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Hydrolysis of Lignocellulosic Biomass in Hot-Compressed Water with Supercritical Carbon Dioxide

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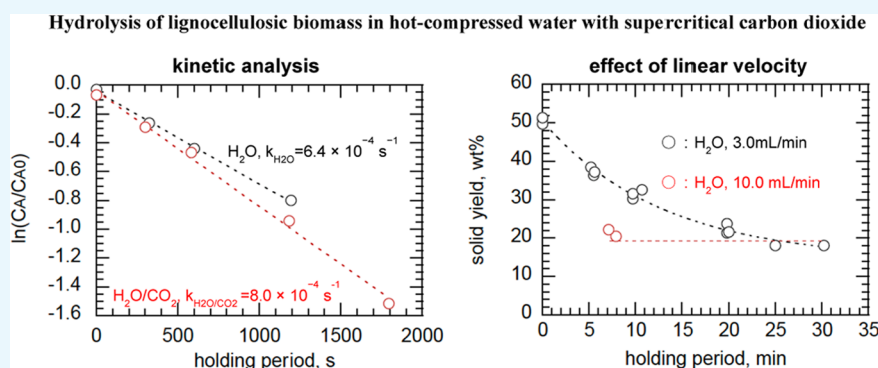Cite This: *ACS Omega* 2021, 6, 14252−14259

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Hydrolysis of lignocellulosic biomass in hot-compressed water with supercritical carbon dioxide

ABSTRACT: This study investigated the decomposition behavior of bamboo under hydrothermal and hydrolysis conditions with H_2O/CO_2 in a semicontinuous-flow reactor at 9.8 MPa. At 255 °C, with and without CO_2, xylan in bamboo completely decomposed into xylo-oligosaccharide (XOD). The yield of glucan degradation products with CO_2 was significantly higher compared with that under the hydrothermal reaction (25.7 vs 14.9 wt %, respectively). The reaction rate of glucan decomposition with CO_2 was slightly higher than the rate of hydrothermal reaction ($k_{H_2O/CO_2}/k_{H_2O} = 1.3$). Increasing the fluid velocity of the hydrothermal reaction (3−10 mL/min) significantly accelerated the solubilization rate, but the ultimate yield of the soluble fraction was unchanged. The ultimate yield of the soluble fraction was slightly affected by physical effects. Hydrolysis with CO_2 under severe conditions exhibited effective degradation of glucan. The catalytic activity of the H_2O/CO_2 system under hydrolysis can be explained by the system's chemical effect.

1. INTRODUCTION

The conversion of lignocellulosic biomass into chemicals has attracted mounting interest during the last 20 years. Considering that <10% consumption of crude oil is attributed to the production chemicals,[1,2] synthesizing chemicals using lignocellulosic biomass would not contribute to decreasing greenhouse gas emissions. However, because of its substitutable molecules, biomass has high potential as renewable feedstock for chemical production that requires fewer steps compared with chemical production of fossil fuels.[1] Sustainable chemical production from biomass should reinforce the public's confidence in the chemical industry.[2] Moreover, the development of flexible and integrated biorefineries to produce biofuels and bioproducts from renewable biomass sources represents a key tool to perform the transition from a petroleum-based economy to a novel bioeconomy that looks for a more efficient and sustainable global development.[3,4] Therefore, converting biomass into useful chemicals through economically viable processes is crucial for sustainable development.[5]

Depolymerization typically involves a pretreatment process (one of the most important steps in the use of lignocellulosic materials), since it improves the efficiency and economy of the overall process.[6,7] Available biomass pretreatment techniques include dilute acid,[8] alkaline hydrolysis,[9] ammonia fiber explosion (AFEX),[10] ionic liquids,[11,12] hot-compressed water (HCW) hydrolysis,[13−16] and CO_2.[17−31] HCW has unique physical and chemical properties.[32,33] The ionic product (K_w) of water changes as the temperature changes. HCW can be used simultaneously as a solvent and a reactant in applications of biomass, such as lignocellulosic pretreatment.[13,14] Previous studies revealed that HCW can completely solubilize hemicellulose from biomass.[15] However, the robust crystalline structure of cellulose creates an obstacle for hydrolysis. The

cellulose hydrolysis rate and glucose yield are much lower in cellulose hydrolysis in HCW compared with acid hydrolysis.[9] The hydrothermal reaction requires a relatively high temperature (>250 °C) or an acidic catalyst, which accelerates the degradation of sugar products.

