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Kinetics of Cellobiose Decomposition under Subcritical and Supercritical Water in Continuous Flow System

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Abstract−The effects of reaction temperature, pressure and residence time were investigated with a flow apparatus. Cellobiose decomposition kinetics and products in sub- and supercritical water were examined at temperatures from 320 to 420 °C at pressures from 25 to 40 MPa, and at residence times within 3 sec. Cellobiose was found to decompose via hydrolysis and pyrolysis. The yield of desired hydrolysis product, glucose, was the maximum value of 36.8% at 320 °C, 35 MPa, but the amount of 5-(hydroxymethyl)furfural (HMF), fermentation inhibitor increased too because residence time increased in the subcritical region owing to decrease of reaction rate. Meanwhile, though the yield of glucose is low in the supercritical region, the yield of HMF decreased compared with the subcritical region; and at the minimum yield of HMF (380 °C, 25 MPa), the yield of glucose was 21.4%. The decomposition of cellobiose followed first-order kinetics and the activation energy for the decomposition of cellobiose was 51.05 kJ/mol at 40 MPa.

Key words: Cellobiose Decomposition, Hydrolysis, Sub- and Supercritical Water, Continuous Flow Apparatus, Activation Energy

INTRODUCTION

Although the acid-catalyzed hydrolysis of cellulosic materials was industrialized almost a century ago, the study of the chemical reaction and kinetics of cellulose is still a focus of research interest today because the products of cellulose hydrolysis have the potential to replace many intermediates synthesized from petrochemistry [Fengel et al., 1989]. From glucose, for example, ethanol can be produced by fermentation or vitamin C by hydrogenation. Acid treatment of glucose forms HMF which can be used to make polyamides, polyesters and epoxides [Kabyemela et al., 1998].

Until now, the main techniques for converting cellulose to glucose and oligomers were acid-catalyzed hydrolysis and enzyme treatment process. Acid-catalyzed hydrolysis [Mok et al., 1992] was the conventional process but had drawbacks of low reaction rates, the corrosion of reactor by acid and treatment of acid waste and was little used recently. The enzymatic treatment process [Mandel et al., 1974] was proposed as an alternative method, but the obstacles to this process were slower reaction rate (it can take 2 days for 100% conversion) than acid-catalyzed process and the narrow operating ranges under which cellulase such as *Trichoderma reesei* grows [Park et al., 2001]. In addition, the waste carbon produced under enzymatic treatment may affect enzyme activity. Therefore, noncatalytic hydrolysis of cellulose has been investigated to improve the above-mentioned problem. Recently, one very interesting and yet not fully studied cellulose conversion technique has been developed using sub- and supercritical water as a reaction medium by an advanced country. For this case, water acts as the solvent and this hydrolysis process using sub- and supercritical water has no environmental problems, and high product yield can be obtained compared with the conventional process by using physical and chemical properties of water such as dielectric constant, and density in critical region.

In this work, cellobiose was selected as a model compound of cellulose, and experiments were conducted in the sub- and supercritical region of water with variations of temperature, pressure and retention time to examine conversion of cellobiose and product yield. The objective of this work is to elucidate the reaction pathway and kinetics in reaction condition.

EXPERIMENTAL

1. Materials

Raw materials used in the experiments and product calibration were obtained from Aldrich Cooperation. and these chemicals were the following: D-cellobiose (99%), α-D-glucose (99%+), D-fructose (99%), DL-glyceraldehyde (95%), pyruvaldehyde (40%), glycolaldehyde dimer, 1,6-anhydro-β-glucose (99%), 1,3-dihydroxyacetone dimer (97%), D-erythrose (60%), 5-hydroxymethyl furfural (99%).

2. Apparatus and Procedure

A schematic diagram of a continuous apparatus using supercritical water is shown in Fig. 1. The apparatus was divided into five sectors such as supplying unit, preheater, reactor, cooler and product separator. Supplying unit consisted of reservoir for water, slurry pump for high pressure, pressure gauge and check valve. The deionized water prepared by pure water fabricator (Milipore Co.) was used during the experiments; and after dissolved oxygen was removed with degasser (Jour Research, X-ActTM), the water was supplied into the preheater by high pressure pump (GL Science Co. PUS-11). Reactant, cellobiose, was supplied into the reactor by high pressure slurry pump (max. pressure-45 MPa). To avoid a counterflow and pulse, check valve (SS-CHS4-1, Swagelok.) and damper were equipped at the line of reactant and in addition, a relief valve (SS4R3A, Swagelok) was installed at this line in view of safety for over-pressure. Preheater was composed of furnace and electric heat-

