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Pyrolysis of cellulose in aromatic solvents: Reactivity, product yield, and char morphology

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ABSTRACT

Aromatic solvents are known to stabilize levoglucosan (1,6-anhydro-β-D-glucopyranose), the major pyrolysis intermediate of cellulose, against thermal degradation including char formation. In this article, pyrolysis of cellulose, a crystalline component of biomass, was investigated in the aromatic solvents 1,3-diphenoxybenzene, diphenyl sulfide, and benzophenone under nitrogen at 280 °C. Thermal degradation of cellulose (Whatman filter paper) was markedly delayed in the aromatic solvents and gave thin film-like char after the removal of unreacted cellulose through hydrolysis. The yields of levoglucosan and 5-hydroxymethylfurfural were greatly enhanced in the aromatic solvents. These observations are discussed at the molecular level in terms of the interactions of cellulose crystallites and the pyrolysis products with the aromatic solvents. A possible char formation mechanism via 5-hydroxymethylfurfural involving the ultrastructure of the cell wall is also discussed. This study provides insight into the molecular-based cellulose pyrolysis mechanisms and efficient and selective thermochemical production of bio-based materials and chemicals.

1. Introduction

Pyrolysis is defined as thermal degradation occurring under limited oxygen supply and is the fundamental basis of various thermochemical conversion technologies, like fast pyrolysis, gasification, carbonization, and torrefaction, for production of biofuels, biochemicals, and biomaterials from biomass resources. However, these technologies are limited by their low product selectivity, which usually makes their practical application difficult. For example, separation of desired products from a complex pyrolysis mixture is a tedious and costly process for biochemical production, and char formation makes the composition more complex along with decreasing productivity. Better understanding of the chemistry involved in biomass pyrolysis could provide insights to aid the development of controlled pyrolysis systems for sustainable utilization of biomass, which is the only renewable organic resource on Earth.

Pyrolysis of cellulose, the most abundant component of biomass, produces a substantial yield of levoglucosan (LG, 1,6-anhydro-β-D-glucopyranose) [1,2], which is an important intermediate. Thus, LG and related compounds are promising biochemicals. However, the efficient production of LG is not easy, because thermal polymerization and dehydration reactions of LG occur at > 250 °C [3,4], which is much lower than the temperature required for the formation of LG from cellulose (around 350 °C) [5]. Accordingly, cellulose-derived pyrolysis vapor forms coke by changing into the molten phase through cooling [6]. This apparently contradicting observation can be explained by the stability of gaseous LG [7], in which intermolecular hydrogen bonding is much less effective than in the molten LG, because the pyrolysis reactions of molten LG are believed to be promoted by hydrogen bonding [3,5,8–12]. Intermolecular hydrogen bonds act as an acid catalyst to promote transglycosylation and dehydration reactions. Such features may also exhibit complex effects on the mass-transfer efficiency of LG out of the cell wall, which affects the progression of secondary reactions including char formation.

LG and other glycosides are known to be stabilized in aromatic [3,13] and polyether [8] solvents up to around 350 °C. Hosoya et al. [13] reported that the stabilization efficiency increased in direct correlation with the π-electron density of aromatic solvents. This is because π electrons of aromatic solvents [3] and ether oxygens of polyethers [8] act as hydrogen bond acceptors for hydroxyl groups of these glycosides, inhibiting proton donation to the carbohydrate molecules. Based on this stabilization mechanism, complete solvation of carbohydrate molecules would be critical to maximize this stabilization effect, so insoluble cellulose is expected to behave very differently to soluble compounds.

The ultrastructure of cellulose may affect its pyrolysis behavior. The cotton cellulose used in this study has cell walls consisting of cellulose microfibrils. Cellulose pyrolysis starts with a decrease of the degree of

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polymerization (DP) to around 200 [14–16], corresponding to the length of cellulose crystallites [17–21], and subsequent thermal decomposition occurs from the crystallite surface [22–24]. Accordingly, the formation of primary pyrolysis products and their secondary reactions including char formation occur inside the cell wall. Thus, the aromatic solvent must penetrate into the cell wall to control the pyrolysis reactions.

Shoji et al. [25] reported that cellulose was completely converted into volatile products by fast pyrolysis of cellulose–aromatic solvent mixtures with the complete inhibition of char formation. They also claimed that polar aromatic substituents are necessary to realize this behavior. Such substituents may help the aromatic compound to penetrate into the space between crystallites. Nevertheless, the action of aromatic solvents on the cell wall remains unclear. In this paper, the influences of aromatic solvents during cellulose pyrolysis are investigated focusing on the accessibility of the solvent to the cellulose crystallite surface by careful analysis of the pyrolyzed cellulose obtained in the presence of aromatic solvents in nitrogen at 280 °C.

2. Experimental

2.1. Materials

Whatman No. 42 filter paper (Whatman PLC, UK, cotton, moisture content: 4.9 wt%, dry basis) was used as a cellulose sample. Diphenyl sulfide [DPS, melting point (mp) −40 °C, boiling point (bp) 296 °C], 1,3-diphenoxybenzene (DPB, mp 166–171 °C, bp 375 °C), and benzophenone (BPH, mp 47–51 °C, bp 305 °C) were purchased from Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan), Wako Pure Chemical Industries, Ltd. (Osaka, Japan) and Nacalai Tesque, Inc (Kyoto, Japan), respectively, (Fig. 1) and used without further purification. DPS is a thioether derivative with lower molar mass than that of DPB, while BPH has a carbonyl substituent that is expected to interact effectively with the hydrophilic surface of cellulose crystallites. Although DPB and BPH are solids at room temperature, they melted during the heating process to form liquids. All these solvents were stable up to the temperatures corresponding to their respective bp.