Carbon dioxide is nontoxic, nonflammable, and inexpensive reagents.[34] Adding CO_2 to lignocellulosic treatments has two effects, which are physical and chemical.[35] As a physical effect, a high CO_2 pressure can easily penetrate small pores of the lignocellulosic structure, which results in structural changes in feedstock.[29] In addition, the supercritical CO_2 phase offers high diffusivity and has a swelling effect on plant materials.[31]

On the other hand, water and carbon dioxide form carbonic acid

$$H_2O + CO_2 \leftrightharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

$$\leftrightharpoons 2H^+ + CO_3^{2-} \tag{1}$$
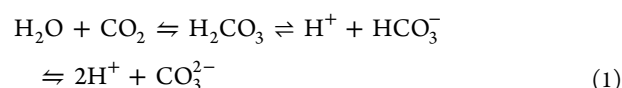
The pH of the H_2O/CO_2 mixture decreases to ~2.9, which creates a strongly acidic environment that facilitates biomass hydrolysis.[36] Studies have reported differences in the effects of CO_2 on aspen wood[21] and corn stover.[22] Van Walsum found that CO_2 in the pretreatment of corn stover enhances xylose and furan concentrations.[22] There are numerous studies for hemicellulose or xylan decomposition with CO_2.[37−42] Bogel-Lukasik and co-workers demonstrated that pretreatment of lignocellulosic biomass (wheat straw) with H_2O/CO_2 in a batch reactor[28−30] produces a liquid fraction that is rich in hemicellulose (mainly in oligomer form) and a solid mainly containing glucan and lignin. A decrease in the solid product yield was also observed using the H_2O/CO_2 system. On the other hand, a continuous-flow reactor used in pretreatment with H_2O/CO_2 at 100 bar did not enhance the degree of biomass (rye straw) dissolution.[27]

In a previous paper,[43] hydrolysis with CO_2 under severe conditions exhibited a remarkable decrease in the solid yield. A linear relationship existed between the catalytic activity of the H_2O/CO_2 system and the severity factor. This study investigated H_2O/CO_2 hydrolysis of bamboo in a semicontinuous (percolating) flow reactor at 9.8 MPa pressure. The research focus was on the catalytic function of supercritical CO_2 for hydrolysis of lignocellulosic material as a function of glucan and xylan degradation. In addition, we considered the effect of fluid velocity on the yield of solid products for hydrothermal reactions.

2. RESULTS AND DISCUSSION

2.1. Effect of the Heating Period at 255 °C on Solid Yield.
A series of hydrolysis experiments were conducted under variable holding periods with and without CO_2. Figure 1 illustrates the solid yield of hydrolysis at 255 °C as a function of the holding period. We did not observe a difference in the solid yield of hydrolysis with or without CO_2 at 0 min of the holding period. However, this difference gradually increased as the holding period increased. At 30 min, the solid yield of hydrolysis with CO_2 was substantially lower compared with that of the hydrothermal reaction. The solid yields at 30 min were consistent with the results of our preceding paper.[43]

Results of hydrolysis with and without CO_2 are summarized in Table 1. For the hydrothermal reaction (without CO_2), the liquid yield was calculated using the carbon yield, which was also specified in this table. The liquid product yield was calculated using the weight of the sample after freeze-drying.
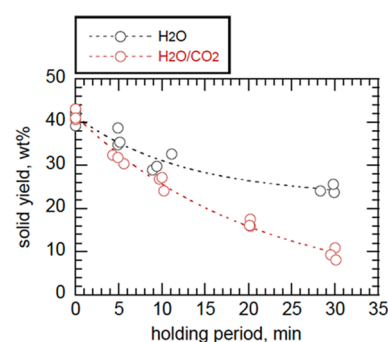

Figure 1. Solid yields of bamboo in a semicontinuous-flow reactor at 255 °C, 9.8 MPa, depending on a holding period.

The sum of the solid and liquid yields was ~93%. However, the liquid product yield estimated by the carbon yield of eluents was much higher compared with freeze-drying. Approximately 100 wt % of feed material was recovered as solid and liquid (carbon yield) products up to 10 min of the holding period. Losses observed in yield for freeze-drying were attributed to the formation of lower-M_w compounds, such as the hydroxymethylfurfural (HMF) and furfural,[14] which easily evaporate under freeze-drying conditions. However, the loss obtained at 30 min for the hydrothermal reaction was ascribed to gaseous products.

2.2. Decomposition Behavior of Xylan. CO_2 addition in hydrolysis at 255 °C enhanced the biomass dissolution degree as a function of the solid yield. To reveal the effect of CO_2 addition on lignocellulosic materials dissolution, we focused on xylan decomposition. Figure 2 illustrates the xylo-oligosaccharide (XOD) yield of hydrolysis as a function of the holding period. All values of the XOD yield were constant and located at approximately 24 wt %. The broken line in Figure 2 indicated the inherent content of xylan in feed material. In addition, we did not detect xylose in the liquid products of any of the cases. These data provide evidence that xylan degradation completely proceeded to XOD even under hydrothermal reaction (without CO_2) at 255 °C. This result was consistent with the fact that CO_2-enhanced biomass dissolution was attributed to the degradation of another component, such as glucan.

