Mechanism and Kinetics of Cellobiose Decomposition in Sub- and Supercritical Water

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Cellobiose decomposition kinetics and products in sub- and supercritical water were studied with a flow apparatus at temperatures from 300 to 400 °C at pressures from 25 to 40 MPa, and at short residence times (0.04−2 s). Cellobiose was found to decompose via hydrolysis of the glycosidic bond and via pyrolysis of the reducing end. Pyrolysis products were glycosylerythrose (GE) and glycosylglycolaldehyde (GG) which were confirmed by FAB-MS. Hydrolysis products were glucose, erythrose, and glycolaldehyde from cellobiose, GE, and GG, respectively, as well as glucose decomposition products. The kinetics from glucose decomposition were used to fit the experimental results and evaluate rate constants of hydrolysis (k_H) and pyrolysis rate constants (k_1 and k_2). The activation energy for the hydrolysis of cellobiose and pyrolysis products GG and GE was found to be 108.6, 110.5, and 106.1 kJ/mol, respectively. In the supercritical region, there was a decrease in the pyrolysis rates k_1 and k_2 and a corresponding increase in hydrolysis selectivity from 85% to 95% as the pressure increased from 30 to 40 MPa.

Introduction

Cellulose hydrolysis products have the potential to replace many intermediates that are being synthesized from petroleum fractions (Fengel and Wegener, 1989). The production of glucose by hydrolysis is an important step of cellulose conversion, from which a wide range of chemicals can be synthesized, including polymers. From glucose, for example, one can form ethanol by fermentation or sorbitol and vitamin C from hydrogenation. Acid treatment of glucose forms 5-(hydroxymethyl)furfural which can be used to make polyamides, polyesters, and epoxides.

To date, however, few techniques exist for converting cellulose to hydrolysis products in a rapid and selective manner. We have performed a number of related studies with the aim of understanding cellulose decomposition. In previous works (Adschiri et al., 1993; Malaluan, 1995; Sasaki et al., 1997), we conducted a study on the cellulose reactions in sub- and supercritical water conditions (300−400 °C). At these conditions and at short residence times (0.04−2 s), we found that a rapid reaction occurs giving high yields of hydrolysis products with the subsequent formation and decomposition of glucose. We have also conducted a study on the decomposition of glucose at these conditions (Kabyemela et al., 1997a) as well as some of its decomposition products such as glyceraldehyde and dihydroxyacetone (Kabyemela et al., 1997b). Limited kinetic data exists on the hydrolysis of intermediate oligomers in sub- and supercritical water. This study focuses on cellobiose, which is a disaccharide of glucose linked by $\beta(1-4)$ glycosidic bonds similar to cellulose.

Bobleter and Bonn (1983) conducted a study on the hydrothermolysis of cellobiose in the range of 180−249 °C in an autoclave, but were only able to follow the formation of glucose as an intermediate compound. Reaction times were in the order of 1−14 min, and the product analysis was able to account for 60% of the cellobiose decomposition products.

The aim of this work is to elucidate the reaction pathways, evaluate the reaction kinetics of cellobiose in sub- and supercritical water conditions. We also examine the pressure dependence of cellobiose product selectivity in the supercritical region.

Experimental Section

Materials. Chemicals used in the experiments and calibration were the following: cellobiose (99%+), obtained from Fluka (Tokyo); glucose (99+%), fructose (99+%), glyceraldehyde (97+%), erythrose (60%), pyruvaldehyde (40%), and dihydroxyacetone (99+%) obtained from Wako (Osaka); and 1,6-anhydroglucose (99+%) obtained from Tokyo Chemical (Tokyo).

