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Glucose Decomposition in Water under Supercritical Pressure at 448-498 K

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The behavior of glucose under hydrothermal conditions is of great interest in the development of processes for supercritical water gasification and the hydrothermal pretreatment of lignocellulosics. Our group examined this behavior in a series of glucose decomposition experiments in water at a pressure of 25 MPa in the temperature range of 448-498 K. The rate parameters of the reactions from glucose to the decomposition products were determined by the least squares method. The reaction order of unity for glucose decomposition was found to be the result of several reactions of various reaction orders proceeding in parallel. The reaction orders for the decompositions of fructose, erythrose, glyceraldehyde, and 1,6-anhydroglucose can be considered unity without large error. By examining the selectivity of glucose conversion reactions, we determined that almost all of the glucose was initially converted into fructose, but at 498 K, 1,6-anhydroglucose and erythrose selectivity matched that of fructose. The kinetic parameters determined in our experiments should be useful for predicting the reaction taking place in the pre-heating section of the supercritical water gasification process and in the hydrothermal pretreatment reactor used for the saccharification of cellulosic materials.

Key Words

Glucose, Decomposition, Subcritical water

Introduction

The behavior of glucose under hydrothermal reaction conditions has been of interest to biomass researchers seeking to make effective use of lignocellulosics^{1) ~ 7)}. Glucose, a monomer of cellulose, is an important intermediate to final products such as ethanol and combustible gas. The rapid hydrolysis of cellulose is a target in the pretreatment of lignocellulosics for ethanol fermentation under hydrothermal conditions, while the further decomposition of glucose in the hydrothermal reaction field should be strictly prohibited^{8) ~ 12)}. Sasaki et al. proved that hydrolysis takes place rapidly by experimentally demonstrating the dissolution of cellulose in supercritical water¹³⁾. The further decomposition of glucose is also rapid, however, and it ultimately leads to the production of fermentation inhibitors such as 5-hydroxymethylfurfural⁸⁾. This is why Sakaki's group decided to use a semi-batch reactor for the fraction-

ation of lignocellulosics¹⁴⁾. The heating rate in the process of supercritical water gasification is known to influence the efficiency of carbon gasification. The authors, for example, have found that a high heating rate improves the efficiency of glucose gasification in supercritical water¹⁵⁾. Sinag et al. managed to increase the gas yield and reduce furfural production by applying a high heating rate in glucose hydropyrolysis experiments in supercritical water¹⁶⁾. Not long afterwards, Watanabe et al. confirmed that a high heating rate significantly improved the gas production from glucose in hot compressed water¹⁷⁾. Taken in sum, these findings confirm that the heating rate confers important effects on glucose decomposition in hydrothermal conditions and on the final products yielded. The only way to gain a fuller understanding of the effects of the heating rate henceforth will be to collect more data on the reaction mechanism, including the reaction rate parameters covering the entire temperature range throughout the heating period.

Other work has focused on the reaction mechanism and kinetics of glucose decomposition under hydrothermal conditions. Kabyemela et al. proposed a detailed scheme of the

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glucose decomposition pathway based on the results of decomposition experiments using glucose aqueous solution and a series of aqueous solutions of compounds derived from glucose degradation in the temperature range of 573–673 K⁽⁴⁾⁽⁵⁾⁽¹⁸⁾⁽¹⁹⁾. In a glucose decomposition experiment conducted at 25 MPa in the temperature range of 448–673 K, our group found that the reaction order of glucose decomposition changed from unity to lower values as the temperature rose⁽²⁰⁾. This result implied that the reaction mechanism changed with the change in the reaction temperature.

The present study was conducted to investigate glucose decomposition under a hydrothermal condition at a pressure of 25 MPa in a lower temperature range of 448–498 K. This temperature range corresponds to the first-order decomposition of glucose⁽²⁰⁾ and is important for hydrothermal pretreatment for ethanol fermentation. We selected the reaction pressure of 25 MPa in consideration of the pre-heating region of the supercritical water gasification. Judging from the changes in the dielectric constant and water density, however, the pressure was not anticipated to have a substantial effect in the temperature range studied. The 5-hydroxymethylfurfural produced in this temperature range also plays important roles as an inhibitor of ethanol fermentation and as a precursor for tarry material production in the supercritical water gasification. The reaction parameters determined based on our experimental results make it possible to predict the glucose behavior in these processes.