To determine the effect of CO_2 on xylan degradation, feed material was hydrolyzed at a relatively low reaction temperature (<200 °C) for 30 min. Figure 3 illustrates the solid yield as a function of the reaction temperature.

The solid yield of hydrolysis with and without CO_2 gradually decreased as the reaction temperature increased. These data are summarized in Table 2. We did not observe this difference at 200 °C. Hydrolysis reactions with CO_2 at a lower reaction temperature had a small effect on biomass dissolution. Typical posthydrolysis results for the solid products are summarized in Table 3. Hydrolysis with CO_2 at 136 °C did not show degradation of xylan, nor a hydrothermal reaction (without CO_2). At 200 °C, the degradation of xylan completely proceeded irrespective of whether CO_2 was present or not. Therefore, xylan in the biomass was easily decomposed by a hydrothermal reaction at 200 °C. Our result is consistent with reports from Mok[15] and Allen et al.[44] On the other hand, solubilization of glucan did not occur at 200 °C in either case. Fockink et al.[45] found that the CO_2/H_2O system used in pretreatment contributed positively to the selective removal of hemicelluloses from sugarcane bagasse. Our results specified in

Table 1. Results of Solid and Liquid Yields by Hydrolysis with and without CO_2

holding period, min	log($R0$)	solvent	solid yield, wt %	liquid yield, wt %	total yield, wt %	difference[a]	liquid yield (TOC), wt %	solid + liquid (TOC), wt %
0.0	4.87	H_2O	41.2	54.3	95.5	4.5	60.2	101.4
5.0	4.98	H_2O	36.3	56.8	93.1	6.9	64.4	100.7
9.8	5.01	H_2O	30.5	63.5	94.0	6.0	70.0	100.5
29.3	5.29	H_2O	24.5	70.3	94.8	5.2	70.7	95.2
0.0	4.87	H_2O/CO_2	41.6	52.8	94.4	5.6		
4.9	4.98	H_2O/CO_2	31.6	64.3	95.9	4.1		
10.0	5.03	H_2O/CO_2	26.1	69.1	95.2	4.8		
20.2	5.15	H_2O/CO_2	16.5	76.4	92.9	7.1		
29.9	5.24	H_2O/CO_2	9.4	83.3	92.7	7.3		

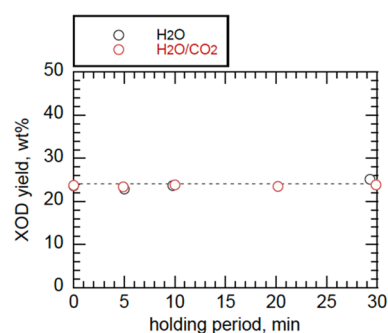[a]Difference = 100-(solid yield + liquid yield).

Figure 2. Yields of xylo-oligosaccharides (XOS) at 255 °C as a function of the holding period.
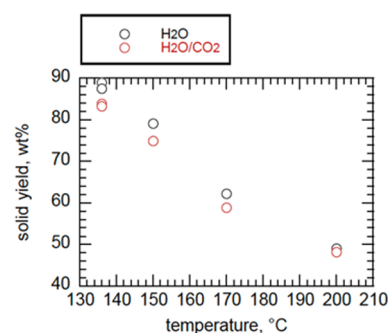

Figure 3. Solid yields of bamboo at 9.8 MPa of pressure, depending on the reaction temperature.

Table 2. Results of Solid and Liquid Yields at Lower Temperatures

	solid yield, wt %		
reaction temperature, °C	H_2O	H_2O/CO_2	difference[a]
136	88.3	83.6	4.7
150	79.1	74.9	4.2
170	62.2	58.9	3.3
200	49.0	48.2	0.8

[a]Difference = solid yield of H_2O − solid yield of H_2O/CO_2.

Table 3. Results of Xylan and Glucan Yields after Hydrolysis

	xylan yield, wt %		glucan yield, wt %	
reaction temperature, °C	H_2O	H_2O/CO_2	H_2O	H_2O/CO_2
136	87.2	79.4	98.5	98.8
200	2.5	3.3	98.3	95.8

Table 3, over 96 wt % of xylan were removed at 200 °C even for hydrothermal reaction. The solid products after hydrothermal reaction with a high content of glucan would easily convert to glucose subsequent enzymatic reaction.