Apparatus and Procedure. Details on the apparatus can be obtained in our previous work (Kabyemela et al., 1997a). Briefly aqueous solutions were mixed with sub- or supercritical water at a tee and were fed continuously into a reactor (0.077 cm i.d. for supercritical conditions and 0.118 cm i.d. for subcritical conditions) constructed of 316 stainless steel and then rapidly quenched. The aqueous solution feed rate was 2 g/min. Preheated water that was mixed with the aqueous solution had a feed rate of 14 g/min. Mixing of the feed in this manner allowed a rapid heating up to the reaction temperature. The temperature was measured 2 cm below the mixing tee by a chromel−alumel thermocouple. At the exit of the reactor, the mixture was quickly cooled to terminate the reaction by injecting water into the line at 14 g/min and externally by a cooling water jacket. The pressure in the system was controlled by a back pressure regulator at the exit of the cooling jacket. Products were sampled and analyzed by the HPLC. The temperature distribution along the reactor was usually between 1 and 2 °C, and so the reaction volume (V) could be precisely

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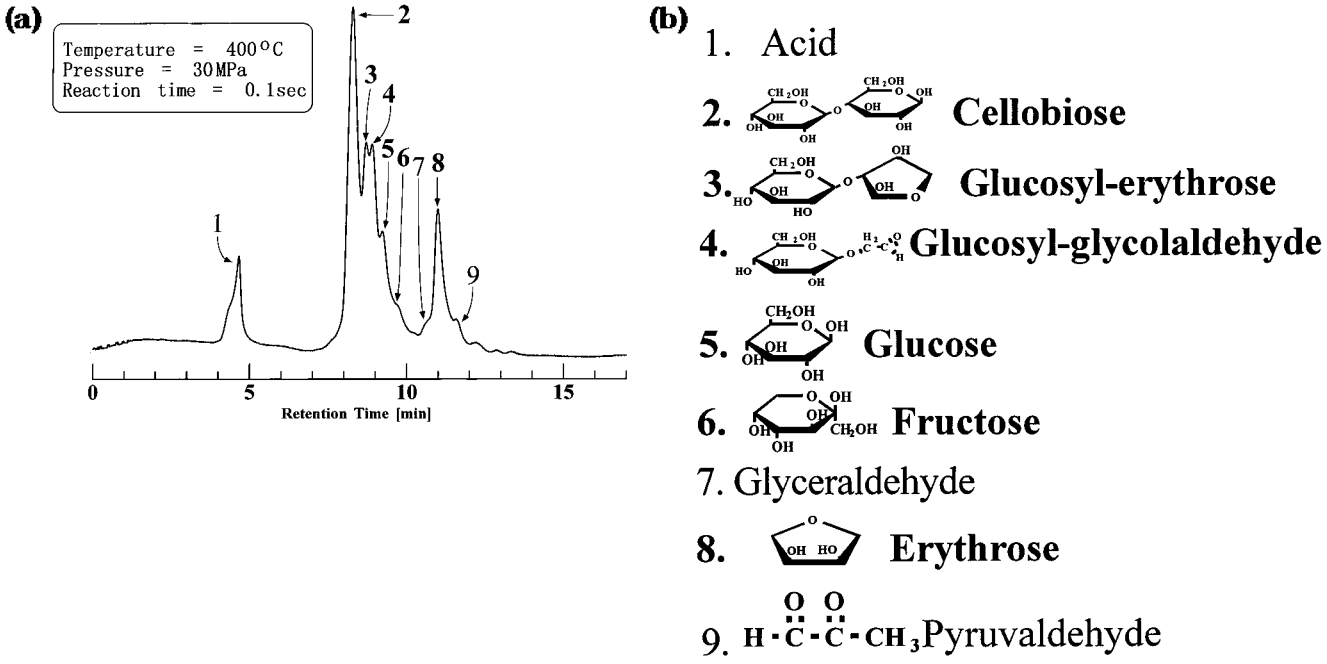

Figure 1. HPLC chromatograph of typical products of cellobiose decomposition.

