NONCATALYTIC CONVERSION OF CELLULOSE IN SUPERCRITICAL AND SUBCRITICAL WATER

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This paper describes the noncatalytic conversion of cellulose in supercritical and subcritical water. First, it was demonstrated that even without any acid catalyst, cellulose was rapidly converted to water soluble species with a relatively high glucose yield in near critical water and glucose yield increased with elevating temperature. Then the rate constants for cellulose decomposition and glucose decomposition were evaluated at a pressure of 25 MPa over a temperature ranging from 473 K to 673 K by using semi-batch reactor and a flow reactor, respectively. From the reported cellulose pyrolysis rate constant and the evaluated cellulose decomposition rate constant, cellulose hydrolysis rate constant was evaluated. By using the cellulose hydrolysis rate, cellulose pyrolysis rate and the glucose decomposition rate, glucose yield obtained in the semi-batch experiment was reasonably explained.

Introduction

Biomass is expected to be valuable renewable resources for energy, chemicals, food and feedstock. Cellulose (a major component of biomass) conversion to glucose from which most of the petroleum products can be produced is a key step[2].

One method which can process a large amount of cellulosic materials at a high rate is acid-catalyzed hydrolysis. So far, a concentrated acid process (50-75 % H_2SO_4, 298.5-313 K)[3] and a dilute acid process (0.1-5 % HCl, 443-463 K)[6] have been proposed. Kinetic studies have been done also over the temperature range from 423 to 523 K[1, 3, 6] for the development of these processes. Recently, Mok and Antal[4] reported that extremely high glucose yield (around 71 %) was obtained at 488 K, 34.5 MPa and 0.05 % H_2SO_4, although the reaction rate was moderately slow. However, the problems of the acid catalyzed hydrolysis are (1) not sufficiently high reaction rate (0.1 min^{-1} at the maximum), (2) corrosion of the reactor and (3) required processing of the waste water.

In this study, we are developing a high temperature noncatalytic biomass conversion process. At elevated temperature water itself works as an acid catalyst, because of its high ionization product. Furthermore at supercritical water (Tc = 647.3 K, Pc = 22.12 MPa), its physical and chemical properties can be controlled and manipulated with pressure; this may lead to the control of product distribution.

The objectives of this study are (1) to examine the noncatalyzed cellulose conversion in near critical water, (2) to evaluate the kinetics of cellulose hydrolysis and glucose decomposition, and (3) to explain the cellulose conversion obtained by using these evaluated rates and cellulose pyrolyis rate previously reported.

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1. Experimental

1.1 Semi-batch reactor for cellulose decomposition

A schematic diagram of an apparatus is shown in **Fig. 1a**. A reactor (0.85cm i.d. × 10 cm length) was made of stainless steel (SUS 316). About 120 mg of dried cellulose powder (40-100 mesh, ADVANTEC Co.) was loaded in the reactor and was sandwiched with glass wool to prevent it from flowing out. Water was fed to the reactor at a rate of 10 ml/min by a high pressure pump (Nihon Seimitsu Co., Model NP-AX-15) and then the system was pressurized up to 25 MPa. The pressure was controlled by a back pressure regulator (Tescom, Model 26-1721-24).

The reactor was heated by an electric furnace (Shinkuriko Co. Model RHL-965C-P). Temperature of the sample and that of the outside wall of the reactor were monitored by chromel-alumel thermocouples. After the sample temperature reached 473 K, hot water or HCl aqueous solution (0.02-0.7 wt%), which had been already heated up to the reaction temperature by flowing through Line 2, was fed to the reactor (Line 1). By using this method a high heating rate (15 seconds from 473 K to 673 K) was attained. Products were recovered through the back pressure regulator along with water. When terminating the reaction, the stream was changed to Line 2 and simultaneously cool water was showered at the outside of the reactor. The quick quench was done by this method. The residue in the reactor was dried and

