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Hydroxymethylfurfural as an Intermediate of Cellulose Carbonization

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Hydrogen bond donor solvents such as aromatic solvents inhibit the secondary degradation of cellulose-derived primary pyrolysis products. In a previous study, we found that the formation of solid carbonized products was completely inhibited during cellulose pyrolysis in aromatic solvents, with 5-hydroxymethylfurfural (5-HMF) recovered in certain yields instead. This indicated that 5-HMF is an intermediate in cellulose carbonization. To confirm this hypothesis, the thermal reactivity of 5-HMF was investigated. At 280 °C, pure 5-HMF polymerized into a hard glassy substance through OH group elimination, but further conversion was slow. When pyrolyzed in the presence of glycerol, a model of coexisting primary pyrolysis products from cellulose, a coupling reaction proceeded. Reactions characteristic of cellulose carbonization then occurred, including the formation of acidic groups and benzene-type structures in the solid products. These results confirmed the above hypothesis. The molecular mechanism of cellulose carbonization is discussed, focusing on the crystalline nature.

1. Introduction

Cellulose is among the most abundant renewable polymeric organic chemicals on earth. Therefore, the development of efficient conversion methods to expand cellulose use and help establish the use of sustainable resources is important. Thermochemical conversion technologies, such as pyrolysis, gasification, and carbonization, are potential methods. In such thermochemical conversion techniques, the composition of the final products depends on the progress of the secondary reactions of the primary pyrolysis products from cellulose. Reactions that form solid carbonized products are particularly important. Promoting these reactions results in more efficient production of charcoal, which can also be used as biochar for carbon capture and storage to mitigate global warming. However, inhibiting the reactions that form solid carbonized products leads to the efficient production of bio-oil, which can be used to produce liquid fuels and industrial chemicals. Therefore, elucidating the molecular mechanism of carbonization in cellulose pyrolysis is important for reaction control.

Changes in the chemical structure of cellulose char during pyrolysis have been studied by infrared (IR) spectroscopy,[1–4] elemental analysis,[1] solid ^{13}C nuclear magnetic resonance (NMR),[2,4–6] pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS),[4] and other techniques. Characteristic IR bands appear at 1600 and 1700 cm^{-1} early in cellulose pyrolysis.[1–4] These bands have been assigned to conjugated C=C bonds, such as in benzene rings, and carbonyl (C=O) groups, respectively, both of which are considered to form through dehydration reactions,[1–4] although the mechanistic details are currently unknown. Based on the van Krevelen diagram, dehydration has been reported to be the major process during cellulose pyrolysis in the temperature range of 200–280 °C,[7] as also confirmed by the production of large amounts of water.[8]

As a result of dehydration reaction, benzene-ring structures are formed in cellulose char.[2,4–6,9,10] Smith and Howard[9] reported the formation of benzenecarboxylic acids from cellulose char by alkali permanganate oxidation as evidence of the benzene rings found in cellulose char prepared at temperatures above 200 °C. Shafizadeh and Sekiguchi[10] reported that, under fast pyrolysis conditions, benzene rings developed rapidly in the temperature range of 350–400 °C.

Pastrova et al. have indicated the roles of furan-type intermediates in benzene ring formation during cellulose pyrolysis.[4] The authors characterized cellulose chars prepared at different temperatures using Py-GC/MS. Although 1,6-anhydro-β-D-glucopyranose (levoglucosan) was the major product detected from cellulose char prepared at 250 °C, by increasing the pyrolysis temperature of char preparation, the major compounds changed to furans and benzenes in the temperature range of 270–350 °C and to benzenes above 350 °C, which has also been supported by solid ^{13}C NMR. Based on these results, they concluded that the chemical structure of cellulose char changes from cellulose→furan→benzene types with the progress of carbonization. However, no further studies have been reported on the mechanism of cellulose carbonization.

In the hydrothermal carbonization of reducing sugars, furfural and 5-hydroxymethylfurfural (5-HMF) have been suggested as intermediates in the formation of solid carbonized products, known as hydrothermal char.[11–14] However, the

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treatment conditions are different, and the reducing sugars used for treatment are different from cellulose, which is a crystalline polysaccharide. Accordingly, direct evidence is needed to determine whether furfural and 5-HMF are involved in cellulose carbonization.

We recently reported the negative relationship between the yields of 5-HMF and solid carbonized products in cellulose pyrolysis under nitrogen or in various aromatic solvents.[15] Aromatic solvents were used to stabilize the cellulose-derived primary pyrolysis products, such as levoglucosan, by forming OH-π hydrogen bonds, which inhibit the formation of intermolecular hydrogen bonds that act as acid and base catalysts during pyrolysis.[15,16] For example, when cellulose was pyrolyzed in benzophenone at 280 °C for 60 min, the yield of 5-HMF increased from 0.0 wt% (under N_2) to 6.4 wt%, while that of solid carbonized products, obtained as the hydrolysis residue, was decreased from 50.7 wt% (under N_2) to 0.0 wt%. Although any 5-HMF was not detected under N_2, 5-HMF was thought to decompose into carbonized products rather than evaporate at 280 °C, which is below the estimated boiling point, 291.5 ± 30.0 °C.[17] In pyrolysis of cellulose, 5-HMF is known to be produced.[18,19] We do not believe that the functional groups of aromatic solvents, namely the benzene ring, ether oxygen, and carbonyl (in the case of benzophenone), greatly influenced the formation of 5-HMF during the pyrolysis of cellulose. From these results, we hypothesized that solid carbonized products were formed via 5-HMF in cellulose pyrolysis.