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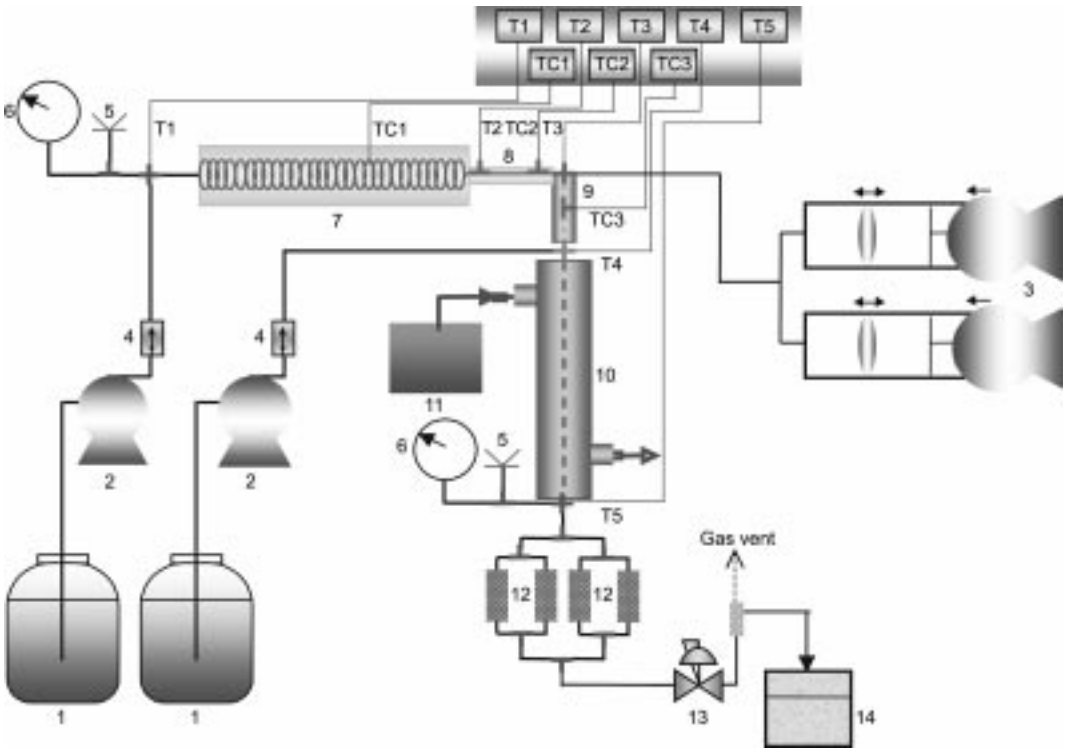

Fig. 1. Schematic diagram of continuous process for hydrolysis of cellobiose.

1. Distilled water storage
2. High pressure pump
3. High pressure slurry pump
4. Check valve
5. Relief valve
6. High pressure gauge
7. High temp. furnace
8. Heating tape
9. Reactor
10. Heat exchange
11. Cooling water bath
12. Line filters
13. Back pressure regulator
14. Sample collector

ing tape with PID controller. Water was heated in the preheater until the water temperature reached a reaction temperature. Cellobiose slurry was mixed with sub- or supercritical water passed preheater at a tee and were fed continuously into a reactor. The reactor was made of stainless steel and the reactor temperature was controlled to maintain a distribution of ±1 °C along the length of the reactor. At the exit of the reactor, the mixture of products and water was quickly cooled to avoid pyrolysis reaction of hydrolysis product by using a cooling jacket as well as direct injecting of water at room temperature. When the system cooled to room temperature, the reactor was depressurized by back-pressure regulator and the residue and products were collected by line filter (SS-8TF-05, pore size 0.5 μm) in the separator and sample collector, respectively.

The volumes of reactors were from the mixing point of reactant and heating water to the cooling point. Changing the length of the reactor allowed for different volumes such as 0.03046, 0.1325, 0.3632, 0.5209 cm^3 and different residence times and each residence time (τ) was calculated by mass flow rate of feed (F), volume of reactor (V) and density of sub- and supercritical water (ρ) using following equation.

$$\tau = \frac{V\rho}{F} \quad (1)$$

The density was assumed to be the density of pure water because very dilute slurry solutions (1 wt%) were used.

Cellobiose decompositions in sub- and supercritical water were conducted at temperatures from 320 to 420 °C at pressures from 25 to 40 MPa, and at residence times within 3 sec.