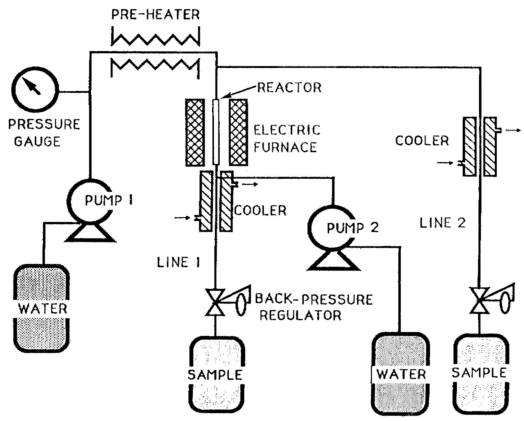


Fig. 1a Semi-batch reactor for cellulose decomposition

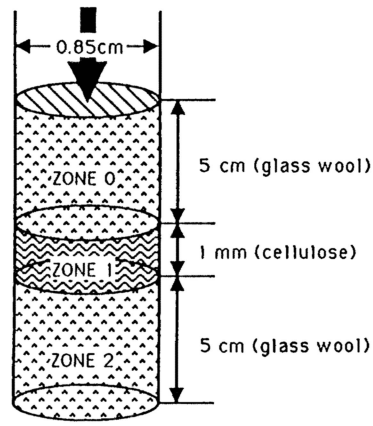


Fig. 1b Reaction zones in the reactor

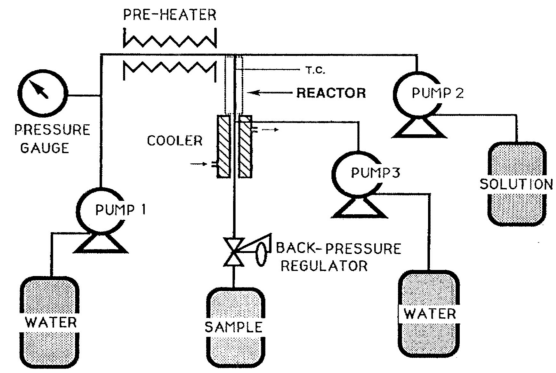


Fig. 2 Flow-type reactor for glucose decomposition

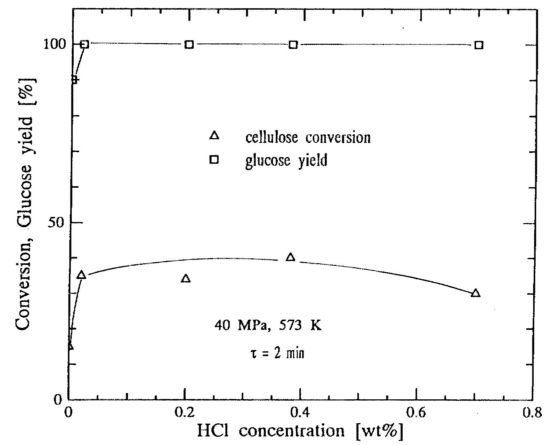


Fig. 3 Effect of HCl concentration on cellulose conversion and glucose yield

weighed. Glucose concentration of the recovered products was measured by high performance liquid chromatography (HPLC).

1.2 Flow reactor for glucose decomposition

In order to evaluate the decomposition rate of glucose in near critical water, a flow type reactor shown in **Fig. 2** was employed. Glucose used was obtained from Wako Pure Chemical Industries, LTD. Glucose aqueous solution (0.35-2 g/l) was fed to the reactor at a feed rate of 10 ml/min by a high pressure pump (GL Science Co., Model PUS-3). Preheated water was fed from another line at the feed rate of 10 ml/min and mixed with the glucose aqueous solution. Thus at this mixing point glucose aqueous solution was rapidly heated up to the reaction temperature and the reaction initiated. The temperature at the mixing point was measured by an alumel-chromel thermocouple. The reactor temperature was controlled by an electric furnace with a PID controller. At the exit of the reactor cool water was injected in order to terminate the reaction immediately. Thus, the reaction volume was accurately determined by this method. The residence time of the solution in the reactor was estimated from the volume of the reactor, the flow rate and the density of solution. In this analysis the density of solution was assumed to be the same as pure water density, because the glucose concentration was less than 0.2 wt%. Pressure of the system was controlled by a back pressure regulator (Tescom, Model 26-1721-24). Products were continuously recovered through the back pressure regulator. The concentration of glucose was evaluated by HPLC.