In the present study, to test our hypothesis, the pyrolytic reactivity of 5-HMF was evaluated by comparing the chemical structures in the resulting char with those in cellulose char using IR, acid titration, and Py-GC/MS. Finally, a mechanism for cellulose carbonization via 5-HMF was proposed and discussed in terms of the crystalline nature of cellulose.

Figure 1. Examples of spectra from in situ IR measurement of cellulose and 5-HMF under nitrogen.

2. Results and Discussion

2.1. In Situ IR Spectroscopy

Figure 1 shows some examples of IR spectra of cellulose and 5-HMF obtained by in situ measurement using a GladiATR system at a heating rate of 10 °C/min. This system allowed continuous monitoring of the spectrum during heating, which enabled identification of the temperature range in which the spectrum changed. The cellulose spectrum began to change at 280 °C, with signals characteristic of cellulose carbonization appearing at 1600 cm^{-1} (C=C) and 1700 cm^{-1} (C=O).[1–4] Furthermore, the hydroxyl group signal (3000–3500 cm^{-1}) gradually shifted toward a higher wavenumber with increasing temperature, attributed to hydrogen bond cleavage.[20–22] After heating for 60 min at 280 °C, the shape of the OH signal changed to be characteristic of carboxyl groups.[23]

When 5-HMF was heated, the signal assigned to OH groups (3000–3500 cm^{-1}) disappeared completely at around 170 °C, which indicates that the OH group in 5-HMF was removed in this temperature range. When the temperature was raised further, the OH signal reappeared at 225 °C, but the shape was
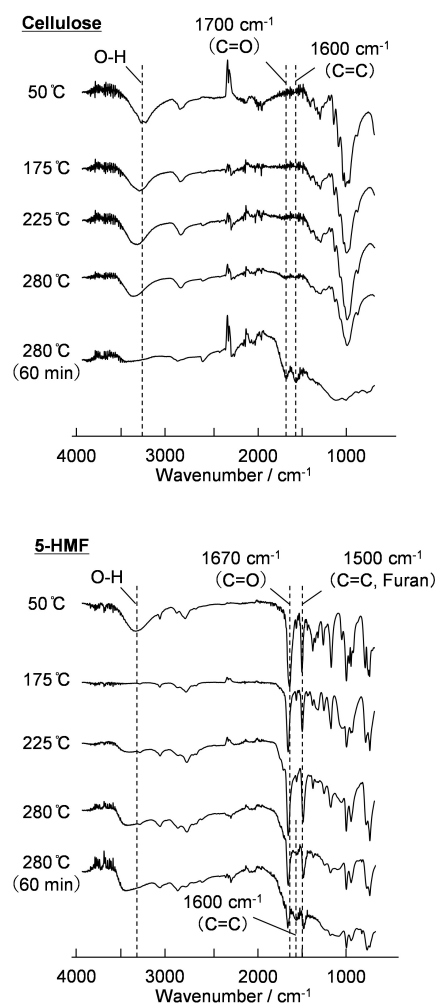
now characteristic of carboxyl groups. As observed in cellulose, the signals at 1600 and 1700 cm^{-1} were broad, but those assigned to the furan ring (1670 cm^{-1}) and aldehyde group (1700 cm^{-1}) of 5-HMF were retained, even after heating at 280 °C for 60 min. Therefore, 5-HMF underwent similar structural changes to cellulose, as reflected in the IR spectra, although 5-HMF showed slower conversion.

2.2. Thermal Polymerization of 5-HMF

As in situ IR measurements indicated OH group removal from 5-HMF at around 170 °C, polymerization reactions were expected to occur. 5-HMF is a potential feedstock for the production of renewable plastics, but most related studies have utilized 5-HMF derivatives, such as 2,5-bis(hydroxymethyl)furan and 2,5-furandicarboxylic acid.[24–27] Accordingly, information on the polymerization of 5-HMF by heating is limited.[28] Therefore, the polymerization behavior of 5-HMF was evaluated at 280 °C.