3. Product Analysis

After solid residue obtained in separator was dried in vacuum

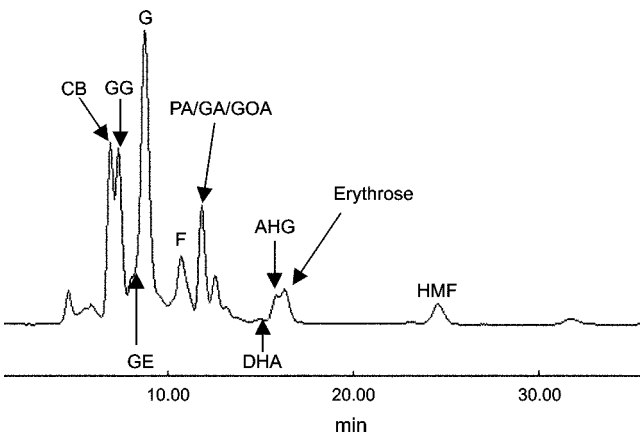

Fig. 2. HPLC chromatography of typical products of cellobiose decomposition.

(CB: Cellobiose, GG: Glycosyl Glycoladehyde, GE: Glycosyl Erythrose, G: Glucose, HMF: 5-Hydroxymethyl furfural, F: Fructose, DHA/AHG/E: 1,3-Dihydroxy acetone/1,6-Anhydro-β-glucose/Erythrose, PA/GA/GOA: Pyruvaldehyde/Glyceraldehyde/Glycolaldehyde)

oven for 24 hours, the weight was measured to calculate conversion of cellobiose. Conversion of cellobiose is represented as

$$X = \frac{W_0 - W}{W_0} \quad (2)$$

where the initial weight of cellobiose is W_0 and the weight of unconverted cellobiose is W.

Reaction products of sample collector were analyzed by using HPLC 2690 Alliance system (Waters Co.) equipped with Sugarpak 1 (Waters Co.) column and RI detector (M2410). The flow rate of water solvent was 0.55 ml/min and the temperature of column and RI detector was 80 and 45 °C, respectively. A sample of 100 μl was injected into the HPLC and the products were analyzed by external standard method using peak height response.

RESULTS AND DISCUSSION

1. Decomposition of Cellobiose

To certify reliability of the experimental apparatus, the experiments were repeated three times under same conditions to calculate the conversion ratios of reactant, yields of hydrolysis products such as glucose, fructose and pyrolysis products such as glucosylerythrose (GE), glucosylglycolaldehyde (GG) pyruvaldehye (PA), glyceraldehyde (GA), glycolaldehyde (GOA), dihydroxyacetone (DHA), 1,6-anhydro-β-glucose (AHG), erythrose, hydroxymethyl furfural (HMF). The standard deviation of the yield about each product was in the range of 0.0167-0.434. This indicated that the data obtained from the apparatus is reliable if the conditions are same. Fig. 2 shows the typical results from the HPLC analysis. As known from the chromatogram, quantitative analysis was conducted using peak height because some peaks of product overlapped. In addition, because pyrolysis products such as GA, PA and GOA had similar retention time, the yield of these products was calculated with mean value, 6.18, obtained from the response factor of each product.

The yields of products and conversion of cellobiose as to retention time under sub- and supercritical region are shown in Fig. 3 and Fig. 4, respectively. It was known that in the case of subcritical region, retention time to approach 50% of cellobiose conversion decreased with increase of temperature and pressure and that in supercritical region, the retention time shortened dramatically to be 0.1 sec under.

At Fig. 3, in the case of 320 °C, reactant decreased continuously with increase of reaction time and the yield of GG, intermediate