1.3 Analysis

The chromatographic equipment (HPLC) consists of high pressure pump (Spectra-Physics Isochrom), column (Shodex, Ionpak KS802) and refractive index (RI) detector (ERC, Model 7515A). HPLC was operated at 80°C with 1.0 ml/min flow of water as a carrier solvent.

Glucose yield, $Y(t)$ [weight of carbon in recovered glucose/initial weight of carbon in cellulose], was evaluated from the measured glucose concentration, $C_G(t)$, as follows

$$Y(t) = \frac{a}{b} \int_0^t \frac{C_G(t) F}{\rho W_0} dt \qquad (1)$$

where a (= 0.4) and b (= 0.444) are respectively the weight fraction of carbon in glucose and that in cellulose, F is flow rate, t is time, W_0 is the initial weight of cellulose and ρ is the density of water.

Based on the retention time (HPLC analysis) of products, the cellulose decomposition products were considered to be glucose, fructose, levoglucosan, erythrose, glyceraldehyde, dihydroxyacetone, pyruvaldehyde

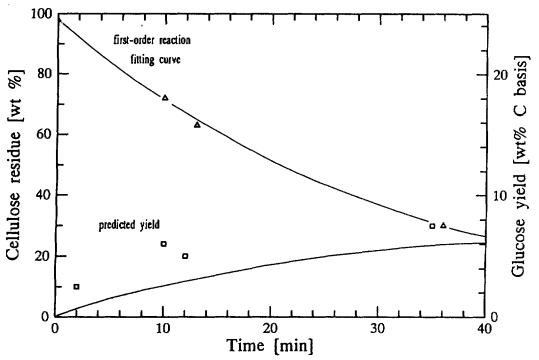


Fig. 4 Cellulose residue and glucose yield vs. reaction time at 523 K

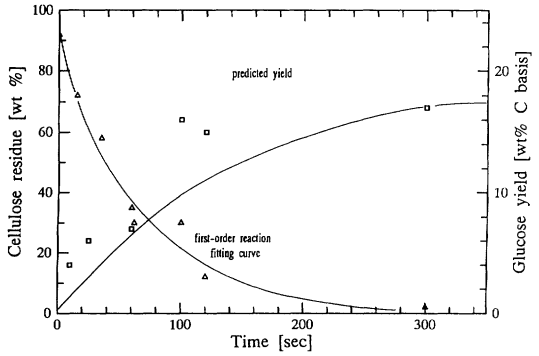


Fig. 5 Cellulose residue and glucose yield vs. reaction time at 573 K

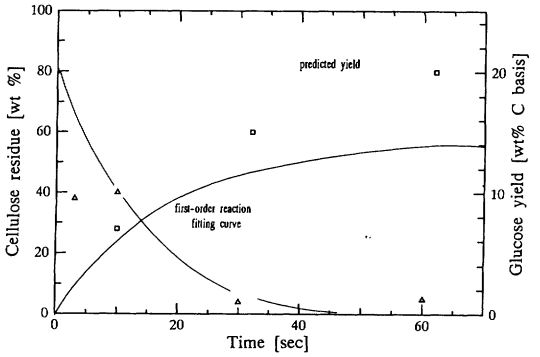


Fig. 6 Cellulose residue and glucose yield vs. reaction time at 593 K

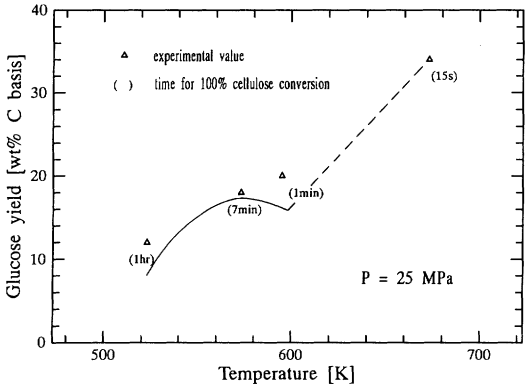


Fig. 7 Glucose yield vs. temperature at 100% cellulose conversion

and acids but the accurate identification of these products (e.g. by NMR analysis) were not conducted and for this reason, mass balance was not evaluated. However, glucose yield (glucose peak was completely separated from other product peaks and was confirmed by NMR analysis) was accurately monitored and measured.