2.2. Pyrolysis and characterization of low-molecular-weight products

Cellulose (40 mg, 38 mg dry basis) and aromatic solvent (400 mg) were placed at the bottom of a Pyrex glass tube reactor (internal diameter 8.0 mm, wall thickness 1.0 mm, length 300 mm), and then the reactor was connected to a nitrogen bag through a three-way tap. After the air inside the reactor was replaced with nitrogen using an aspirator, the reactor was inserted into a muffle furnace preheated to 280 °C. After heating for 60 min, the reactor was removed from the furnace and immediately cooled with an air flow.

The resulting pyrolysis mixture was extracted in dimethylsulfoxide (DMSO)-d_6 (0.7 mL) containing maleic acid as an internal standard and hydroxylamine hydrochloride (10 mg), an oximation reagent. The soluble portion was analyzed by ^{1}H NMR spectroscopy with a Bruker AC-400 (400 MHz) spectrometer. The residue was washed successively

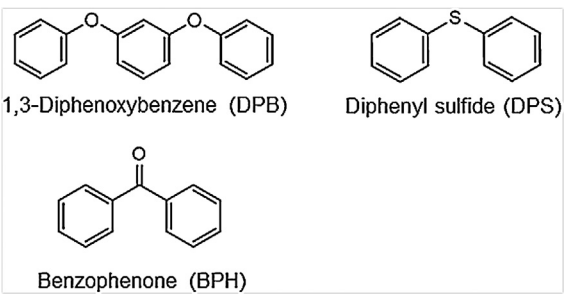

Fig. 1. Chemical structures of aromatic solvents used in cellulose pyrolysis experiments.

with chloroform (5 mL, five times) and methanol (5 mL, five times), dried in an oven at 105 °C for 24 h, and then analyzed by the various methods described in Section 2.3.

To determinate the low-molecular-weight products, the pyrolyzed cellulose was extracted with a binary mixture of D_2O (1.0 mL) and $CDCl_3$ (1.0 mL) containing maleic acid (internal standard) and the oximation reagent (10 mg). With this procedure, the aromatic solvents were nicely separated into the $CDCl_3$-solbule fraction, whereas the cellulose-derived pyrolysis products were recovered in the D_2O-soluble fractions. The resulting residues were further extracted with DMSO-d_6 (1.0 mL) containing the oximation reagent (10 mg). The cellulose-derived products were determined with the first D_2O-soluble and second DMSO-d_6-soluble fractions by ^{1}H NMR spectroscopy. Identification of the products was conducted by comparing the spectra with those of authentic compounds.

Control experiments were conducted in a similar manner without the addition of aromatic solvent. A heating period of 58 min was used for the control experiments because the presence of aromatic solvent delayed the heating process by 2 min based on the results of direct temperature measurement with a fine thermocouple (0.25 mm in diameter, type K, Shinnetsu Co., Ltd., Ibaraki, Japan). Experiments with a shorter pyrolysis period (10 min in aromatic solvent and 8 min for control) at 280 °C were also conducted following a similar process. All experiments were repeated at least twice to confirm the reproducibility of the results, although the data have not been treated statistically.

2.3. Characterization of the pyrolysis residue

Unreacted cellulose was determined as anhydroglucose that was obtained by the acid hydrolysis of the pyrolysis residue. First, aq. H_2SO_4 (72 wt%, 0.1 mL) was added to the residue and then the mixture was heated at 30 °C for 60 min with frequent agitation by a glass rod. The resulting transparent liquid was diluted with water (2.8 mL) and then heated in an autoclave at 121 °C for an additional 60 min. The hydrolyzate (1.0 mL) was added to a vial and diluted with water (9.0 mL). After removing the sulfuric acid in the solution using an OnGuard II/A ion-exchange cartridge (Dionex, Sunnyvale, USA), the glucose yield in the solution was determined by ion chromatography (IC) on an ICS-3000 ion chromatograph (Dionex) under the following conditions: column, CarboPac PA1 (4 × 250 mm, Dionex); column temperature, 25 °C; eluent, 2 M NaOH (8%) in ion-exchanged water; flow rate, 1.0 mL min^{-1}; carrier gas, N_2. The obtained glucose yield was converted to that corresponding to anhydroglucose by multiplying by 162/180.

Small portions of pyrolysis residue and the residue after acid hydrolysis were sampled using a micromanipulator (Micro Support Co., Ltd., Shizuoka, Japan). Their infrared (IR) spectra were recorded in transmission mode with a Nicolet Continuum FT-IR microscope attached to a Nicolet iS10 FT-IR spectrometer (Thermo Scientific, Madison, WI, USA).

The color of cellulose and its pyrolysis residue was measured with a ZE6000 color meter (Nippon Denshoku Industries Co., Ltd., Tokyo, Japan). CIELAB parameters [brightness (L^*), redness (a^*), and yellowness (b^*)] were determined in reflectance mode according to standard JIS Z-8722 using illuminant C and an observation angle of 2°. Total color difference (ΔE^*) was calculated from the following equation:

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{\frac{1}{2}} \quad (1)$$

Molecular weight (MW) distribution was evaluated by gel-permeation chromatography (GPC) for phenyl carbamate derivatives of cellulose and its pyrolysis residues. Phenyl isocyanate (0.2 mL) was added to a suspension of each sample (5 mg) in pyridine (2 mL), and then the mixture was stirred at 80 °C. After reaction for 24 h, the mixture formed a transparent solution. Methanol (0.5 mL) was added to the reaction mixture to terminate the reaction, and then the solvent was removed by