Table 1. Cellobiose Decomposition Data in Sub- and Supercritical Water[a]

residence time [s]	conv.	CB [M] × 10^{-3}	GE [M] × 10^{-5}	GG [M] × 10^{-5}	Glu [M] × 10^{-4}	Fru [M] × 10^{-5}	Ery [M] × 10^{-4}
(a) Temperature 300 °C, Pressure 25 MPa							
0.146	0.07	2.24	2.80	4.70	1.57	4.71	1.25
0.292	0.13	2.09	2.12	2.25	2.48	6.93	1.59
0.839*	0.17	2.01	3.67	3.85	4.44	8.30	1.77
0.878*	0.17	2.02	4.15	4.39	3.86	10.4	1.86
1.102	0.21	1.91	4.74	5.02	5.25	13.3	1.91
residence time [s]	conv.	CB [M] × 10^{-3}	GE [M] × 10^{-4}	GG [M] × 10^{-4}	Glu [M] × 10^{-4}	Fru [M] × 10^{-4}	Ery [M] × 10^{-4}
(b) Temperature 350 °C, Pressure 25 MPa							
0.122	0.25	1.81	1.46	1.55	4.54	1.07	3.61
0.142	0.28	1.74	1.63	1.73	4.07	1.22	3.35
0.245	0.36	1.54	1.57	1.67	6.17	1.66	4.97
0.569	0.57	1.04	1.41	1.49	7.30	2.64	7.19
0.730	0.66	0.81	1.62	1.72	8.33	3.25	8.56
0.918*	0.72	0.68	1.48	1.57	8.43	3.38	9.81
1.046*	0.73	0.65	1.30	1.37	7.68	3.52	11.8
1.402	0.80	0.49	0.85	0.89	5.34	2.88	13.1
residence time [s]	conv.	CB [M] × 10^{-3}	GE [M] × 10^{-4}	GG [M] × 10^{-4}	Glu [M] × 10^{-4}	Fru [M] × 10^{-4}	Ery [M] × 10^{-4}
(c) Temperature 400 °C, Pressure 30 MPa							
0.030*	0.54	1.12	2.61	2.77	5.47	2.54	7.85
0.029*	0.59	0.99	2.36	2.50	6.54	2.69	7.37
0.030*	0.55	1.09	2.60	2.75	8.09	3.21	7.54
0.029*	0.58	1.01	2.44	2.38	4.58	2.04	7.64
0.078	0.63	0.90	2.30	2.68	5.37	2.39	10.7
0.098	0.70	0.72	2.03	2.35	5.52	2.69	13.0
0.147	0.76	0.59	2.24	2.37	5.36	2.65	15.5
residence time [s]	conv.	CB [M] × 10^{-3}	GE [M] × 10^{-4}	GG [M] × 10^{-4}	Glu [M] × 10^{-4}	Fru [M] × 10^{-4}	Ery [M] × 10^{-4}
(d) Temperature 400 °C, Pressure 40 MPa							
0.043*	0.62	0.92	1.73	1.84	6.15	2.68	7.83
0.043*	0.60	0.96	1.83	1.95	6.21	3.03	8.03
0.043*	0.60	0.96	2.02	2.14	6.19	3.75	7.93
0.073	0.69	0.76	1.74	1.85	6.38	3.10	8.35
0.113	0.75	0.61	1.74	1.86	6.01	2.97	11.9
0.144	0.79	0.50	1.29	1.49	5.43	2.60	12.6

[a] Symbols: CB, cellobiose; GE, glycosylerythrose; GG, glycosylglycolaldehyde; Glu, glucose; Fru, fructose; Ery, erythrose. Runs marked with asterisks are those used for estimation of experimental error. Cellobiose feed = 0.002 41 M.

evaluated. The residence time (τ) was calculated by $\tau = V\rho/F$, where the mass flow rate is F and the density of the reaction mixture is ρ. The density was assumed to be the density of pure water because very dilute samples were used. Cellobiose feed was 0.6 wt %. Reaction temperatures ranged from 300 to 400 °C with pressures from 25 to 40 MPa and residence times of 0.04−2 s.