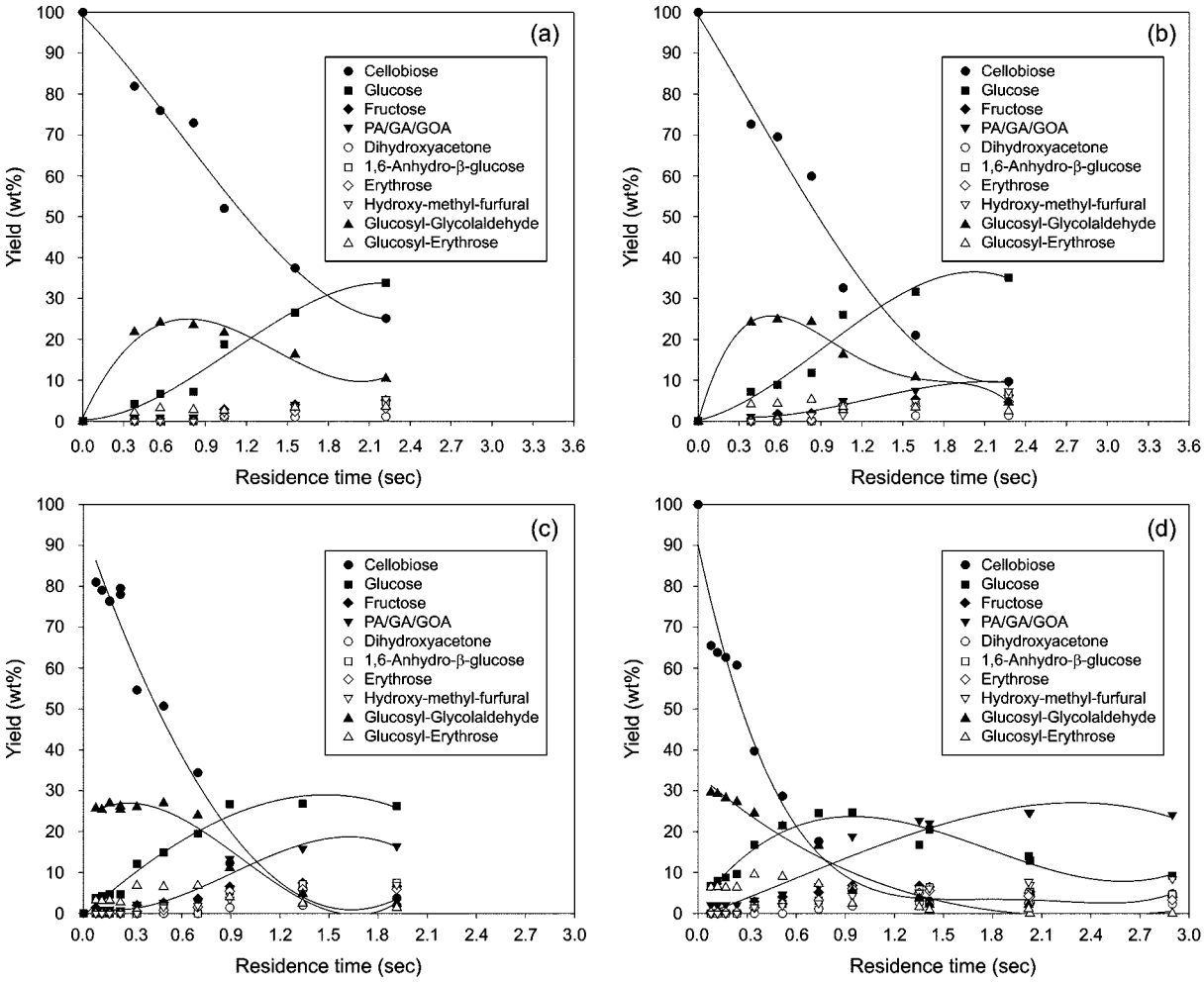

Fig. 3. Products yield versus residence time for cellobiose decomposition in subcritical region.
(a) at 320 °C, 30 MPa (b) at 320 °C, 40 MPa (c) at 360 °C, 30 MPa (d) at 360 °C, 40 MPa