Experimental

Fig. 1 shows the experimental setup used in this study. The glucose solution was fed to the reactor by an HPLC pump (Pump A). Water from the pre-heater was fed to the reactor by a second HPLC pump (Pump B) and mixed with the glucose solution whose temperature was kept at room temperature using the heat exchanger at the reactor inlet. The reactor was composed of stainless steel tubing (SS316)

with an inner diameter of 1.0 mm and an adjustable length to allow modification of the residence time in accordance with the allowable flow rate of the HPLC pumps. After passing through the reactor, the effluent was mixed with cooling water from a third pump (Pump C), and it was further cooled using a cooling jacket all the way down to room temperature. The temperature at the exit mixing tee was below 100°C. Once cool, the effluent was depressurized by a backpressure regulator and sampled for analysis. The flow ratio of the glucose solution and preheated water was set at around 1 to 4 by weight. A thermocouple was inserted into the union cross to diminish the dead volume of the mixing point and detect the temperature of the solution just after the mixing point. The flow ratio of the effluent from the reactor and cooling water was 1 to 3 by weight.

The effluent was analyzed by HPLC using a SUGAR KS-802 column (Shodex) for separation and a refractive index detector (Shimadzu, RID-10A) for detection. A TOC analysis indicated a carbon balance of higher than 0.95 in most cases, thereby confirming that the levels of gas produced were negligible under our experimental conditions.

Our glucose decomposition experiments were conducted under a pressure of 25 MPa at three different temperatures, i.e., 448 K, 473 K, and 498 K. Five initial glucose concentrations were tested separately at each temperature. The concentration of the glucose solution ranged from 0.017 to 0.54 mol dm⁻³. The residence time in the reactor ranged from 40 s to 320 s. The reaction parameters and concentration dependency were determined using the data obtained under the 15 different experimental conditions thus arranged. Detailed discussion follows below.

Results and Discussion

Fig. 2 shows the typical yield changes with time for the compounds examined. Five products were observed: fructose produced by epimerization, and erythrose, glyceraldehyde, 1,6-anhydroglucose, and 5-hydroxymethylfurfural (5-HMF) produced by decomposition or dehydration. Kabyemela et al. proposed a detailed pathway of glucose decomposition based on data obtained by experimentally decomposing glucose and other materials in subcritical and supercritical water⁽⁴⁾. Referring to their reaction pathway, we assumed that glucose decomposition can be expressed as shown in Fig. 3. Having observed, from an earlier study, that glucose decomposition takes place as a first-order reaction in the temperature range of 448–498 K⁽²⁰⁾, we assumed that all of the reactions in Fig. 3 were first-order reactions. Equations 1–6 are the rate equations for the respective compounds identified and determined in our ex-

Fig. 1 Experimental set-up

Fig. 2 Typical yield change with residence time (498 K, 0.51 mol dm⁻³)

Fig. 3 Glucose decomposition scheme assumed in this study

periments. The Arrhenius rate constant shown in Eq. 7 can be used to express each reaction rate constant by defining the pre-exponential factor and activation energy.

$$\frac{dC_{glu}}{dt} = -(K_g + K_{gf} + K_{ga} + K_{ge} + K_{ggl} + K_{g5}) \times C_{glu} \quad (1)$$

$$\frac{dC_{fru}}{dt} = K_{gf} \times C_{glu} - (K_f + K_{fe} + K_{fgl} + K_{f5}) \times C_{fru} \quad (2)$$

$$\frac{dC_{ery}}{dt} = K_{ge} \times C_{glu} + K_{fe} \times C_{fru} - K_e \times C_{ery} \quad (3)$$