2. Results and Discussion

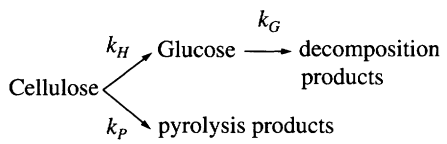
2.1 Cellulose conversion and glucose yield in near critical water

(1) Effect of HCl concentration **Figure 3** shows the effect of acid catalyst (HCl) concentration on both cellulose conversion and glucose yield at 573 K, 40MPa, and 2 min of reaction time. Although HCl concentration was very low, cellulose was completely converted with relatively high glucose yield. Furthermore, even without catalyst, 90 % of cellulose was converted under the same condition. In the following experiments, cellulose conversion and glucose yield in near critical water without any catalyst was intensively studied.

(2) Noncatalyzed reaction The weight change of cellulose and the glucose yield with time at 523 K, 573 K and 593 K are shown in **Figs. 4** to **6**, respectively. The glucose yield at 100 % cellulose conversion was plotted against temperature in **Fig. 7**. The time required for the complete conversion of cellulose is shown in parentheses. The reaction time decreased with elevating temperature. When the reactor temperature was raised up to 673 K, cellulose was converted during the heating up period in just less than 15 sec. The result demonstrates that in near critical water, rapid cellulose conversion can be achieved without any catalyst. Furthermore, glucose yield increases with elevating temperature.

2.2 Evaluation of reaction rate constants

(1) Reaction scheme According to previous studies[4, 5], the reaction scheme is considered as follows



Glucose is produced through hydrolysis of cellulose. As a parallel reaction of the hydrolysis, thermal decomposition of cellulose takes place to produce pyrolysis products for which glucose cannot be produced. The produced glucose further decomposed into various species, including fructose, 1,6-anhydro *D*-glucose, erythrose, glycolaldehyde, glyceraldehyde, dihydroxyacetone, pyruvaldehyde and acids. Thus, the glucose yield is determined by the balance of these three reaction rate constants (k_H, k_P and k_G). For the description of the temperature dependence of glucose yield in Fig. 7, evaluation of these three rate constants is required.

(2) Cellulose decomposition rate Decomposition rate of cellulose in near critical water was evaluated by

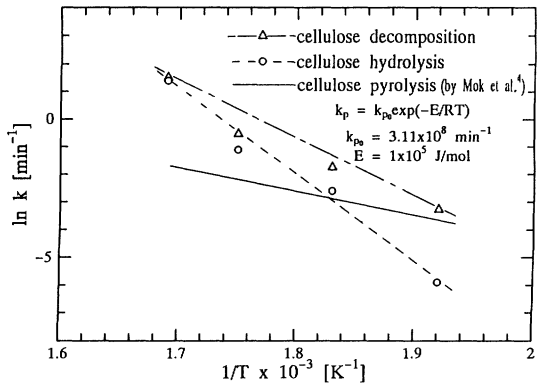


Fig. 8 Arrhenius plot for cellulose decomposition, cellulose pyrolysis and cellulose hydrolysis

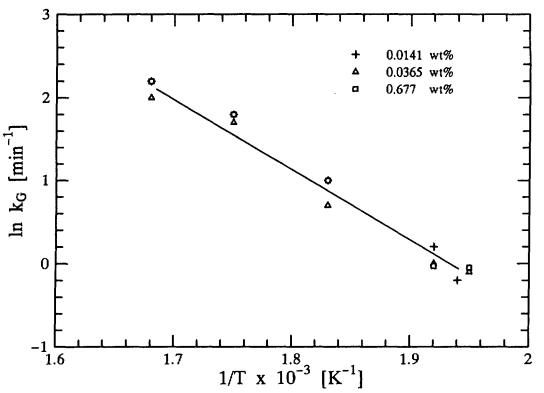


Fig. 9 Arrhenius plots for glucose decomposition

assuming the first order reaction with respect to the residual amount of cellulose, $W(t)$, at time t as follows

$$dW(t)/dt = -k_T W(t) \tag{2}$$

where k_T is the overall reaction rate constant.