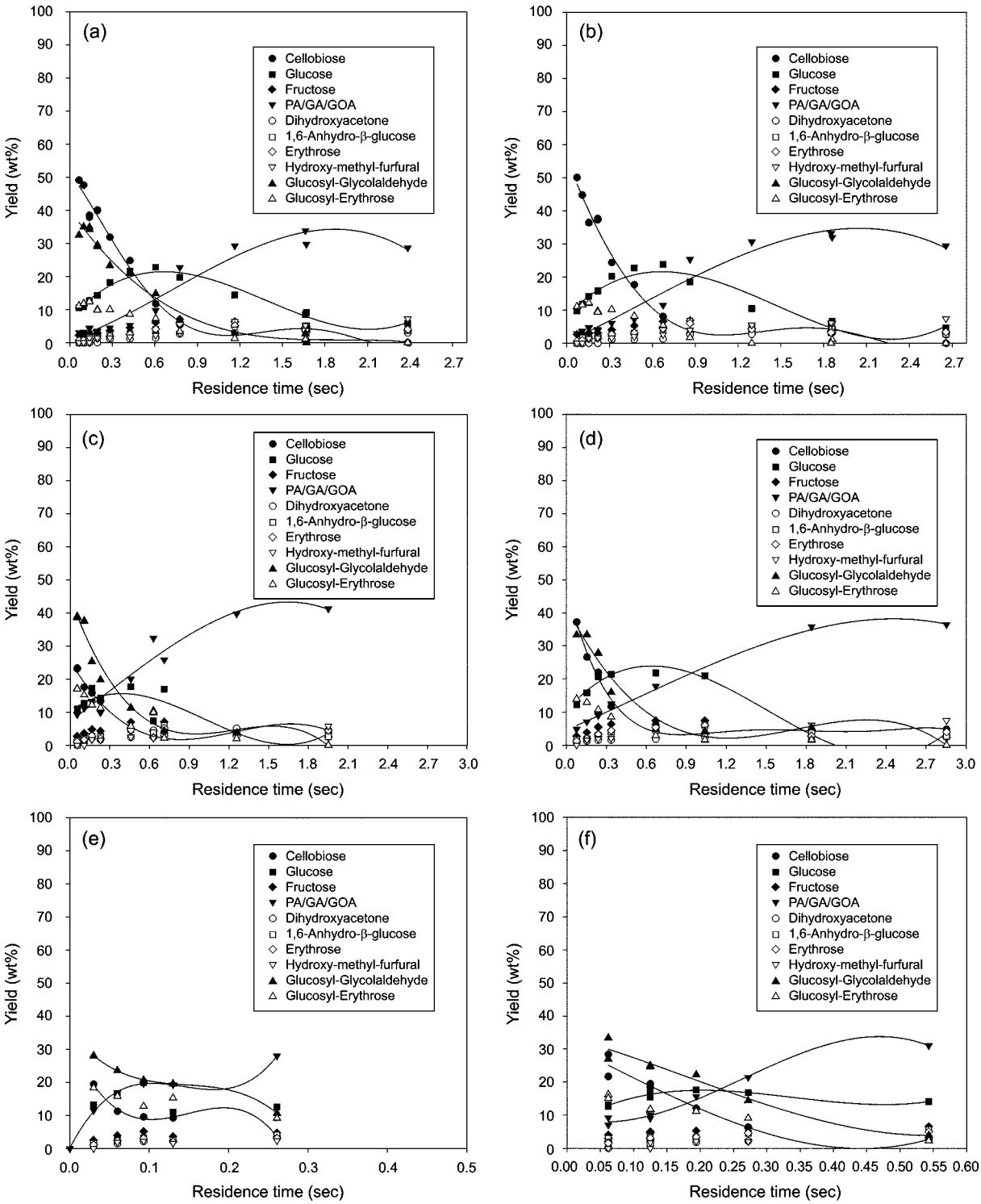

Fig. 4. Products yield versus residence time for cellobiose decomposition in supercritical region.
(a) at 380 °C, 30 MPa, (b) at 380 °C, 40 MPa, (c) at 400 °C, 30 MPa, (d) at 400 °C, 40 MPa, (e) at 420 °C, 30 MPa (f) at 420 °C, 40 MPa

increased until 0.9 sec and then decreased because of second pyrolysis. The yield of glucose increased continuously and the maximum yield was 33.8% after 2 sec of residence time. Parts (c) and (d) of Fig. 3 show the yields of products at 360 °C, at 30 and 40 MPa. As the temperature of reaction increased, the yield of GG was about 30% within 0.3 sec of reaction time, and the time of maximum glucose yield decreased from 1.5 to 0.9 sec with increase of pressure. Especially, the yields of pyrolysis products such as PA/GA/GOA and HMF increased in contrast with results of 320 °C. It indicated that pyrolysis accelerated somewhat more at 360 °C than 320 °C.

In the case of supercritical region of Fig. 4, the yields of cellobiose and GG behaved in the similar manner of the subcritical region,

Table 1. HMF yield according to maximum yield of glucose at experimental conditions

T (°C)	P (MPa)	RT (sec)	Yield (wt%)	
			Glucose (Max)	HMF
320	25	2.191	33.8	5.1
	30	2.222	33.8	5.4
	35	2.251	36.8	6.5
	40	2.276	35.1	7.3
360	25	1.835	24.5	6.3
	30	1.339	26.8	5.0
	35	0.920	27.0	3.9
	40	0.943	24.7	4.3
380	25	0.511	21.4	1.9
	30	0.606	22.8	2.2
	35	0.647	24.7	2.4
	40	0.675	23.8	2.6
400	25	0.214	15.7	2.4
	30	0.459	17.7	2.5
	35	0.609	22.4	3.1
	40	0.671	21.8	3.5
420	25	0.060	18.8	2.4
	30	0.093	19.9	2.3
	35	0.149	21.9	2.1
	40	0.194	17.6	2.1

but the yield of glucose formed a volcano curve and the yield of the pyrolysis product of PA/GA/GOA increased considerably in comparison with the subcritical region.

