Glucose decomposition in sub- and supercritical water: Effect of glucose concentration

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Abstract

Supercritical water gasification is suitable for wet biomass gasification. It is thought that dry matter content of feedstock has some effects on its reactivity, while the effects and mechanism are still unclear. In this study, we focused on dry matter content of feedstock and its effect on reactivity and decomposition products. We employed glucose solution as a model feedstock of biomass. The experimental setup was customized to realize rapid heating up and cooling down, which minimized the effect of heating up and cooling down process. It was founded that the reaction rate became lower when the glucose concentration became higher. And its effect became small when the reaction temperature was lower than 523 K.

Introduction

Biomass is a carbon neutral resource and its utilization as an energy resource can diminish CO2 emission from fossil fuel. Biomass is a material originated from plants or animals. Therefore many kinds of biomass contain much water so that direct combustion of them is difficult and we call them wet biomass. Because of its high water content, wet biomass must be dried when it is used as an energy resource.

Supercritical water gasification (SCWG) is one of options to convert biomass to gas for energy use and it is favorable process for gasification of wet biomass because there is no need to dry wet biomass in this process. Furthermore, it allows thermochemical gasification of wet biomass in a short residence time. For these reasons, many researches regarding supercritical water gasification of biomass have been conducted. Yu et al.[1] conducted gasification of glucose solution in supercritical water. Xu et al.[2] gasified glucose and bagasse at 873 K and 35.4 MPa with carbonaceous catalyst and showed complete gasification could achieve with in a few minutes. Kruse et al.[3] conducted gasification of carrots and potatoes in CSTR at 773 K and 30 MPa with NaOH catalyst and the gasification efficiency they obtained were up to 60 %.

Some papers mentioned the reactant concentration effect on gasification ratio. Yu et al.[1] showed that total carbon in product gas decreased as the glucose concentration increased in their experiments of SCWG using flow reactor. Kruse et al.[3] showed higher gas yield was obtained at higher dry matter content in their SCTR experiments, on the other hand, phenol yield increased with increases in the dry matter content. From these facts, we can say that reactant content has a good deal of effect on its reaction in SCWG.

The objective of this study is to elucidate the concentration effect on decomposition of glucose in sub- and supercritical water at temperature rang 448 to 673 K and at pressure of 25 MPa.

Experimental

Figure 1 shows the experimental setup employed in this work. The glucose solution was fed to the reactor by an HPLC pump (Pump A). Another HPLC pump (Pump B) fed water that was delivered to the pre-heater and mixed with glucose solution at the inlet of the reactor. The reactor was stainless tubing (SUS316) with inner diameter of 1.0 mm, and the length was changed so that desired residence time could be achieved within the range of the allowable flow rate of the HPLC pumps. After passing through the reactor, cooling water fed by Pump C was added to the effluent and following cooling jacket cooled the effluent to as low as room temperature. Then the effluent was depressurized at backpressure regulator and sampled to be analyzed. Rapid heating of reactant could be achieved by mixing with preheated water in front of the reactor. The flow ratio of glucose solution and preheated water was set around 1:4 by weight. The effluent from the reactor was mixed with cool water just after the reactor. The flow ratio of the effluent from the reactor and cooling water was 1:3 by weight. The concentration of the glucose solution ranged from 0.02 M to 1.2 M at room temperature.