$$\frac{dC_{AHG}}{dt} = K_{ga} \times C_{glu} - K_a \times C_{AHG} \quad (4)$$

$$\frac{dC_{gly}}{dt} = K_{ggl} \times C_{glu} + K_{fgl} \times C_{fru} - K_{gl} \times C_{gly} \quad (5)$$

$$\frac{dC_{HMF}}{dt} = K_{g5} \times C_{glu} + K_{f5} \times C_{fru} - K_5 \times C_{HMF} \quad (6)$$

$$K_i = A_i \exp\left(\frac{-\Delta E_i}{RT}\right) \quad (7)$$

Table 1 shows the frequency factor and activation energy of each reaction, obtained by fitting all of the parameters to the experimental data set by the least squares method. The reaction rate constant K_g is negligible in our result, hence we can conclude that the first step of glucose decomposition is conversion into the five substances in Fig. 3, i.e., fructose, 1,6-anhydroglucose, erythrose, glyceralde-

Table 1 Reaction rate parameters for first-order reactions

	A [s ⁻¹]	Δ E [kJ mol ⁻¹]
Kg	0	-
Kf	5.71E+04	62.4
Kgf	1.54E+05	78.6
Kga	1.21E+17	193.2
Kge	2.70E+06	96.2
Kggl	6.59E+06	95.6
Kg5	8.19E+08	125.9
Kfe	0	-
Kfgl	0	-
Kf5	0	-
Ka	2.79E+21	226.9
Ke	4.27E+29	591.5
Kgl	4.71E+03	43.8
K5	0	-

hyde, or 5-HMF. This conclusion, we should note, rests on the premise that the mass balance is closed among these six compounds and stands even when the reactions are not of first order. The reactions from fructose to erythrose, glyceraldehydes, and 5-HMF are also negligible, possibly due to the low temperature. Fig. 4 presents the experimental yield and the yield calculated by the parameters determined. As the figures show, the calculated glucose yields accurately reproduce the experimental data. For the other compounds such as fructose and 1,6-anhydroglucose, the agreement between the calculated and experimental values is rather poor. While the initial glucose concentration is assumed to have no influence when a first-order reaction is assumed, the experimental results reveal that it actually alters the yields of both fructose, erythrose and 1,6-anhydroglucose.

For improved predictability, we also tried n-th order reaction equations to reproduce the experimental yields. Equations 8-13 are the rate equations for this purpose. Table 2 shows the reaction parameters for these equations obtained by the least squares method.

$$\begin{aligned} \frac{dC_{glu}}{dt} = & -K_g \times (C_{glu})^{ng} - K_{gf} \times (C_{glu})^{ngf} - K_{ga} \times (C_{glu})^{nga} \\ & - K_{ge} \times (C_{glu})^{nge} - K_{ggl} \times (C_{glu})^{nggl} - K_{g5} \times (C_{glu})^{ng5} \end{aligned} \quad (8)$$

$$\begin{aligned} \frac{dC_{fru}}{dt} = & K_{gf} \times (C_{glu})^{ngf} - K_f \times (C_{fru})^{nf} - K_{fe} \times (C_{fru})^{nfe} \\ & - K_{fgl} \times (C_{fru})^{nfgl} - K_{f5} \times (C_{fru})^{nf5} \end{aligned} \quad (9)$$

$$\frac{dC_{ery}}{dt} = K_{ge} \times (C_{glu})^{nge} + K_{fe} \times (C_{fru})^{nfe} - K_e \times (C_{ery})^{ne} \quad (10)$$

$$\frac{dC_{AHG}}{dt} = K_{ga} \times (C_{glu})^{nga} - K_a \times (C_{AHG})^{na} \quad (11)$$

$$\frac{dC_{gly}}{dt} = K_{ggl} \times (C_{glu})^{nggl} + K_{fgl} \times (C_{fru})^{nfgl} - K_{gl} \times (C_{gly})^{ngl} \quad (12)$$