As HMF was known as inhibitor for fermentation [Abatzoglou, 1986], it was found that fermentation of glucose was favored when the HMF concentration was low at the condition of maximum glucose yield. Table 1 shows the HMF yield at the residence time at which glucose has the maximum yield with respect to variation of pressure. As the reaction condition shifted to the subcritical region, the HMF yield at maximum glucose yield had high value in comparison with the supercritical region. On the contrary, though the yield of glucose was under 25% in the supercritical region, the yield of HMF also had lower value. It may be explained as follows. As the reaction condition moved to supercritical region, the pyrolysis rate accelerated considerably so that the yield of glucose decreased. However as the residence time to approach maximum glucose yield also decreased in supercritical condition, HMF might not have been formed yet within the short residence time. Because the fermentation could be possible for hydrolysis solution diluted by two times with hydrolyzate [Park et al., 2001], it was important to find the condition to be able to obtain high concentration of glucose at lower HMF concentration. Therefore, it was found that the optimum condition to consider fermentation was 380 in supercritical region.

2. Hydrolysis Model of Cellobiose and Kinetic Constant

Fig. 5 shows the plots of $-\ln(1-X)$ versus residence time for cellobiose. The straight line means that decomposition of cellobiose depends on first-order kinetics. In the subcritical region of Fig. 5(a) and (b), these lines pass through the origin. However, though linearity formed in the case of the supercritical region, these lines do not pass the origin. Uhl and Gray [Uhl et al., 1986] have summarized the studies on the mixing of liquid and gas stream. For the case of opposed flow tee, complete mixing is achieved at feed mixing lengths of up to 5 tube diameters for gases, while for liquids they are typically 10-40 tube diameters. But a detailed analysis on the optimum reactor for mixing of fluid and liquid stream is not presently carried out. Moreover, because the difference of densities for liquid and fluid stream exist, perfect mixing may not be available. So long contact time is needed to mix these streams homogeneously.

Table 2. Rate constants for cellobiose decomposition in sub- and supercritical water

Pressure		320 °C	360 °C	380 °C	400 °C	420 °C
30 MPa	k	0.6408	1.7133	2.7593	3.5703	6.4726
	intercept	−0.03	−0.04	0.46	1.29	1.62
	reliability	0.99	0.99	0.98	0.99	0.94
35 MPa	k	0.8625	1.7444	2.4719	2.8739	6.0438
	intercept	−0.05	0.10	0.5	0.88	1.11
	reliability	0.99	0.99	0.95	0.96	0.99
40 MPa	k	1.0481	2.3984	3.3592	3.6105	4.7944
	intercept	−0.06	0.08	0.37	0.75	1.14
	reliability	0.99	0.99	0.97	0.98	0.96

In this experiment, since residence time is considerably shorter in the supercritical reaction and the length of reactor also is not long enough to achieve perfect mixing, the decomposition in the supercritical region is thought not to be a homogeneous reaction. This may partially explain the irregularities that the plot of first order kinetics for the decomposition of cellobiose do not pass the origin.

The rate constants obtained from the slopes of Fig. 5 are summarized in Table 2. As shown by the intercept, the deviation from the origin was little in the subcritical region, whereas the condition moved to the supercritical region, the deviation was rather larger. Futhermore, under the same pressure, as the temperature increased, reaction rate also increased; but under same temperature, reaction rate increased or/and decreased as the pressure increased. Namely, in the subcritical region of 320 and 360 °C, reaction rate increased with increasing pressure without regard to temperature whereas in supercritical region of 380 and 400 °C, reaction rate decreased in the range from 30 to 35 MPa and reaction rate increased at 40 MPa. In addition, at 420 °C, reaction rate decreased according to increase of pressure contrary to the results of subcritical region.

These phenomena to reverse trend of reaction rate might be ascribed to the shift of mechanism from ionic reaction to free radical reaction. Antal and Roy [1987] reported that the reaction chemistry in supercritical water can be described by heterolytic (ionic) mechanisms when the ion product K_w of the supercritical water exceeds 10^{-14} and by homolytic (free radical) mechanisms when $K_w \ll 10^{-14}$. K_w values at this experimental condition were determined using the chart [Bernard, 1998] about K_w dependence of temperature and pressure and summarized at Table 3. As shown at Table 3, it was confirmed that all reactions in the subcritical region (320, 360 °C) corresponded to ionic mechanism due to $K_w \gg 10^{-13}$ and that in the cases of 25, 30 MPa at 380 °C, 30, 35 MPa at 400 °C and 35, 40 MPa at 420 °C, reaction mechanism shifted from ionic to free radical reaction with decreasing pressure. In comparison with K_w trend and rate

