9.1 min. Figure 5 illustrates the ^{1}H-NMR spectrum of the water-soluble fraction (300°C/2 min) after acetylation. A broad signal observed around 2 ppm is assigned to the methyl proton of the acetyl group. Several broad signals around 3–6 ppm are observed in a magnetic field similar to that of the ring and C_6 protons of penta-O-acetyl-D-glucopyranose, which was used as a model compound. Furthermore, the ratio of the peak areas for these two signals was close to the theoretical value (acetyl methyl proton/ring and C_6 protons 9:7) for the acetylated linear glucose–polymer linked through glycosidic linkage. These GPC and NMR analyses indicate that the water-soluble fraction is mainly composed of polysaccharides formed through ring-opening polymerization of levoglucosan. Two peaks at 8.2 and 9.1 min observed on chromatogram *b* in Fig. 4 may correspond to oligosaccharides.
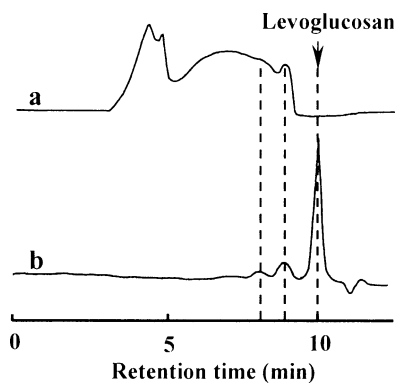
Fig. 4. Gel permeation chromatography (GPC) of the pyrolysis products from levoglucosan. **a** Water-soluble fraction (300°C/2 min). **b** MeOH-soluble fraction (300°C/2 min)
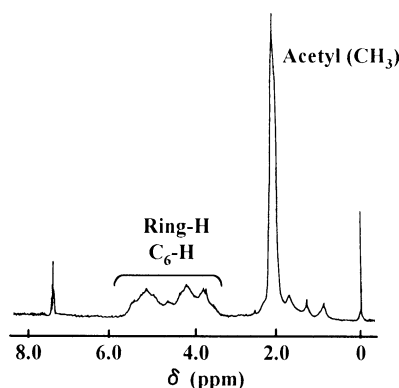

Fig. 5. Proton nuclear magnetic resonance (^{1}H-NMR) spectrum of the water-soluble fraction (300°C/2 min) after acetylation

Although further investigation is necessary to establish the detailed structure of the water-soluble fraction, polysaccharide formation by ring-opening polymerization of levoglucosan has been reported.[16–19] Ponder and Richards[19] prepared polysaccharide by thermal polymerization of levoglucosan in the presence of monochloroacetic acid at 170°C and reported the structure to have an α/β ratio of 2:1, with linkages including 1 → 6 (40%), 1 → 4 (22%), 1 → 3 (18%), and 1 → 2 (20%). Polysaccharides also have been isolated from tar fractions obtained by pyrolysis of cellulose[9] and cellobiose,[20] and their structures have been characterized as randomly linked polysaccharides without a reducing end-group.

Consequently, the change in the product composition in Fig. 2 (levoglucosan → MeOH-soluble fraction) is explained by two simultaneously occurring reactions: transformation to volatile LMW products and ring-opening polymerization into oligosaccharides. The subsequent change (MeOH-soluble → water-soluble fraction) is explained by the polymerization from oligosaccharides soluble in MeOH to polysaccharides soluble in water.

Insoluble fractions were not soluble in the usual solvents, including CHCl₃, dioxane, tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), dimethylsulfoxide (DMSO), and ethanol. Moreover, they showed characteristic IR spectra as observed during the carbonization of cellulose,[21,22]
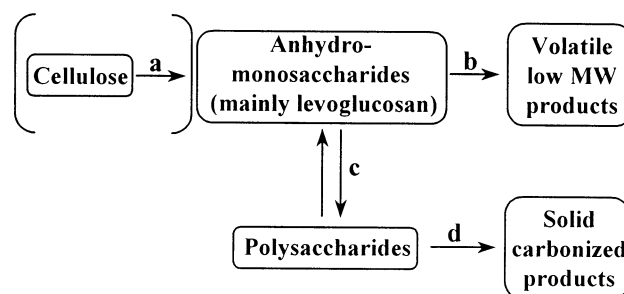

Fig. 6. Proposed pathway (*a–d*) of cellulose pyrolysis via anhydromonosaccharide. *MW*, molecular weight

including absorption around 1640 and 1700 cm^{-1}, which are assigned to conjugated double bond and carbonyl groups, respectively, with decreased absorption around 900–1200 cm^{-1} corresponding to C—O stretching. These observations indicate that change in the product composition in Fig. 2 (water-soluble → insoluble fractions) corresponds to the conversion from polysaccharides to carbonized products.

Polymerization reaction of levoglucosan

To obtain more detailed information about polymerization of levoglucosan, the water-soluble (polysaccharide) fraction was also pyrolyzed. After confirming the complete removal of levoglucosan using GC, the water-soluble fraction (300°C/2 min) was pyrolyzed again at 400°C for 1 min. As a result, closely similar results were obtained between levoglucosan pyrolysis and polysaccharide pyrolysis. Interestingly, HPLC chromatograms were almost identical even for the minor products; furthermore, levoglucosan was also determined in a 7.0% yield from GC analysis of the MeOH-soluble fraction obtained from polysaccharide pyrolysis. These results strongly indicate that the polymerization reaction of levoglucosan is reversible and that levoglucosan and polysaccharides exist as an equilibrium mixture during pyrolysis before other reactions occur, including dehydration and fragmentation.

Pathway of cellulose pyrolysis via anhydromonosaccharide

A pathway of cellulose pyrolysis via anhydromonosaccharide (Fig. 6) is proposed. Anhydromonosaccharide, mainly levoglucosan, which is the primary product formed during cellulose pyrolysis, undergoes two simultaneous reactions: transformation into volatile LMW products (Fig. 6, *b*) and ring-opening polymerization into polysaccharides (Fig. 6, *c*, a reversible reaction). Polysaccharides are then successively converted to the solid carbonized products (Fig. 6, *d*).

Although transformations *b* and *d* in Fig. 6 may include similar reactions (e.g., dehydration and fragmentation) to produce conjugated structures, their effects on the resulting products are quite different. Transformation *b* for

anhydromonosaccharides leads to the formation of volatile LMW products because it enhances the volatility of the products by lowering the boiling point, which results in quick removal from the heated zone. In contrast, transformation *d* in the nonvolatile polysaccharides leads to irreversible formation of solid carbonized products by staying in the heated zone. Thus, with this pathway, equilibrium between anhydromonosaccharide (monomer) and polysaccharide in reaction *c* is important for the resulting product composition. Under favorable conditions for anhydromonosaccharides volatile LMW products are preferentially produced, whereas under favorable conditions for polysaccharides the formation of solid carbonized products is favored.

This proposed pathway, which includes the polymerization reaction of anhydromonosaccharides as a key reaction for carbonized product formation, was also supported by the experimental result that pyrolysis of levoglucosan (10.0 mg) at 300°C in sulfolane (tetrahydrothiophene 1,1-dioxide) (1.0 ml), a good solvent for levoglucosan with a high boiling point (285°C), produced completely soluble products without formation of any insoluble carbonized products even after 5 min of pyrolysis. Anhydromonosaccharide is expected to stabilize for polymerization in sulfolane by dispersing anhydromonosaccharide molecules in solution. This proposed pathway can provide useful information for exploiting the more selective conversion process of cellulosic biomass into fuels and chemicals based on effective thermochemical reactions.

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