Products Analysis. Reaction products were analyzed by using a liquid chromatography (LC) system

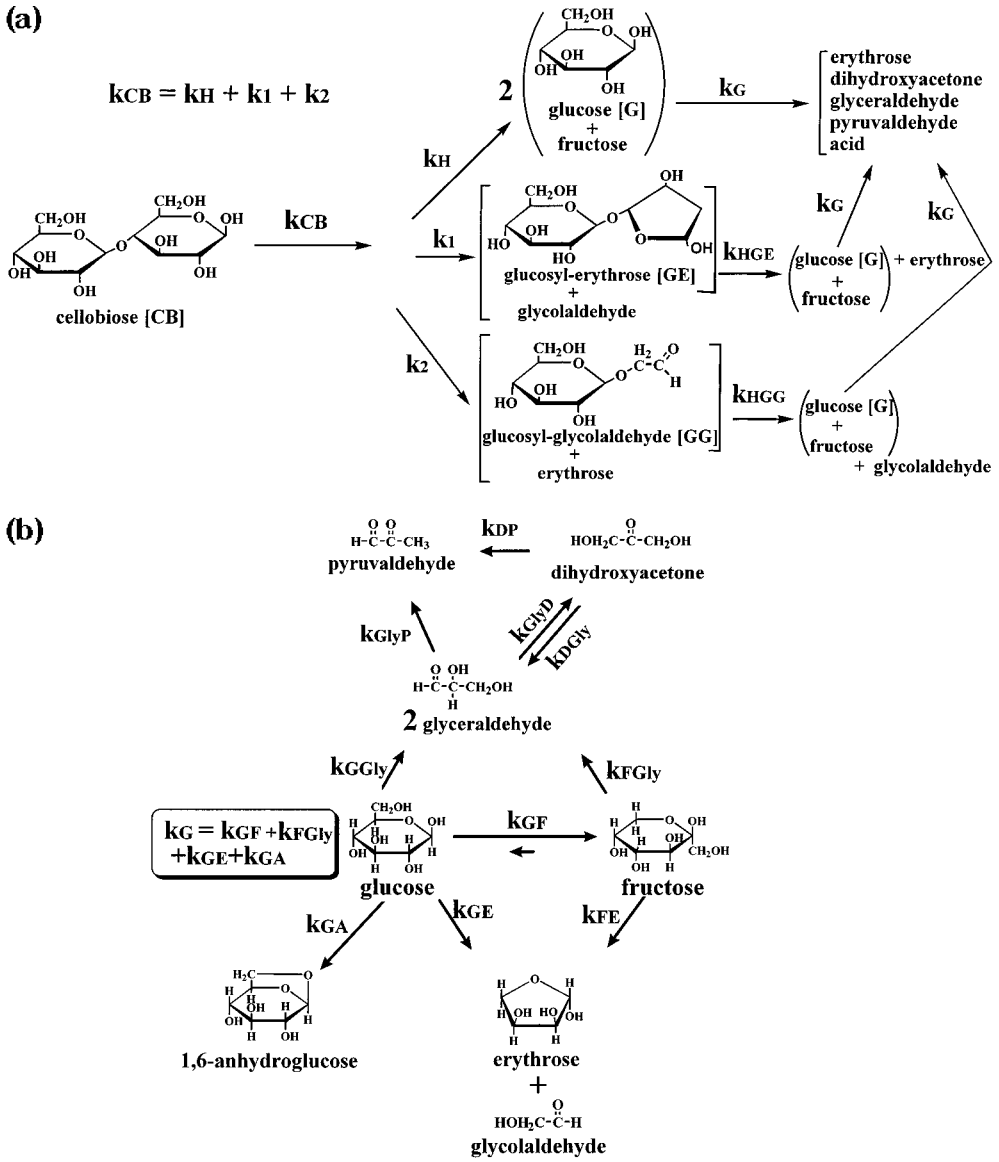

Figure 2. (a) Cellobiose decomposition pathway. (b) Glucose decomposition pathway.

with an ionpak KS 802 (Shodex) column operated at 80 °C with a 1 mL/min flow of water solvent. The detectors used were an ultraviolet (UV) (Thermoseparations Products, model Spectra 100) detector set at 290 nm and a refractive index (RI) (ERC, model 7515A) detector.