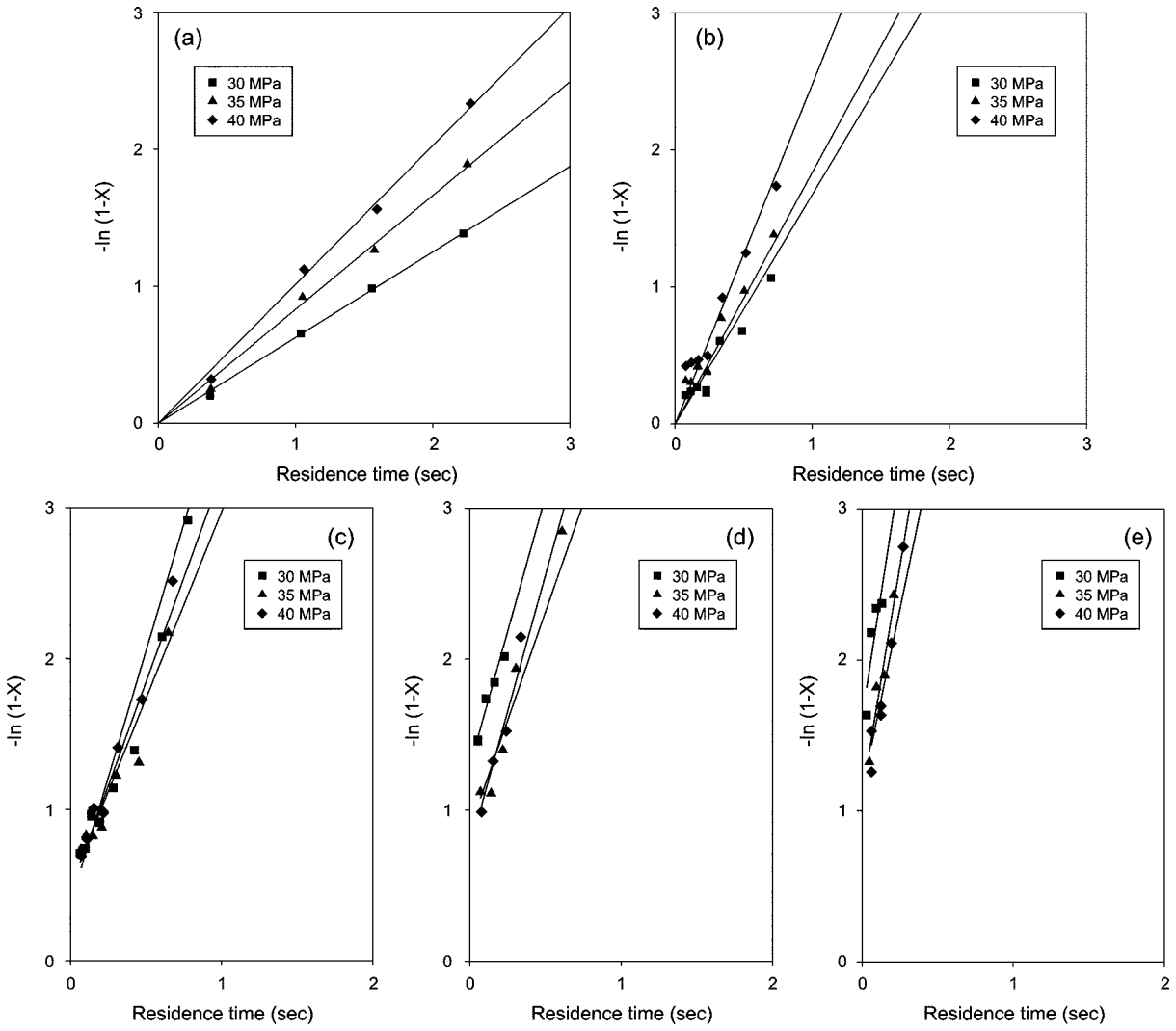

Fig. 5. −ln(1−X) versus residence time for cellobiose according to reaction temperature and pressure.
(a) 320 °C, (b) 360 °C, (c) 380 °C, (d) 400 °C, (e) 420 °C

Table 3. Ion product variation according to temperature and pressure

	320 °C	360 °C	380 °C	400 °C	420 °C
25 MPa	$K_w \approx 10^{-11.4}$	$K_w \approx 10^{-12.28}$	$K_w \approx 10^{-15.65}$	$K_w \approx 10^{-19.7}$	$K_w \approx 10^{-20.9}$
30 MPa	$K_w \approx 10^{-11.3}$	$K_w \approx 10^{-11.92}$	$K_w \approx 10^{-13.01}$	$K_w \approx 10^{-15.28}$	$K_w \approx 10^{-18.2}$
35 MPa	$K_w \approx 10^{-11.15}$	$K_w \approx 10^{-11.7}$	$K_w \approx 10^{-12.35}$	$K_w \approx 10^{-13.2}$	$K_w \approx 10^{-15.1}$
40 MPa	$K_w \approx 10^{-11.05}$	$K_w \approx 10^{-11.5}$	$K_w \approx 10^{-11.92}$	$K_w \approx 10^{-12.53}$	$K_w \approx 10^{-13.6}$