2.3. Decomposition Behavior of Glucan. Figure 4 illustrates typical changes in glucan decomposition products
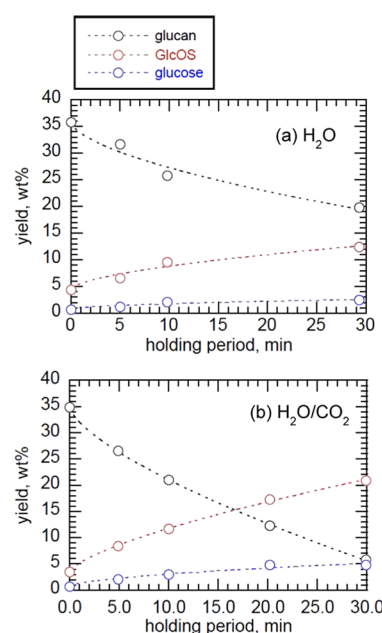

Figure 4. Typical change in the holding period for testing glucan degradation products at 255 °C, 9.8 MPa.

over time. The glucan yield of the hydrothermal reaction (without CO_2) decreased with the increasing holding period, as shown in Figure 4a. The GlcOS yield increased corresponding to the decreasing yield of glucan. The glucose yields after the hydrothermal reaction were less than 3 wt % based on feed. The degradation behaviors for CO_2 addition (Figure 4b) were analogous to those for the hydrothermal reaction. However, the absolute yield value of GlcOS remarkably increased with the addition of CO_2. These data are summarized in Table 4. At 30 min, the liquid yield drastically increased from 70 to 83 wt % with the addition of CO_2. The increments of liquid yield (13 wt %) roughly corresponded to increasing yields of GlcOS and glucose (11 wt %). To exhibit the effect of CO_2 addition on biomass degradation, we carried out kinetic analysis of the glucan decomposition reaction.

Table 4. Results of Degradation Products Yields by Posthydrolysis of Products

holding period, min	log(R0)	solvent	solid yield, wt %	liquid yield, wt %	total yield, wt %	difference[a]	glucan, wt %	GlcOS, wt %	glucose, wt %	XOS, wt %
0.0	4.87	H_2O	41.2	54.3	95.5	4.5	35.8	4.4	0.7[b]	23.6
5.0	4.98	H_2O	36.3	56.8	93.1	6.9	31.7	6.6	1.2[b]	22.9
9.8	5.01	H_2O	30.5	63.5	94.0	6.0	25.8	9.6	2.1[b]	23.7
29.3	5.29	H_2O	24.5	70.3	94.8	5.2	19.8	12.4	2.5[b]	25.2
0.0	4.87	H_2O/CO_2	41.6	52.8	94.4	5.6	34.9	3.5	0.7[b]	23.8
4.9	4.98	H_2O/CO_2	31.6	64.3	95.9	4.1	26.6	8.4	2.1[b]	23.4
10.0	5.03	H_2O/CO_2	26.1	69.1	95.2	4.8	21.0	11.7	3.0	23.9
20.2	5.15	H_2O/CO_2	16.5	76.4	92.9	7.1	12.3	17.3	4.8	23.5
29.9	5.24	H_2O/CO_2	9.4	83.3	92.7	7.3	5.8	20.9	4.8	23.9

[a]Difference = 100 − total yield. [b]Below the detection limit of high-performance liquid chromatography (HPLC).

The glucan concentration in the feed material was 40.4 wt %. The glucan yield at 0 min as a holding period was 35.8 and 34.9 wt %, respectively. Therefore, more than 12 wt % of reactants had already decomposed during the heat-up period. To provide kinetic analysis, the decomposition reaction during the heating period was suppressed as much as possible. One of the methods of suppressing glucan decomposition during the heating period, we have focused on heating rate for the hydrolysis reaction. We examined the hydrolysis reaction with a higher heating rate using the bypass method.

The effects of the bypass method on heating rate are summarized in Table 5. The heating rate using the bypass

Table 5. Comparison of Glucan Yield and Concentration by Heating Method[a]

solvent	method	heating rate, °C/min	glucan yield, wt %	C_A/C_{A0}
H_2O	normal	7.1	35.8	0.884
H_2O	bypass	21.2	39.4	0.973
H_2O/CO_2	normal	7.5	34.9	0.862
H_2O/CO_2	bypass	21.2	37.8	0.933

[a]Feed: glucan contents = 40.5 wt %.