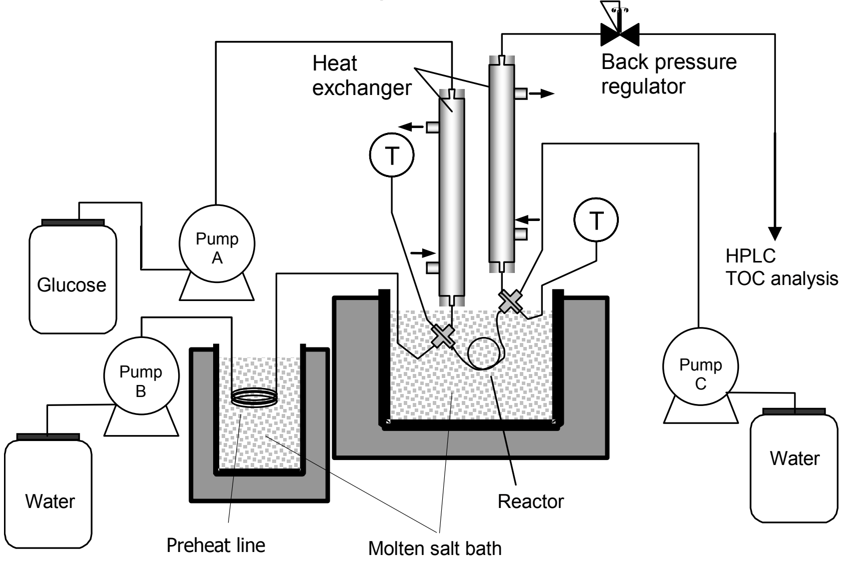

Figure 1 Experimental setup

The effluent was analyzed by HPLC equipped with a refractive index detector (Shimadzu, RID-10A) and SUGAR KS-802 (Shodex). TOC analyses were also conducted and carbon balance was higher than 0.95 in most cases, which showed that the gas production in this study was negligible.

Results and Discussions

Reaction Order of Glucose Decomposition

Figure 2 shows the results of glucose yields in glucose decomposition experiments at temperature ranging from 448 K to 498 K. Although different concentration glucose solutions were used in these experiments, reaction rates don't have definite dependency on the glucose concentrations. Therefore we assumed that the glucose decomposition was first order in glucose concentration at this temperature range and its reaction rate is represented as following equation.

$$-\frac{d[G]}{dt} = K\,[G]$$

[G]	glucose concentration in the reactor (mol/L)
K	reaction rate constant (s-1)

By fitting rate constant K to the experimental data at each temperature condition by least squares method, we obtained the rate constant showed in Table 1.

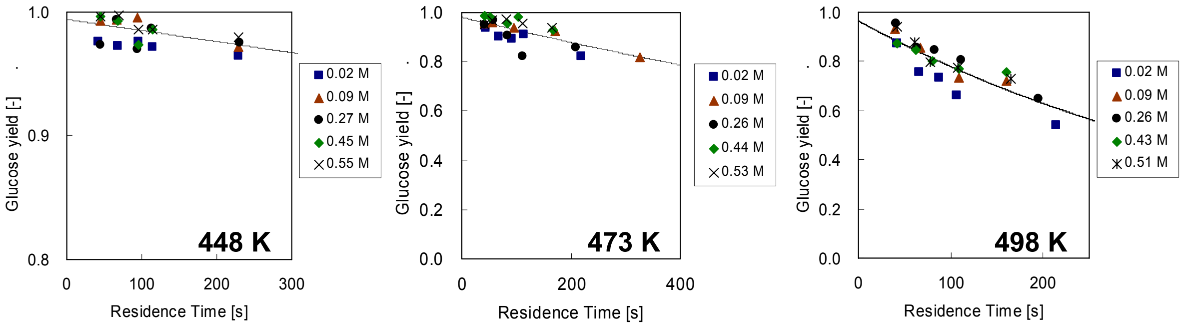

Figure 2 Glucose decomposition result: Temperature and initial glucose concentration dependency on glucose yield (448 - 498 K)

Table 1 Glucose decomposition rate constants (448– 498 K)

T [K]	K [s^{-1}]
448	9.12E-05
473	5.51E-04
498	2.14E-03

The curves in Figure 2 are calculated using the rate constants in Table 1, indicating the constants are adequate.

Figure 3 provides the results of glucose decomposition experiment at the temperature range 523 to 673 K. Obviously, reaction rate of glucose decomposition have dependence on glucose concentration. Thus we assumed that the rate equation was described as following equation in this temperature range.

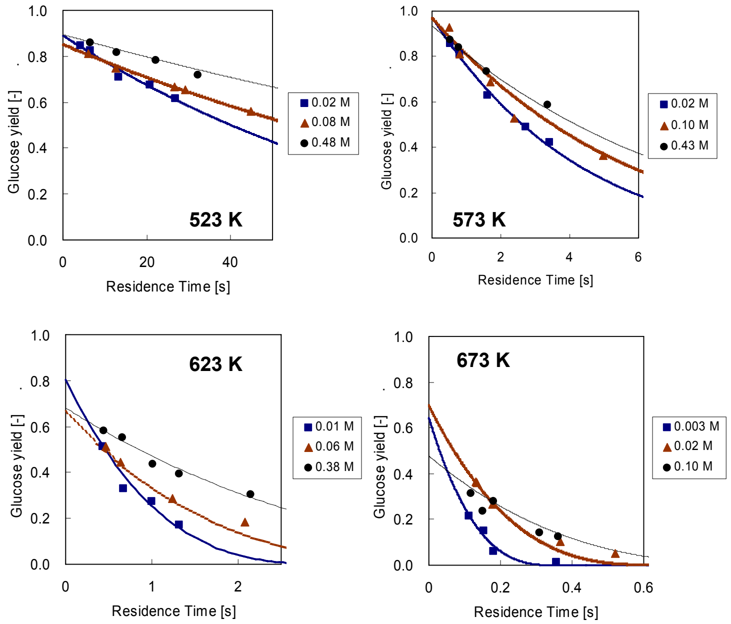

Figure 3 Glucose decomposition result: Temperature and initial glucose concentration dependency on glucose yield (523 - 673 K)

$$-\frac{d[G]}{dt} = K\,[G]^n$$

n reaction order (-)