Details on the analytical procedure are described in our previous work (Kabyemela et al., 1997a). Typical results from the HPLC analysis are shown in Figure 1. The peaks of glycosylerythrose (GE) and glycosylglycolaldehyde (GG) were identified by FAB-MS and quantified by HPLC. Pure samples of glycosylerythrose (GE) and glycosylglycolaldehyde (GG) were not available. Their respective response factors were estimated from the correlation of the response factors of the known similar compounds such as cellobiose, cellotriose, cellopentaose, and cellohexaose to their molecular weight. These compounds had a response factor ranging from 5.279×10^{-6} to 6.868×10^{-6}. The correlation was quadratic and gave a standard deviation of 2.74×10^{-7} to the actual response factors. The carbon balance closure was between 85% and 100% based on the compounds detected by the HPLC. Higher carbon balance closure was obtained at shorter reaction times (<0.1 s) since product identification was more certain. The lack of carbon closure at longer residence times is mainly due to the formation of further decomposition products, probably acids, which could not be quantified. Total organic carbon results on selected samples showed a carbon balance between 95% and 100%.

Results and Discussion

The product concentrations obtained from the experiments are shown in Table 1. At 300 °C, the conversion was up to about 20% at the residence times of up to 1.1 s, with the intermediate products being formed without their subsequent decomposition. At 350 °C, the conversion reached 80% at a residence time of 1.4 s. Products such as glucose and fructose go through a maximum and erythrose reaches the highest concentration among the products. Erythrose may be formed from the hydrolysis of GE and GG, whose concentrations seem to be constant. At 400 °C, the conversion reaches about 80% in about 0.15 s. There is a rapid formation and subsequent decomposition of the products glucose, fructose, GG, and GE while the concentration of erythrose seems to increase. Similar results were obtained at similar conditions for erythrose in the study of glucose

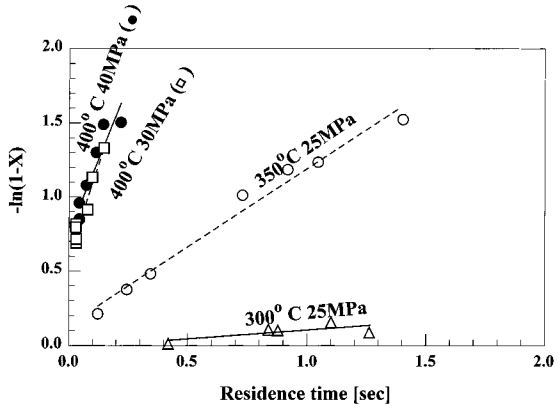

Figure 3. $-\ln(1 - X)$ versus residence time for cellobiose decomposition.

Table 2. Reaction Rate Constants for Cellobiose Decomposition in Sub- and Supercritical Water

rate constant [s^{-1}]	300 °C, 25 MPa	350 °C, 25 MPa	400 °C, 30 MPa	400 °C, 40 MPa	E_a [kJ/mol]
k_{CB}	0.21	1.06	4.9	4.0	96.4
k_1	0.03	0.05	0.25	0.08	30.4
k_2	0.04	0.11	0.35	0.1	69.3
k_H	0.14	0.9	4.3	3.8	108.6
k_{HGE}	0.15	0.9	3.7	3.1	106.1
k_{HGG}	0.17	1.1	3.5	3.2	110.5

decomposition (Kabyemela et al., 1997a). The standard deviation for the data is in the range of $5-7 \times 10^{-5}$ in concentration based on the runs indicated in Table 1.