The heat-treatment product of 5-HMF was extracted with acetone to separate soluble and residual constituents. The

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residue was obtained as a glassy material and was insoluble in other solvents, such as methanol, tetrahydrofuran, dimethyl sulfoxide, and chloroform, which indicated a highly condensed product. Gel-permeation chromatography (GPC) of the acetone-soluble portions (Figure 2), conducted after heating at 280 °C
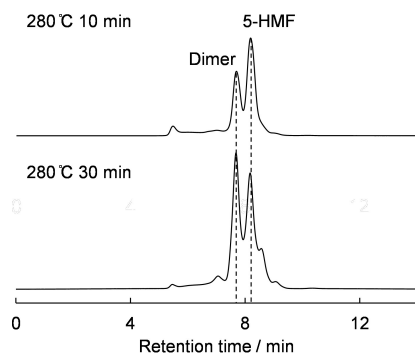

Figure 2. GPC chromatograms of acetone-soluble portions of 5-HMF pyrolysis mixtures (280 °C, 10 and 30 min).
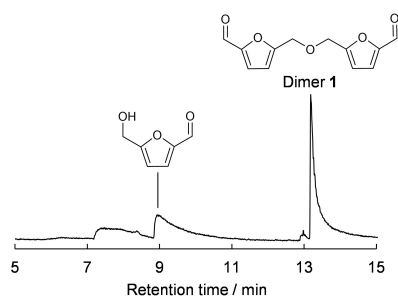

Figure 3. Total-ion chromatogram of acetone-soluble portion of 5-HMF pyrolysis mixture (280 °C, 30 min).
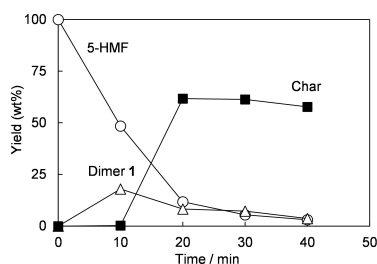

Figure 4. Time-course change of pyrolysis products from 5-HMF at 280 °C. ○: 5-HMF, △: dimer **1**, ■: char

for 10 and 30 min heating, exhibited two large signals corresponding to unreacted 5-HMF and a dimer.

This was confirmed by GC/MS analysis (Figure 3). Using thin layer chromatography (TLC; solvent system, ethyl acetate/hexane = 1:2), a 5-HMF dimer, 5,5'(oxy-bis(methylene))bis-2-furfural (**1**), was isolated and identified by ^{1}H NMR, ^{13}C NMR, and GC/MS (Figure S1 in the Supporting Information). Dimer **1** has been reported from treating 5-HMF under acidic conditions[29–31] or by heating at 210 °C.[28]

Figure 4 shows the effect of the heating period on the yields of dimer **1**, insoluble residue (char), and unreacted 5-HMF. At 10 min, no char was detected, but the amount of 5-HMF was reduced by about half and dimer **1** was produced in a 17.9 wt% yield. This indicated that dimer **1** was formed initially, and then char was generated. When extended to 30 min, char was produced in 61.3 wt% yield, but the principle components detected in the GPC chromatogram were dimer **1** and unreacted 5-HMF (Figure 2). Therefore, the polymerization of 5-HMF proceeded quickly to give insoluble char, and small amounts of polymerization products that were soluble in acetone, except for dimer **1**, although the role of the dimer is currently unknown. In situ IR measurement of 5-HMF (Figure 1) showed that unreacted 5-HMF completely disappeared at 175 °C. Unreacted 5-HMF (estimated boiling point, 291.5 ± 30.0 °C)[17] was removed by evaporation during in situ IR measurements, because the polymerization reactivity of 5-HMF at 175 °C was lower according to the results in Figure 4.

Next, glycerol was used as a model compound for cellulose-derived pyrolysis products that were expected to coexist with 5-HMF in cellulose pyrolysis, as discussed later. Accordingly, the polymerization reactivity of 5-HMF in the presence of glycerol was investigated at 280 °C. The heat-treated mixture of 5-HMF (200 mg) and glycerol (200 mg) was separated using a binary solvent system of water and ethyl acetate. The resulting water-soluble portion was separated by TLC using 5% MeOH/CHCl$_3$ and subsequently 7% MeOH/CHCl$_3$ (five times) to give coupling product 5-[(2,3-dihydroxypropyoxy)methyl]-2-furaldehyde (**2**) in 14.4 mol% yield. No glassy solid products were produced in the presence of glycerol, which indicates that the polymerization of 5-HMF was inhibited by glycerol.

The ^{1}H NMR spectrum of the coupling product is shown in Figure 5 and compared with that of the acetate derivative (also see Figure S2 in the Supporting Information). The protons assigned to the aldehyde (H$_1$, 9.62 ppm) and furan ring (H$_2$,
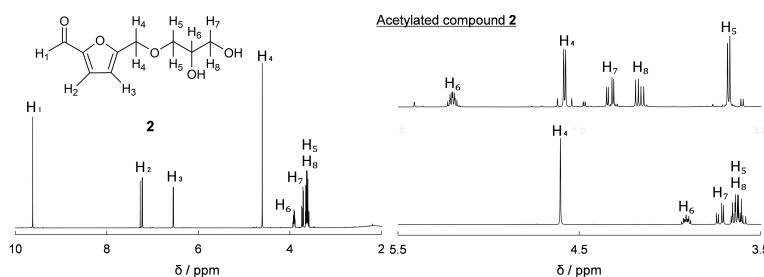

Figure 5. ^{1}H NMR spectrum of compound **2** obtained from the pyrolysis of 5-HMF and glycerol at 280 °C for 20 min, as compared with the spectrum of acetylated compound **2**.