The results obtained in Figs. 4 to 6 were fitted with Eq. (2) to evaluate the rate constant, k_T. The solid curves in these figures are the correlated results. Weight change of cellulose with time was fairly well described by Eq. (2), which implies the soundness of the first order reaction assumption. The evaluated rate constants are plotted against reciprocal temperature in **Fig. 8**. Since the dynamic change of cellulose can be described by first order reaction, we think that the solid residue has more or less the same property with the cellulose (without further verification).

(3) Pyrolysis rate and hydrolysis rate of cellulose The hydrolysis rate constant, k_H, was evaluated as the difference of k_T and k_P. For the pyrolysis rate constant, k_P, reported in the recent work of dilute acid hydrolysis of cellulose[4] was used. The result is shown in Fig. 8. As shown in this figure the ratio of cellulose hydrolysis rate against cellulose pyrolysis rate increased with elevating temperature. This suggests that the selectivity of glucose production from cellulose increases with elevating temperature.

(4) Glucose decomposition rate Glucose decomposition can be expressed by the first order reaction [Eq. (3)], since conversion of glucose at the exit of the flow reactor was almost the same, irrespective of the initial glucose concentration [0.041, 0.0365, 0.677 wt%].

$$dC_G/dt = -k_G C_G \tag{3}$$

The rate constant, k_G, was evaluated from the glucose conversion at the exit of the reactor, as follows

$$k_G = -F\ln(C_{Gout}/C_{Gin})/(V\rho) \tag{4}$$

where the density of solution was assumed to be the same as that of pure water, $\rho(T, P)$. The evaluated k_G is shown in **Fig. 9**.

2.3 Description of reaction in near critical water

For the description of the reaction in near critical water, we have the following assumptions: (1) reaction in the reactor is divided into 3 zones as shown in Fig. 1b, (2) cellulose conversion takes place in zone 1 (1 mm length), (3) glucose is the only one primary product of cellulose hydrolysis and (4) glucose decomposition in zone 1 is neglected because of very short residence time and (5) glucose (produced in zone 1) further decomposes into lighter species in zone 2 (5 cm length).

Weight change of cellulose with time, $W(t)$, can be written as

$$W(t) = W_0\exp(k_T t) \tag{5}$$

Since we assume that glucose is produced by the hydrolysis of cellulose, primary production rate of glucose in zone 1, $dG(t)/dt$ [g-carbon in glucose/s], is described as

$$dG(t)/dt = bk_H W(t) \tag{6}$$

$$dG(t)/dt = bk_H W_0\exp(-k_T t) \tag{7}$$

Thus, the concentration of glucose [g-glucose/cm^3] at the inlet of zone 2 at time θ can be written as

$$C_G(\theta, 0) = \frac{b\rho k_H W_0\exp(-k_T\theta)}{aF} \tag{8}$$

A portion of the produced glucose decomposes in zone 2 with the residence time, τ. The concentration of glucose at the exit of zone 2, $C_G(\theta, L)$, can be described as

$$0 \le \theta < \tau$$
$$C_G(\theta, L) = 0 \tag{9}$$

$$\theta \ge \tau$$
$$C_G(\theta, L) = C_G(\theta-\tau, 0)\exp(-k_G\tau) \tag{10}$$

$$\theta \ge \tau$$
$$C_G(\theta, L) = \frac{b\rho k_H W_0\exp(-k_G\tau)\exp[-k_T(\theta-\tau)]}{aF} \tag{11}$$

It follows that the glucose yield, $Y_G(t)$ [g-glucose/g-initial weight of cellulose], until sampling time, ϕ, is

$$Y_G(\phi) = \int_\tau^\phi \frac{F}{\rho W_0} C_G(\theta, L)\, d\theta \tag{12}$$

$$Y_G(\phi) = \frac{bk_H \exp(-k_G \tau)}{ak_T} \{1 - \exp[-k_T(\phi - \tau)]\} \quad (13)$$