On the basis of these results, the reaction pathway elucidated through the analysis of products distribution with reaction time is shown in Figure 2a. Cellobiose undergoes parallel reaction via hydrolysis (k_H) and pyrolysis (k_1 and k_2). Hydrolysis forms glucose and pyrolysis forms GG and GE which hydrolyze via k_{HGG} and k_{HGE} to form glucose plus glycolaldehyde and glucose plus erythrose, respectively. Similar pyrolytic products were obtained by Ponder and Richards (1993) in the study of the pyrolysis of inulin (a polysaccharide; soluble in water; molecular formula = $(C_7H_{10}O_5)_6$) and also by Koll et al. (1990) in the pyrolysis of cellulose. In both cases, the pyrolytic products formed were a result of pyrolysis at the reducing end. The products GG and GE were not detected in the earlier work on cellobiose (Bobleter and Bonn, 1983) probably due to the type of analytical methods used and the range of temperatures. Glucose that is formed undergoes further decomposition to other products (Kabyemela et al., 1997a) as shown in Figure 2b.

Figure 3 shows the plots of $-\ln(1 - X)$ versus residence time for cellobiose that were used to evaluate the reaction rate constant k_{CB}. The straight line suggests first-order kinetics, similar to the results of Bobleter and Bonn (1983). However, these lines do not pass through the origin. At the mixing point, we are mixing two lines with different temperature, concentration, and phases (liquid and supercritical). Uhl and Gray (1986) have summarized the studies on the mixing of liquid and gas streams. 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. A study on the mixing of fluid and liquid streams is not presently available. Considering the extreme case of the shortest reactor, high temperature (400 °C) and a conservative value of up to 40 tube diameters mixing length, a maximum of 30% of the actual reactor length would be defined as the mixing zone. This may partially account for the irregularities at the shorter residence times which is similar to the effects of preheat times in batch experiments. In this respect, these effects cannot be avoided and they cause a bias at short residence times.