method was approximately 3 times that of the normal procedure. As a result, the suppression of glucan decomposition during the heating period can be achieved through the reaction with higher heating rate with the bypass method. A series of hydrolysis experiments with higher heating rates were conducted under variable holding periods with and without CO_2. Figure 5 illustrates the solid yield of hydrolysis at 255 °C as a function of the holding period.
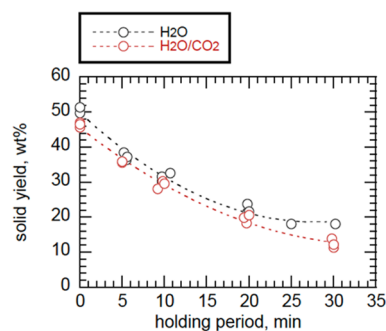

Figure 5. Solid yields of bamboo in a semicontinuous-flow reactor using the bypass method at 255 °C, 9.8 MPa, depending on the holding period.

As an analogy with the former result (Figure 1), the effect of CO_2 addition on biomass decomposition can be observed for hydrolysis with a higher heating rate. Data in Table 6 show the kinetics analysis of a glucan decomposition reaction was examined by assuming a first-order mechanism.

Figure 6 plots the logarithmic function of hydrolysis degradation of glucan versus the holding period, which exhibited a linear relationship in a correlation coefficient of 0.999 and 0.998, respectively. Therefore, glucan was equal by disintegrated in the pseudo-first-order reaction in both cases.

By calculating the rate constant for these experiments, values of $k_{H_2O} = 6.4 \times 10^{-4}$ and $k_{H_2O/CO_2} = 8.0 \times 10^{-4}$ s^{-1} were obtained. Hydrolysis with CO_2 led to a 1.3-fold increase in the constant rate of the glucan decomposition reaction. The effect of CO_2 addition on glucan decomposition caused a modest increase in the rate constant. There are no kinetic data available from the literature on lignocellulosic biomass hydrolysis, especially glucan degradation. These data are significant for future practical reaction designs.

2.4. Effect of the Linear Velocity on Biomass Degradation (Physical Effect). In the H_2O/CO_2 experiments, CO_2 was added to the water flow at 1.0 mL/min. The water flow was fixed at 3.0 mL/min. For this reason, the volume of fluid per unit time of the CO_2 additive experiments was much higher than that of the hydrothermal reaction. Each fluid volume per minute under the experimental condition (255 °C, 9.8 MPa) was 3.8 mL of H_2O and 9.7 mL of CO_2, respectively. The CO_2 volume drastically increased under supercritical conditions due to a remarkable decrease in its density.[46] Therefore, the total volume of fluids was 13.5 mL, which was 3.5-fold of the hydrothermal reaction. This volume, 13.5 mL, did not consider the solubility of CO_2 in water. The solubility of CO_2 in water under experimental conditions was calculated by the estimated formula of Henry's constant proposed by Crovetto.[47]

$$\ln(k_0/\text{bar}) = 1713.53(1 - T^{\#})^{1/3}(T/K)^{-1} + 3.875 \\ + 3680.09(T/K)^{-1} - 1198506.1(T/K)^{-2}$$
(2)

where k_0 is Henry's constant and $T^{\#} = T/T_c$, where T_c is a critical temperature of water. On the basis of Henry's constant from eq 2, we can calculate the molar fraction of CO_2 under experimental conditions. These results are illustrated in Figure 7 and are summarized in Table 7.

The solubility of CO_2 in water was 0.039 g/g-H_2O under 9.8 MPa at 255 °C. The corrected total volume was 12.3 mL, which corresponded to 12.4 mm/s as a linear velocity. To

Table 6. Results of Degradation Products Yields by Posthydrolysis of Products Using the Bypass Method

holding period, min	log($R0$)	solvent	solid yield, wt %	liquid yield, wt %	total, wt %	difference[a]	glucan, wt %	GlcOS, wt %	glucose, wt %
0.0	4.34	H_2O	50.7	43.1	93.8	6.2	39.4	1.1[b]	0.1[b]
5.4	4.71	H_2O	37.4	56.2	93.6	6.4	32.1	6.0	1.3[b]
10.0	4.81	H_2O	31.5	61.1	92.6	7.4	26.1	9.1	2.2[b]
19.9	5.00	H_2O	22.3	69.7	92.0	8.0	18.2	13.5	3.5
25.0	5.08	H_2O	18.1	69.8	87.9	12.1			
30.0	5.15	H_2O	18.1	71.8	89.9	10.1			
0.0	4.44	H_2O/CO_2	46.4	48.2	94.6	5.4	37.8	1.9	0.3[b]
5.0	4.63	H_2O/CO_2	35.7	59.1	94.8	5.2	30.3	6.6	1.7[b]
9.7	4.75	H_2O/CO_2	29.3	66.1	95.4	4.6	25.4	9.5	2.2[b]
19.7	5.01	H_2O/CO_2	19.6	75.7	95.3	4.7	15.8	15.1	3.9
29.9	5.12	H_2O/CO_2	12.2	83.2	95.4	4.6	8.9	20.1	5.9