Fig. 4 Parity plot for first-order reaction parameters

Table 2 Reaction rate parameters for the n-th order reactions

	A [s ⁻¹]	Δ E [kJ mol ⁻¹]	N [-]
Kg	0	-	-
Kf	9.70E+03	50.7	1.13
Kgf	7.07E+04	77.5	0.69
Kga	4.32E+15	178.0	1.37
Kge	1.25E+10	126.0	1.23
Kggl	4.41E+08	120.4	0.56
Kg5	4.41E+08	124.2	0.90
Kfe	0	-	-
Kfgl	0	-	-
Kf5	0	-	-
Ka	9.88E+14	219.9	1.02
Ke	1.93E+06	76.0	1.06
Kgl	8.64E+05	64.2	1.04
K5	0	-	-

$$\frac{dC_{HMF}}{dt} = K_{g5} \times (C_{glu})^{ng5} + K_{f5} \times (C_{fru})^{nf5} - K_5 \times (C_{HMF})^{n5} \quad (13)$$

The reaction orders for the conversion of glucose into fructose and glyceraldehyde are less than unity, while those for the conversions of glucose into 1,6-anhydroglucose and erythrose are larger than unity. The reaction orders for other reactions are close to unity within the 15% difference and can be assumed to be of first order. On this basis, we can presume that the first order of glucose decomposition observed in this temperature range²⁰⁾ results solely from several reactions of different reaction orders proceeding in parallel. Any change in the reaction temperature and pressure can be expected to change the selectivity of each reaction by altering the overall reaction order for glucose decomposition. The decomposition reactions of the other compounds into smaller molecules, on the other hand, are first-order reactions. Fig. 5 compares the experimental data with the data calculated by the parameters in Table 2. The n-th order reaction set has better predictability than the first-order reactions, especially for fructose and 1,6-anhydroglucose.

The selectivity of the glucose conversion reactions, the first steps in the reaction network shown in Fig. 3, is the key to understand the main reaction pathway. Fig. 6 shows the calculated selectivity as a function of the temperature and glucose concentration in the reactor. Basically, most of glucose is converted to fructose. Selectivity of fructose is the highest at 448 and 473 K, but it decreases with increase in temperature and glucose concentration. At glucose concentration of 1 mol dm⁻³, yields of 1,6-anhydroglucose and erythrose match that of fructose. The observed yield of 1,6-anhydroglucose is of the same order as fructose, as shown in Figs. 2 and 4(b). On this basis we can assume that fructose

is quickly decomposed once produced, while 1,6-anhydroglucose remains rather stable in this reaction field. The selectivity for 1,6-anhydroglucose is higher at higher temperatures and at higher glucose concentrations. Given that most of the glucose is converted into fructose at the first step of the conversion, fructose is a key compound for elucidating the behavior of glucose in hydrothermal reaction fields.

The kinetic parameters determined here should be useful for predicting the reactions taking place in the pre-heating section of the supercritical water gasification process and in the hydrothermal pretreatment reactor for the saccharification of cellulosic materials.

Conclusions

We conducted a series of glucose decomposition experiments in water at 25 MPa in the temperature range of 448–498 K. The following results were obtained.

1. The reaction rate parameters (activation energy, frequency factor, and reaction order when necessary) were determined for first-order and n-th order reactions in the glucose-decomposition network by the least squares method.
2. The first step of glucose decomposition is conversion into five substances, i.e., fructose, 1,6-anhydroglucose, erythrose, glyceraldehyde, or 5-HMF.
3. The first-order behavior of glucose decomposition in this temperature range is the result of several reactions of different reaction orders proceeding in parallel. The reaction orders for the conversion of glucose into fructose and glyceraldehyde are less than unity, and those for the conversions of glucose into 1,6-anhydroglucose and erythrose are larger than unity.
4. Basically, most of the glucose is converted into fructose at first. On the basis of these results, we conclude that fructose is a key compound for understanding the behavior of glucose in hydrothermal reaction fields.

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(a) glucose

(b) fructose

(c) erythrose

(d) 1,6-anhydroglucose

(e) glyceraldehyde

(f) 5-hydroxymethylfurfural

Fig. 5 Parity plot for n-th order reaction parameters

Fig. 6 Calculated selectivity of glucose conversion reactions

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