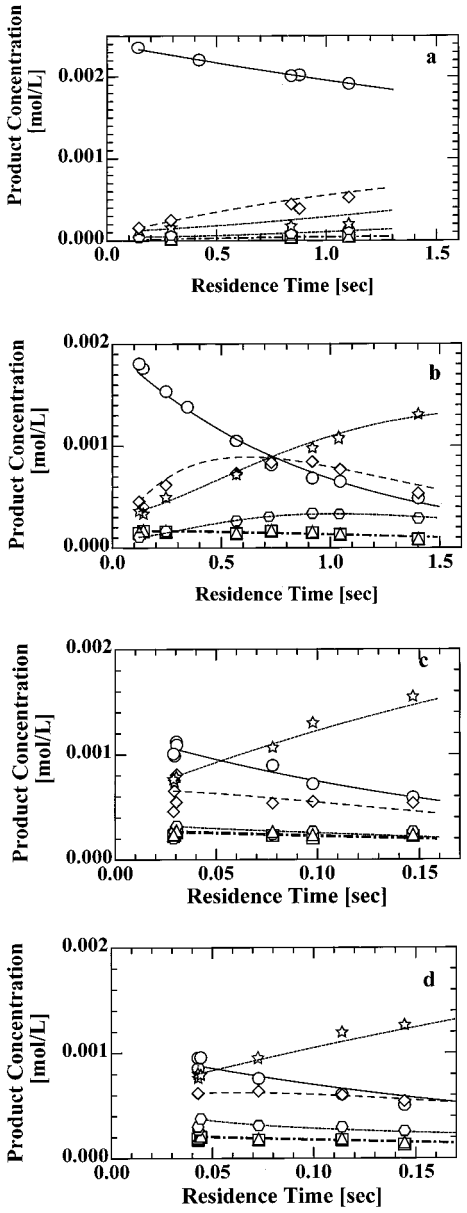

Figure 4. Products concentration versus residence time for cellobiose decomposition. (a) Temperature at 300 °C, pressure at 25 MPa. (b) Temperature at 350 °C, pressure at 25 MPa. (c) Temperature at 400 °C, pressure at 30 MPa. (d) Temperature at 400 °C, pressure at 40 MPa. Symbols: round, cellobiose; triangle, glycosylerythrose; hexagon, fructose; diamond, glucose; square, glycosylglycolaldehyde; star, erythrose.

Using the experimental results, the hydrolysis and pyrolysis pathway shown in Figure 2a, the reaction rates were evaluated and the results are shown in Table 2. The rate constants were evaluated by fitting the cellobiose as well as the product concentrations such as glycosylerythrose, glycosylglycolaldehyde, glucose, fructose, and erythrose. The glucose decomposition rate constants used in the fitting were obtained from our earlier work (Kabyemela et al., 1997a). The kinetics were fitted using the software, modeling laboratory MLAB (Bunow and Knott, 1995; Knott, 1995). The

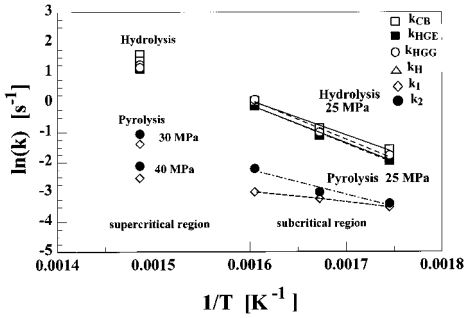

Figure 5. Arrhenius plot for cellobiose reaction rate constants k_{CB}, k_H, k_{HGE}, and k_{HGG}.

fitting results for the cellobiose experiments are shown in Figure 4a−d. An analysis on the residuals between the model and the experimental data was made for the products. The model predicts concentrations that are within the experimental standard deviation which was $5-7 \times 10^{-5}$. The standard deviation of the model residuals for all compounds was in the order of 5×10^{-5} in concentration. The rate constants obtained were plotted against the reciprocal of temperature to obtain the activation energies. These kinetic parameters are summarized in Table 2. The hydrolysis rates k_H, k_{HGG}, and k_{HGE} have almost the same values which may be a result of the similarity in structure and reaction mechanism.

The effect of pressure in the supercritical water region is rather small on the hydrolysis rates k_H, k_{HGG}, and k_{HGE}. The difference in the pressures used of 30−40 MPa may not be large enough to provide a significant change in these hydrolysis reactions. However, at these conditions, the cellobiose pyrolysis rates decreased with an increase in pressure. In other words, the selectivity toward cellobiose hydrolysis increases from 85% to 95% as pressure is increased from 30 to 40 MPa at 400 °C. Pyrolysis essentially arises from the breaking of C−C linkage. The extension of this linkage prior to fragmentation in the transition state is suppressed by the increased local density of water around the molecule as pressure is increased. This cage effect results in the decrease in pyrolysis rate with pressure (Amis and Hinton, 1973).

Conclusion

The reaction pathways of cellobiose in subcritical and supercritical water were elucidated. Decomposition of cellobiose was via hydrolysis to glucose and pyrolysis to glycosylerythrose and glycosylglycolaldehyde which further hydrolyzed to erythrose plus glucose and glycolaldehyde plus glucose, respectively. The hydrolysis and pyrolysis rates for the general decomposition pathway of cellobiose were evaluated. The cellobiose hydrolysis rate was similar to the glycosylerythrose and glycosylglycolaldehyde hydrolysis rates. The pyrolysis rate of cellobiose decreased with pressure in the supercritical water conditions giving an increase in hydrolysis selectivity. This may be a result of the cage effect of the solvent around the transition species that suppresses the decomposition.

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