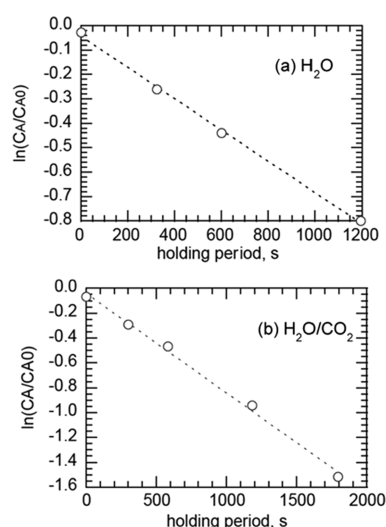[a]Difference = 100 − total yield. [b]Below the detection limit of HPLC.

Figure 6. Determination of the first-order rate constant for the glucan decomposition reaction.
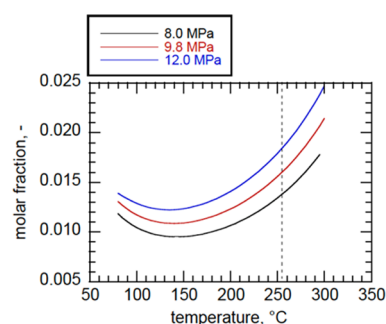

Figure 7. Molar fraction of CO_2 under high pressure as a function of temperature.

Table 7. Summary of Molar Fraction of CO_2 under High Pressure

pressure, MPa	molar fraction, x_B	solubility, g/g-H_2O
8.0	0.014	0.034
9.8	0.016	0.039
12.0	0.018	0.044

reproduce a similar linear velocity with H_2O by itself, the flow rate requires 10.0 mL/min at room temperature. To exhibit the effect of linear velocity on lignocellulosic material dissolution, we focused on a hydrothermal reaction with 10.0 mL/min as

the flow rate. The results of reactions with 10.0 mL/min are depicted in Figure 8 with a red circle. The solid yields with
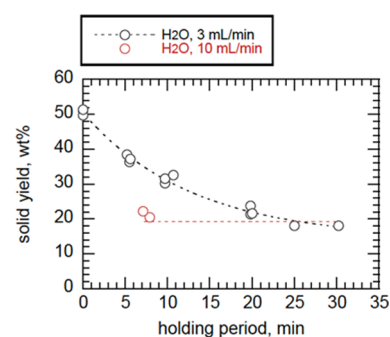

Figure 8. Effects of the flow rate of water on the solid yield of a hydrothermal reaction.

10.0 mL/min were remarkably similar to those observed with 3.0 mL/min for 25 min, which was an equilibrium value of the solid yield at 3.0 mL/min as a flow rate. We did not observe any improvement in biomass degradation with 10.0 mL/min as a function of the solid yield. In addition, water volume during the holding period was approximately 75 mL in both cases. The observation (Figure 8) was consistent with the fact that the degradation of lignocellulosic materials corresponded to the water volume during the holding period. These results suggest that lignocellulosic material dissolution with HCW progresses in a reaction-controlled mechanism. A change in the linear velocity of a reactor was insensitive to the ultimate yield of soluble fractions.

3. CONCLUSIONS

This report detailed the degradation of lignocellulosic material, especially glucan decomposition by H_2O/CO_2, at 255 °C, under high-pressure conditions. For hydrothermal reactions, an increasing flow rate of water resulted in an accelerated degradation reaction, but the ultimate yield of the soluble fraction was unchanged. These results suggested that lignocellulosic material dissolution by HCW progresses as a reaction control mechanism.