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7.22; H3, 6.55 ppm) were observed, along with protons assigned to the glycerol moiety at 3.5–4.0 ppm, which confirms that this was the coupling product of glycerol and 5-HMF. Acetylation caused the signals for H6, H7, and H8 to be shifted downfield because of the influence of electron-withdrawing acetyl groups, while the effect on the chemical shifts of signals assigned to H4 and H5 was small. These results indicated the coupling position between glycerol and 5-HMF moieties in compound **2**. ^{13}C NMR, GC/MS, and UV spectra of compound **2** are shown in Figure S3 in the Supporting Information, as compound **2** has not been reported previously. These results indicated that 5-HMF combined with other cellulose-derived products containing hydroxy groups during cellulose pyrolysis.

Polymerization, dimerization, and coupling reactions between glycerol and 5-HMF would occur via the mechanisms shown in Figure 6. The OH group on 5-HMF is removed, assisted by electron donation from the oxygen in the furan ring. The resulting oxonium intermediate is attacked by the hydroxyl groups of 5-HMF and glycerol to form dimer **1** and glycerol-adduct **2**, respectively. In the absence of glycerol, the homopolymer of 5-HMF (5-HMF char) formed as a glassy solid substance through nucleophilic addition of 5-HMF, containing several nucleophilic sites, to the oxonium intermediate.

2.3. Conversion of 5-HMF in the Presence of Glycerol

In actual cellulose pyrolysis, 5-HMF coexists with other pyrolysis products, including carbohydrates, such as levoglucosan, oligosaccharides, and anhydro-oligosaccharides, fragmentation products, and water. Therefore, the influence of these coexisting materials on the carbonization of 5-HMF must be considered. However, when these compounds are mixed with 5-HMF, it is difficult to determine which lead to the formation of carbonized products. Therefore, glycerol and water were selected to be mixed with 5-HMF to obtain reaction conditions closer to that of actual cellulose. Glycerol contains three hydroxyl groups, but was stable at 280°C.

A mixture of 5-HMF (500 mg) and glycerol (4.0 g) was heated at 280°C for 60 min, and solid char was obtained by washing with water and then oven-drying. Figure 7 shows the appearance and IR spectrum of the resulting char, which was compared with those prepared from cellulose and pure 5-HMF.
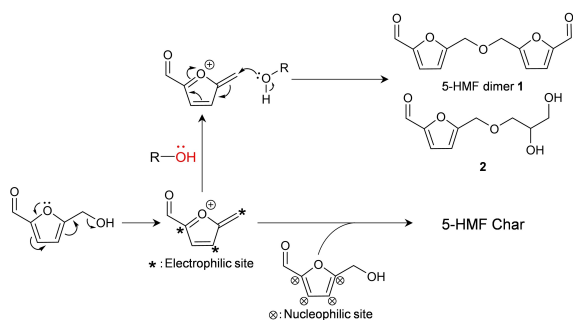

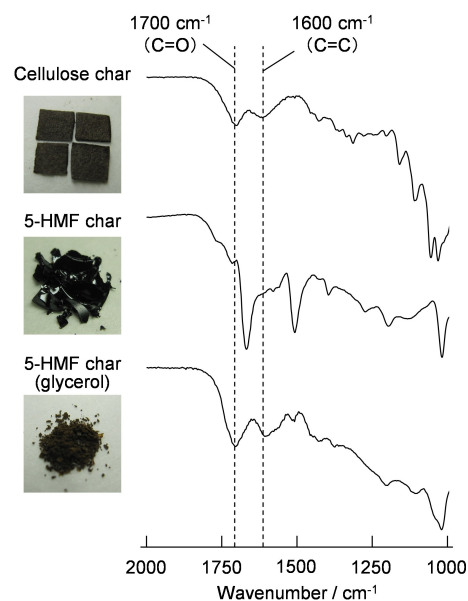**Figure 6.** Proposed condensation mechanisms of 5-HMF during heat treatment.

Figure 7. IR spectra of char fractions obtained from the pyrolysis of cellulose and 5-HMF at 280°C for 60 min.

The char produced in the presence of glycerol is denoted as 5-HMF char (glycerol). By mixing with glycerol, the signals assigned to 5-HMF moieties disappear completely, with two signals appearing at 1600 and 1700 cm^{-1}, which are characteristic of cellulose carbonization. These results indicated that the carbonization reactions of 5-HMF moieties dispersed in the 5-HMF char (glycerol) proceeded efficiently, in contrast to the previously described hard glassy 5-HMF char.