Dark shade: ionic reaction, light shade: transition reaction, no shade: free radical reaction.

constant, the reverse trend of rate constant according to pressure indicates the possibility of mechanism change. Though the exact mechanisms and the shift of mechanism cannot be determined certainly yet because of the short residence time in sub/supercritical water and the error about deviation from origin for obtaining the rate constant, it could be thought that the relationship between K_w and rate constant exists through the above results. And this relationship seems to be a worthwhile subject to study for the future.

It is thought that the reason for increase of reaction rate with pres-

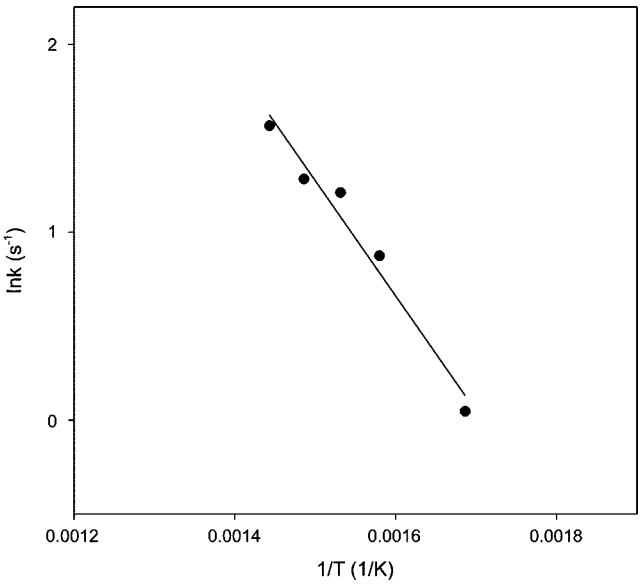

Fig. 6. Arrhenius plot for cellobiose decomposition.

sure increase is the increase of residence time in the subcritical region. Meanwhile, the reaction in the supercritical region shifts into the direction of lower pressure with increasing pressure because the reaction progresses in gas-like phase for supercritical region. Consequently, the reaction proceeds in reverse direction in the supercritical region.

As explained above, because the reaction at 40 MPa only belonged to the same mechanism, ionic reaction as to K_w, the activation energy of cellobiose decomposition was calculated at 40 MPa. The result of the Arrhenius plot is shown in Fig. 6 and the activation energy for cellobiose decomposition was found to be 51.05 kJ/mol.

CONCLUSIONS

Based on the above experimental observations and discussions, we may conclude the following about the decomposition of cellobiose and the reaction mechanism.

1. Cellobiose was found to decompose via hydrolysis and pyrolysis to be glucose, fructose as hydrolysis products and glycosylerythrose, glycosylglycolaldehyde, glycolaldehyde, pyruvaldehye, glyceraldehyde, glycolaldehyde, dihydroxyacetone, 1,6-anhydro-β-glucose, erythrose, hydroxymethyl furfural as pyrolysis products. As the reaction condition shifted to supercritical region, residence time having same conversion decreased, and as pressure and residence time increased at same temperature, pyrolysis products increased.

2. When fermentation inhibitor, HMF, was not considered, maximum yield of glucose was 36.8% at 320 °C, 35 MPa in subcritical region, while at the condition of minimum HMF, maximum yield of glucose was 21.4% at 380 °C, 25 MPa in supercritical region. Namely, in the subcritical region, HMF as well as the yield of glucose was high, but in the supercritical region, though the yield of glucose was lower than subcritical region, the yield of HMF was lower too.

3. The decomposition of cellobiose depended on first-order kinetics. Reaction rate increased in subcritical region and increased and/or decreased in critical point region and decreased in supercritical region with increasing pressure. This might be attributed to the shift of reaction mechanism from ionic mechanism to free radical mechanism.

4. The activation energy for cellobiose decomposition was found to be 51.05 kJ/mol as a result of Arrhenius plot at 40 MPa.

ACKNOWLEDGMENTS

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NOMENCLATURE

F : inlet flow rate [g/min]
V : volume of the reactor [cm^3]
X : conversion of cellulose [-]
W : weight of residual cellulose [g]
W_0 : weight of cellulose before reaction [g]
k : decomposition rate constant [sec^{-1}]
K_w : ionic product (=$[H^+][OH^-]$)$[M^2]$

Greek Letters

ρ : density of water [g/cm^3]
τ : residence time [s]

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