In the case of glucan decomposition, the yield of the products degraded with CO_2 was significantly higher compared with those of the hydrothermal reaction (25.7 vs 14.9 wt %, respectively). The reaction rate of glucan decomposition by CO_2 was slightly higher than that of the hydrothermal reaction ($k_{H_2O/CO_2}/k_{H_2O} = 1.3$). Observation of the effect of linear
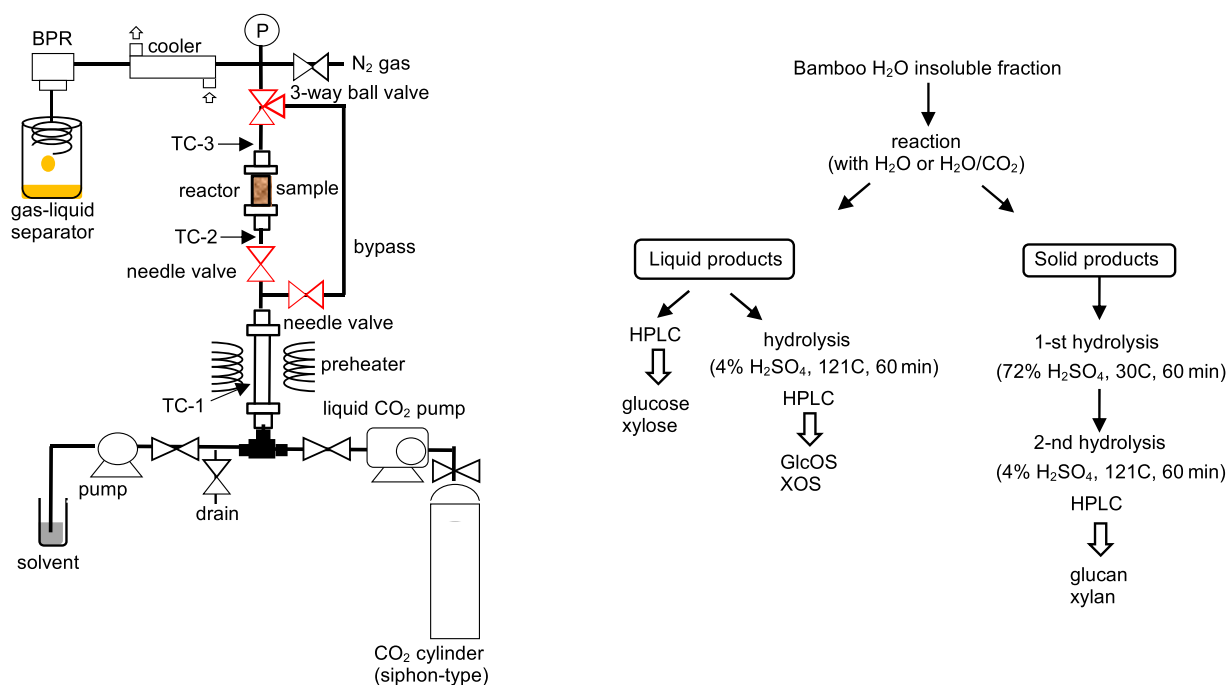
Figure 9. Schematic diagram of the apparatus and posthydrolysis procedure. TC: thermocouple; cooler: duplex-tube-type cooler; BPR: back-pressure regulator.

velocity was consistent with the fact that a change under physical condition, such as flow rate, was insensitive to the ultimate yield of soluble fraction under our experimental condition. The catalytic activity of the H_2O/CO_2 system in hydrolysis can be explained by the system's chemical effect.

We proposed a mechanism for the decomposition of lignocellulosic material in the presence of supercritical CO_2. From the viewpoint of practical pretreatment of lignocellulosic materials, this mechanism should be carried out using a larger particle size sample to consider pulverizing cost. However, these data would be of great importance to future reactor designs.

4. EXPERIMENTAL SECTION

4.1. Materials. The lignocellulosic biomass sample used in this study was dried bamboo (phyllostachys) pulverized to 149−297 μm. The bamboo used in this study consisted of approximately 57% (weight) cellulose, 12% hemicellulose, 25% Klason lignin, 4% diethyl ether extracts, and 12% ash. The bamboo moisture was determined to be 9.2% (weight). To evaluate biomass degradation under hydrothermal conditions, the water-soluble fraction of the sample was removed using a Soxhlet extractor. The water-insoluble yield of the sample was ∼90 wt %. The result of the elemental analysis of the water-insoluble fraction was: C, 48.2 wt %; H, 6.2 wt %; and O (diff.), 4.6 wt %.

4.2. Experimental Apparatus and Procedure. Hydro-thermal and hydrolysis reactions with CO_2 were conducted in a semicontinuous-flow reactor, as described by Mok et al.[15] and Ando et al.[13] Further details of the reactor system design can be found in Sasaki et al.[43] A high-performance liquid chromatography pump delivered the solvent into a preheater, which consisted of a 7.53 mm i.d. × 185 mm, 2.7 mL stainless steel tube (SUS316). Approximately 250 mg of the sample was charged in a 4.6 mm i.d. × 39.4 mm, 0.7 mL reactor (SUS316) capped with gasket filters (average pore size: 5 μm) at the inlet

and outlet. The reactor was covered with heat-insulating material to prevent heat release. The effluent from the reactor was quenched using a duplex-tube-type cooler. Temperature data were measured using thermocouples at three different locations: preheater outside, preheater exit (inside), and reactor exit (inside). The thermocouple of the preheater outside was fixed at the preheater's center and controlled the electric heater output. Pressure in the reactor system was kept constant using a back-pressure regulator (BPR).