2.4. Acidic Group Determination

Table 1 summarizes the results of acidic group titration performed using the Boehm method. This allowed carboxylic acids, phenolic acids, and lactones (carboxyesters) to be quantified separately according to the alkalinity of the solution used for neutralization. Although the relative compositions were different, carboxylic acids, lactones, and phenols were detected in certain amounts from cellulose char and 5-HMF char (glycerol). Consequently, the formation of these functional groups, which are characteristic of cellulose carbonization,[32–36] also occurred by heating 5-HMF in the presence of glycerol.

The formation of carboxylic acids and esters was also confirmed by changes in the IR spectrum caused by neutralization (Figure 8). The signal at 1700 cm^{-1}, assigned to carboxyl

Table 1. Contents of acidic groups in cellulose and 5-HMF char.

(mmol/g)	Carboxylic acid	Lactone	Phenol
Cellulose char	0.556	0.177	2.68
5-HMF char	nd	nd	nd
5-HMF char (glycerol)	0.104	0.273	0.169

nd: not detected.

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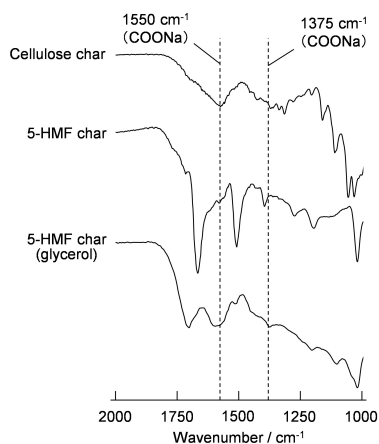European Chemical
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Figure 8. IR spectra of cellulose char and 5-HMF char (280 °C, 30 min) after alkali treatment.

(COOH) and lactone (−COO−) groups, showed reduced intensity, while signals appeared at 1375 and 1550 cm^{-1}, assigned to carboxylate (COO$^-$) groups.

The IR spectrum of the 5-HMF char (Figure 1) prepared from pure 5-HMF contained signals that indicated the formation of carboxylic acids, but these groups could not be titrated (Table 1). The IR spectrum also did not change under treatment with alkaline solution (Figure 8). These results indicated that alkaline solution might not be able to penetrate inside the glassy 5-HMF char.

2.5. Py-GC/MS Analysis

The chemical structure of char obtained from 5-HMF was evaluated by Py-GC/MS analysis, which was performed at 764 °C with a solid heating period of 5 s. Substructures formed in the char were expected to be released and identified using this method. Figures 9 and 10 show the total-ion chromatograms (pyrograms) and chemical structures of the compounds identified, respectively.

When a mixture of 5-HMF and glycerol was directly analyzed by Py-GC/MS without prepyrolysis, large signals of 5-HMF and glycerol were observed, along with a relatively small peak assigned to methylfurfural (**5**). Therefore, most 5-HMF and glycerol evaporated without suffering thermal degradation, although methylfurfural was formed by cleavage of the C−OH bond in 5-HMF through Py-GC/MS analysis.

In the pyrogram of 5-HMF char, the large 5-HMF signal disappeared and methylfuran (**3**) and dimethylfuran (**4**) were produced as furanic compounds, along with methylfurfural (**5**). This indicated that 5-HMF reacted to form other furan-type structures. The formation of benzene-type (benzene (**11**), toluene (**13**), and naphthalene (**17**)) and benzofuran-type (methylbenzofuran (**19**)) compounds indicated that benzene rings were formed in the 5-HMF char, as these types of product were not detected in the pyrogram of 5-HMF + glycerol (untreated).

By adding glycerol, the number of products detected in the pyrogram increased, and methylfurfural (**5**), observed as a large
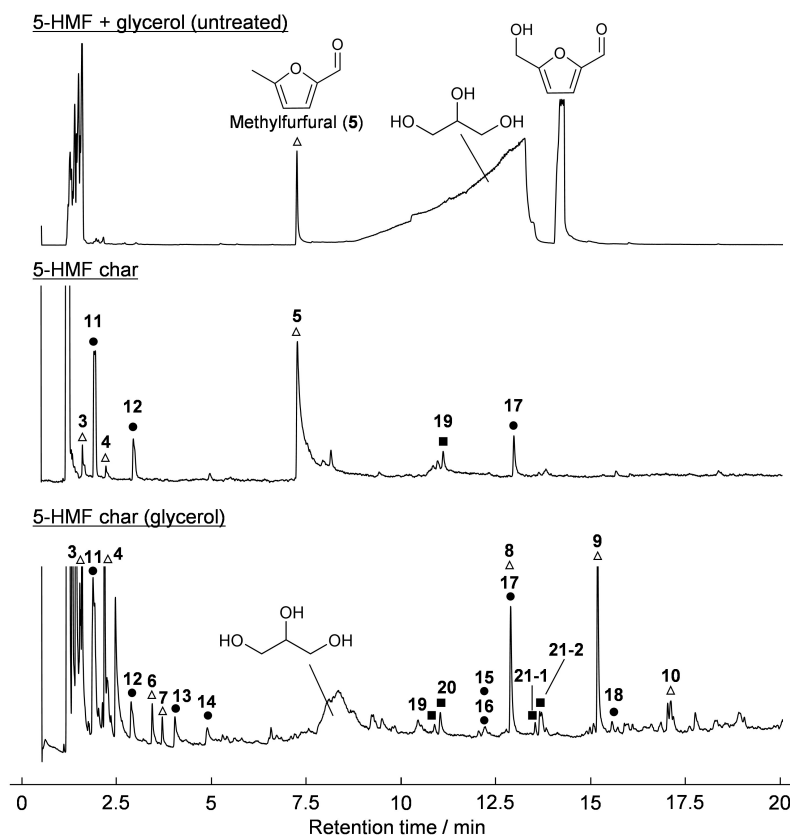