The glucose yield at 100% cellulose conversion is

$$Y_G(\infty) = \frac{bk_H \exp(-k_G \tau)}{ak_T} \quad (14)$$

The variation of glucose yield with time calculated by Eq. (14) using the reported k_P[4] and the evaluated rate constants (k_H, and k_G) is shown as curves in Figs. 4 to 6. The reasons for some deviations from the calculated to experimental values are experimental errors and the assumption that the glucose decomposition rate is equal to cellulose hydrolysis rate. Final glucose yields calculated at the temperature ranging from 473 K to 593 K are shown in Fig. 7 as a solid curve. The tendency of the result can be explained by this analysis. The increase of glucose yield by the elevation of temperature was attributed to the higher hydrolysis rate of cellulose than pyrolysis rate at elevated temperature. This result suggests that at 673 K, glucose yield can be elevated up to 92 % by increasing the flow rate ($\tau \approx 0$).

In this experiment(at 673 K), cellulose was completely converted during the heating period. At this time, there was a temperature distribution in the reactor, since (1) the upper part of the cell (zone 0) was heated up to the supercritical state (673 K) by the SCW fed, thus the fluid largely expanded and (2) cooling jacket was set just below the reactor. As a result the product solution in zone 2 was pushed out from it. It follows that the residence time of the product solution was much shorter than in the steady state experiments.

In the analysis of this particular case, we assume that: (1) cellulose is completely converted at 623 K, (2) the average glucose concentration at the inlet of zone 2 is C_G (0) = $[b\rho k_H W_0 \exp(-E/(RT)]/(ak_T F)$ at 650 K, (3) glucose is converted in zone 2 at 650 K and (4) the residence time in zone 2 during heating up period is averagely shortened by the expansion of the fluid by the increase of its temperature from 623 to 673 K. The estimated result is shown in Fig. 7. Fairly good agreement with the experimental result was obtained.

Conclusion

Cellulose could be rapidly converted to water soluble species in near critical water (473-650 K, 25MPa) even with out any acid catalyst. The overall reaction rate in near critical water was 1 or 2 orders of magnitude higher than that of the conventional acid catalytic process. Furthermore, glucose yield increased with elevating temperature.

Cellulose hydrolysis rate and glucose decomposition rate were evaluated by using semi-batch reactor and a flow reactor, respectively. By using the evaluated rate constants and pyrolysis rate constant in earlier work[4], the obtained results could fairly well be explained. The increase of glucose yield by the elevation of temperature was attributed to the higher hydrolysis rate of cellulose than pyrolysis rate at elevated temperature.

Acknowledgement

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Nomenclature

a	=	weight fraction of carbon in glucose	[g-carbon/g-glucose]
b	=	weight fraction of carbon in cellulose	[g-carbon/g-cellulose]
C_G	=	concentration of glucose	[g/cm^3]
C_{Gin}	=	inlet concentration of glucose	[g/cm^3]
C_{Gout}	=	exit concentration of glucose	[g/cm^3]
E	=	activation energy	[J/mol]
F	=	flow rate of water	[g/min]
G	=	glucose production rate	[g-carbon in glucose/min]
k_G	=	rate constant of glucose decomposition	[1/min]
k_H	=	rate constant of cellulose hydrolysis	[1/min]
k_P	=	rate constant of cellulose pyrolysis	[1/min]
k_T	=	rate constant of cellulose decomposition	[1/min]
L	=	length of zone 2	[5 cm]
m	=	molecular weight of carbon	[g/mol]
R	=	gas constant	[8.314 J/mol/K]
t	=	time	[min]
V	=	volume of the reactor	[cm^3]
W	=	instantaneous weight of cellulose	[g]
W_0	=	initial weight of cellulose	[g]
Y	=	Glucose yield (weight of carbon in glucose/weight of carbon in cellulose)	[-]
ϕ	=	sampling time	[min]
θ	=	time	[min]
ρ	=	density of water in a reactor	[g/cm^3]
τ	=	residence time in a reactor	[min]

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