To define the reaction temperature, we conducted another experiment using a stainless steel tube instead of a reactor. A thermocouple was inserted at the vertical center of the tube and fixed with silver solder welding. The setting temperature and the temperature inside the reactor were measured using the tube to determine the correlation between the two parameters.[43]

First, we loaded ∼250 mg of the sample into the reactor. After the reactor was assembled in the apparatus, we purged it thrice with N_2 gas at 3.0 MPa to remove air. The pump delivered deionized water through the preheater to the reactor at a flow rate of 3.0 mL/min. Next, the BPR was set at 9.8 MPa pressure. Heat was applied at a heating rate of ∼5 °C/min up to the desired temperature, at which it was maintained for 30 min (holding phase). Next, the electric heater was turned off and the reactor cooled to room temperature for 10 min. A siphon-type CO_2 cylinder and a liquid CO_2 pump (PU-2086 plus, JASCO, Tokyo, Japan) were used for hydrolysis with CO_2. A spiral-type gas−liquid separator was used for efficient eluent recovery, and the CO_2 flow rate was fixed at 1.0 mL/min.

Residue in the reactor (solid products) was dried at 80 °C in a vacuum for 8 h, after which the residue yield was calculated using the reactor weight before and after the reaction. Effluents that were collected during heating, holding, and cooling (liquid products) were then freeze-dried and weighed. The exper-

imental error of our reaction procedure was within 3% of each severity.

For solid and liquid products, posthydrolysis using oligomeric reaction products took place in the second half of quantitative saccharification. First, 4% sulfuric acid solution was prepared from the reactor effluent,[48] as shown in Figure 9. The reactant water-insoluble fraction of bamboo was treated with 72 and 4% sulfuric acid[49] for a comparison with the yield of monomeric sugars in liquid products. Solid products after posthydrolysis defined glucan and xylan, respectively. GlcOS and XOS yields were calculated by glucose and xylose yields after posthydrolysis of liquid products.

To conduct a kinetic analysis of the glucan decomposition, a reaction with a higher heating rate was carried out. For higher heating rate experiments, we added a bypass channel around the reactor, as shown in Figure 9. The bypass channel was equipped with two needle valves (Swegelok, SS-3NBS4-G) and a three-way ball valve (Swegelok, SS-H83XPS4), which were resistant to high temperatures and pressures. The pump delivered deionized water to the bypass channel at a flow rate of 3.0 mL/min. Next, the BPR was set at 9.8 MPa pressure. Heat was applied at a heating rate of ∼30 °C/min up to the desired temperature. After the internal temperature (TC-2) was constant (∼60 min), the channel changed from the bypass to the reactor. As a result, the heating rate remarkably increased from 7 °C/min up to 21 °C/min based on the internal temperature (see the temperature profile for the bypass method in the Supporting Information).

4.3. Analytical Method. Liquid products were analyzed for oligosaccharides using a JASCO liquid chromatography system (JASCO) with Shodex sugar KS-804 (Shodex, Tokyo, Japan). Molecular weights of the samples were calculated by Pullulan standards. The posthydrolysis samples were analyzed for glucose (98.0%), xylose (98.0%), arabinose (99.0%), furfural (98%), and 5-hydroxymethylfurfural (5-HMF) (99%) using the same liquid chromatography system as used for Shodex sugar SP-0810 (Shodex). This system was also equipped with an ionic-form H^+/CO_3^- de-ashing guard column (Bio-Rad, CA). Standards for the analysis and reagents were purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan). The carbon concentration in the liquid products was measured using a TOC-5000A total organic carbon (TOC) analyzer (Shimadzu, Tokyo, Japan).

Overend and Chornet first defined the log severity factor.[50] This factor can only be used if the temperature remains constant during the reaction. Therefore, this work aimed to evaluate the temperature effect on the compositions of liquid and solid products as a function of the modified severity factor proposed by Rogalinski et al.[27]

$$R_0 = \int_0^t \exp\left(\frac{T(t) - 100}{14.75}\right)dt \tag{3}$$

where t is the residence time(min), $T(t)$ is the temperature (°C) in dependency on the residence time considering the heat-up period, and 14.75 is an empirical parameter related to temperature and activation energy. In this study, we used the modified severity factor to evaluate the temperature and holding time effects on the decomposition behavior of the H_2O/CO_2 system.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c01026.

    Temperature profiles of bypass method (Figure S1) and reproducibility of preheater inside temperature of bypass method (Figure S2) (PDF)

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Notes

The authors declare no competing financial interest.

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