Figure 9. Pyrograms obtained by Py-GC/MS analysis (764 °C, 5 s) of 5-HMF char obtained by pyrolysis at 280 °C for 60 min.

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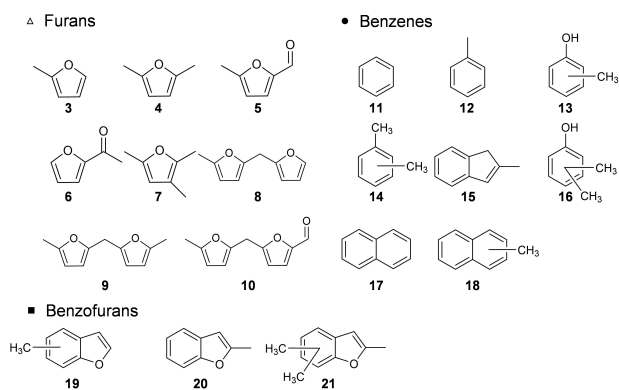European Chemical
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Figure 10. Chemical structures of products identified in Py-GC/MS analysis (764 °C, 5 s) of 5-HMF char obtained by pyrolysis at 280 °C for 60 min.

Figure 11. Proposed cellulose carbonization mechanism focusing on the cell wall ultrastructure and role of 5-HMF.

signal in the 5-HMF char, disappeared completely. These results confirmed that carbonization reactions of 5-HMF proceeded efficiently by dilution with glycerol. The formation of furanic compounds **6–10** also confirmed that condensation reactions of 5-HMF occurred. Indene (**15**) and phenol (**13** and **16**) were also detected, which are known to be substructures of carbonized products from cellulose.[4] Phenol formation was consistent with the acid titration results.

2.6. Role of 5-HMF in Cellulose Carbonization Mechanism

Natural cellulose is a cellular substance with a cell wall several micrometers thick that is an aggregate of hundreds of crystallites (6×6 nm, in cross section[37]). Based on X-ray diffraction analysis,[38–40] the thermal degradation of cellulose crystallites is thought to begin with surface molecules, while the internal molecules are stable. Furthermore, thermal degradation of cellulose was reported to be delayed significantly by removing the reducing end through $NaBH_4$ reduction or thermal glycosylation with glycerol.[41–43] Consequently, on a nanoscale, the thermal degradation of cellulose proceeds heterogeneously in the cell wall, although our previous work on observing cellulose carbonization using UV microscopy showed that cellulose carbonization progressed uniformly within the cell wall at a resolution of 280 nm.[44] These results indicated that pyrolysis begins heterogeneously, but with the area evenly distributed within cell wall. Accordingly, a carbonization reaction mechanism was proposed, as shown in Figure 11.

The first event when heating cellulose is a decrease in the degree of polymerization (DP) to around 200, which corresponds to the size of cellulose crystallites in the length direction.[45,46] The reducing end of the cellulose crystallite then decomposes, because it is more reactive to thermal decomposition than other repeating and non-reducing end groups.[42,43] Our previous report[43] indicated that this process initiates the thermal degradation of cellulose by forming pyrolysis products at the crystallite interface. 5-HMF is among these pyrolysis products, and its formation is reasonably attributed to the reducing ends via the chain structure, which is
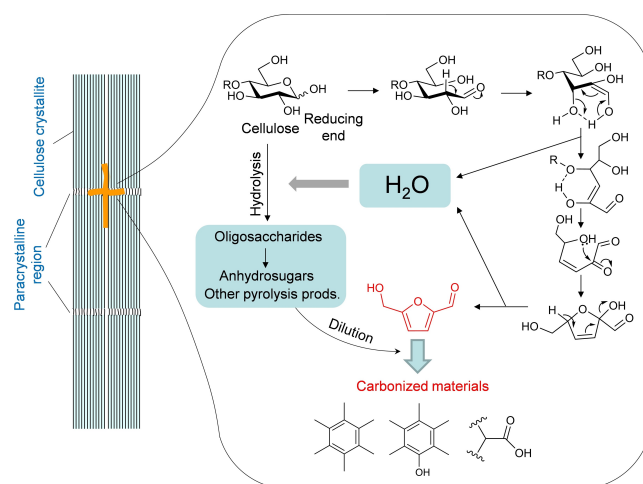
efficiently dehydrated via six-membered transition states.[47,48] This pathway produces 2 mol of water that hydrolyzes cellulose, generating new reducing ends.[43] Therefore, as these reactions proceed, the thermal degradation of cellulose accelerates exponentially.

The present experimental results indicated that the 5-HMF produced was diluted by other degradation products, with their coupling reaction inhibiting formation of a stable homopolymer. Under such conditions, the 5-HMF moiety is efficiently converted into benzene, benzofuran, and indene-type structures, reported as substructures of solid carbonized products.[3–5,9,10,44,49]

Acidic groups, such as carboxylic acids and phenols, are also produced. These acidic groups accelerate cellulose carbonization by catalyzing hydrolysis and dehydration reactions. Consequently, to suppress carbonization, the initial reactions caused by degradation of the reducing end should be prevented. The use of aromatic solvents to effectively suppress the secondary pyrolysis reaction caused suppression of the cellulose carbonization by up to 30% conversion, but control was difficult once carbonization had started.[15]

3. Conclusions

The pyrolysis reactivity of 5-HMF was investigated to determine its role in cellulose carbonization. We found that 5-HMF was converted to stable glassy materials by hydroxyl group removal, while subsequent carbonization reactions were very slow. Furthermore, pyrolysis of 5-HMF in the presence of glycerol, a model of coexisting pyrolysis products, gave the coupling product in a certain yield, which indicates that 5-HMF formed during cellulose pyrolysis binded with other coexisting products, such as anhydrosugars and oligosaccharides. Additionally, upon pyrolysis with glycerol, the 5-HMF moiety was converted to benzene, benzofuran, and indene-type structures, along with carboxylic acids, phenols, and carboxyesters. These are charac-

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teristic structures of carbonized cellulose, which suggests that 5-HMF is an intermediate in cellulose carbonization. Finally, a cellulose carbonization mechanism was proposed and discussed, focusing on the ultrastructure of the cellulose cell wall. Reducing ends might have an important role in the formation of 5-HMF. The carbonization reaction might be accelerated by the action of water and acidic groups generated during carbonization.

Experimental Section

Materials

5-HMF (>95.0%, GC) and dimethyl sulfone (DMSO$_2$, >99.0%, GC) were purchased from Tokyo Chemical Industry, Tokyo, Japan. Before experiments, water was removed from 5-HMF by freeze-drying. Whatman No. 42 filter paper was used as a cellulose sample, which was cut into small sheets (7×7 mm). Glycerol (>99.5%, GC), Na$_2$CO$_3$ (>99.5%, titration) and NaHCO$_3$ (99.5%, titration) were purchased from Nacalai Tesque, Inc., Kyoto, Japan, and used without purification. Aqueous NaOH solution (47–53%, T) and aqueous HCl solution (35–37%, T) were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan) and used without purification.

In Situ IR Spectroscopy

5-HMF or cellulose was heated using a GladiATR system (Pike Technologies, WI, USA) at a heating rate of 10°C/min under nitrogen, and IR spectra were recorded at 25°C intervals in the temperature range of 50–280°C. The temperature was held for 1 min at each interval to measure the IR spectra. ATR-FTIR spectra were recorded by attaching GladiATR to Shimadzu IR Affinity-1 spectrometer (Shimadzu Corp., Kyoto, Japan). The sample chamber in GladiATR was continuously purged with dry nitrogen (99.99%) at a flow rate of 500 mL/min. A total of 45 scans over the range between 400 and 4000 cm^{-1} were collected with a resolution of 4 cm^{-1} (PIKECalc Software, Pike Technologies, Madison, Wisconsin USA).

Pyrolysis of 5-HMF and Cellulose

5-HMF (500 mg) was placed in a Pyrex glass tube reactor (inner diameter, 8.0 mm; wall thickness, 1.0 mm; length, 300 mm). The reactor was purged with nitrogen (99.99%), and then the bottom three-quarters of the reactor were inserted into a muffle furnace preheated at 280°C through a small hole at the top. After heat treatment for 10–40 min, the reactor was removed from the furnace and immediately cooled with air flow. The solid product (char) was washed with water to remove the non-carbonized soluble pyrolysis products and then dried in an oven at 105°C for 24 h. The obtained char was analyzed by Fourier-transform IR spectrometry using a Shimadzu IR Affinity-1 spectrometer (Shimadzu Corp., Kyoto, Japan) in attenuated total reflection mode. A total of 45 scans over the range between 400 and 4000 cm^{-1} were collected with a resolution of 4 cm^{-1}. Similar procedures were performed in the presence of glycerol and for cellulose. Although the experimental results were not statistically evaluated, the reproducibility is confirmed by conducting each experiment twice.

To study the condensation reaction of 5-HMF, the pyrolysis mixture was extracted with acetone, and the soluble portion was analyzed by GPC, GC/MS, and NMR. GPC analysis was performed using an LC-

20 A system (Shimadzu Corp., Kyoto, Japan) under the following conditions: Column, Shodex KF-801 (Showa Denko KK, Yokohama, Japan); column temperature, 40°C; eluent, tetrahydrofuran (THF); flow rate, 1.0 mL/min; detection wavelength, 254 nm. Before analysis, the soluble portion was evaporated with a rotary evaporator, and resulting residue was dissolved in THF (1 mL). GC/ MS analysis (QP2010 Ultra, Shimadzu Corp.) was conducted under the following conditions: Column, Agilent CPSil 8CB (length, 30 m; diameter, 0.25 mm; thickness of the column liquid phase, 0.25 μm); injector temperature, 250°C; split ratio, 1:50; column temperature, 50°C for 5 min, then increased to 300°C at 20°C/min, and held at 300°C for 3 min; carrier gas, hydrogen (72.5 mL/min). MS analysis was conducted under the following conditions: an ion source temperature, 200°C; ionization mode, EI; a filament voltage, 70 eV; emission current, 60 μA; mass range, m/z 35–500. In the GC/MS analysis, 1 μL of acetone solution was injected. ^{1}H and ^{13}C NMR spectra were recorded in CDCl$_3$ (Euriso-Top, Paris, France, 0.03% tetramethylsilane (TMS), 99.80% D) using a Bruker AC-400 spectrometer (Bruker, MA, USA) with tetramethylsilane as an internal standard. Chemical shifts and coupling constants (J) are given in δ (ppm) and Hz, respectively. Component quantification was conducted using dimethyl sulfone (DMSO$_2$) as an internal standard. The concentration of DMSO$_2$ in CDCl$_3$ was 6.86 g/L. The ^{1}H-NMR and ^{13}C-NMR spectra were measured with the following parameters: 30° pulse, relaxation delay of 1.0 s (^{1}H-NMR) and 2.0 s (^{13}C-NMR). The peak integration was conducted manually. The pyrolysis products were separated using preparative TLC on silica gel plates (Kieselgel 60 F254, Merck, Darmstadt, Germany).

5,5′(oxy-bis(methylene))bis-2-furfural (Dimer **1**): ^{1}H NMR (400 MHz, CDCl$_3$): δ = 9.63 (s, 1H), 7.22 (d, 1H, J = 3.56), 6.57 (d, 1H, J = 3.56), 4.64 ppm (s, 1H); ^{13}C NMR (400 MHz, CDCl$_3$): δ = 177.8, 157.3, 152.9, 152.9, 122.0, 112.0, 64.7 ppm; MS (70 eV): m/z (%): 206 (M$^+$, 14), 109 (100), 95 (20), 81 (94), 53 (79), 39 (31).

5-(propanoxy-1,2-diol)-2-furaldehyde (Compound **2**): ^{1}H NMR (400 MHz, CDCl$_3$): δ = 9.62 (s, 1H), 7.22 (d, 1H, J = 3.52), 6.55 (d, 1H, J = 3.52), 3.89–3.93 (m, 1H), 3.72 (dd, 1H, J = 3.92, 11.44), 3.58–3.66 ppm (m, 2H); ^{13}C NMR (400 MHz, CDCl$_3$): δ = 177.9, 157.9, 152.8, 122.2, 111.7, 72.5, 70.2, 65.6, 63.9 ppm; UV (methanol): λ_{max} (ε) = 278 (9333 mol^{-1}dm^{3}cm^{-1}); MS (70 eV): m/z (%): 200 (M$^+$, 6.6), 126 (45), 110 (96), 97 (9.9), 81 (57), 61 (27), 53 (70), 43 (41), 39 (25).

Py-GC/MS Analysis

Py-GC/MS analysis of the 5-HMF char and cellulose char was conducted using a portable Curie-point injector (JCI-22, Japan Analytical Industry Co., Ltd., Tokyo, Japan) coupled with GCMS (QP2010 Ultra, Shimadzu Corp.). The char was rapidly heated to 764°C, and the temperature was held for 5 s. The GC/MS conditions were set as follows: Column, Agilent CPSil 8CB (length, 30 m; diameter, 0.25 mm); injector temperature, 250°C; split ratio, 1:50; column temperature, 50°C for 3 min, increased to 200°C at 6°C/ min, then to 300°C at 30°C/min, and held at 300°C for 5 min; carrier gas, helium. The same MS analysis conditions used in GC/MS analysis were applied for Py-GC/MS.

Boehm Titration

Acidic groups on the char surface were determined using a Boehm titration. The char (50 mg) was added to 0.1 N NaOH, 0.05 N Na$_2$CO$_3$, or 0.1 N NaHCO$_3$ aqueous solution (50 mL). The concentrations of these solutions were confirmed by titration. The vial was sealed and shaken for 24 h. The solution (10 mL) was pipetted and excess base was titrated with 0.1 N HCl. The number of acidic sites was quantified, assuming that NaOH neutralized carboxyl, lactone,

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and phenol groups, Na_2CO_3 neutralized carboxyl and lactone groups, and $NaHCO_3$ neutralized only carboxyl groups. The potentiometric titrator (AT-510, KEM, Japan) was used for titration.

Acknowledgments

Conflict of Interest

The authors declare no conflict of interest.

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