By least squares fitting rate constant K to the experimental data at each temperature condition using least squares method, we obtained the rate constant showed in Table 2.

Table 2 Rate constants and reaction orders of glucose decomposition (523– 673 K)

T [K]	K [$M^{(1-n)}$ s^{-1}]	n
523	4.42E-03	0.740
573	1.22E-01	0.844
623	2.19E-01	0.707
673	1.48E+00	0.782

The curves in Figure 3, which are calculated by rate constants and reaction order shown in Table 2, reproduce the experimental results in each temperature and each glucose concentration.

The difference of reaction order between reactions at lower temperature and higher temperature than 523 K implies change in reaction mechanism with the change of reaction temperature under 25 MPa.

Reaction Parameters of Each Reaction

Kabyemela et al.[4-6] made systematic study regarding glucose decomposition and proposed a reaction scheme in detail. Referring their scheme, we presumed glucose decomposition scheme as shown Figure 4. We have determined yields of not only glucose but also some other products including fructose, erythrose, anhydroglucose, glyceraldehyde, and 5-hydroxymethylfurfral, which enabled us to determine each reaction parameter such as activation energy and frequency factor of each reaction in Figure 4. Because there is the change in reaction mechanism, first we determined parameters for lower temperature using the experimental results at lower than 498 K. The parameters we obtained are shown in Table 3.

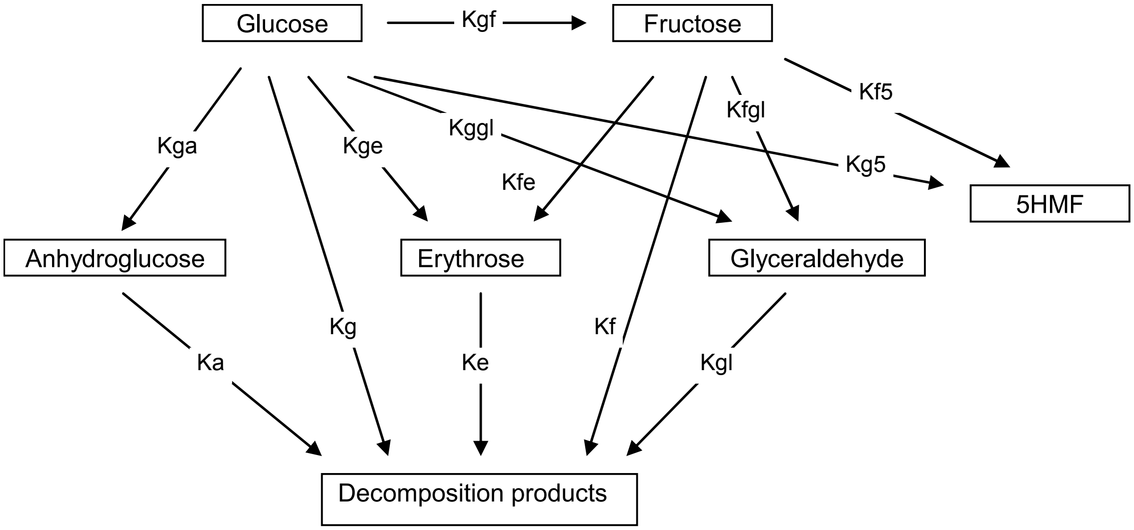

Figure 4 Glucose decomposition scheme presumed in this study

Table 3 Reaction parameters of each reaction at 448 - 498 K

	A (s^{-1})	Δ E (kJ/mol)
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	-

As for higher temperature experiments, reaction order of each reaction was also considered. And we also determined the reaction parameter including reaction order for higher temperature, which shown in Table 4. Some reaction rate parameters for reactions in Figure 5 are omitted in Tables 3, 4 because they are negligible.

Table 4 Reaction parameters of each reaction at 523 - 673 K

	A [$M^{(1-n)}$ s^{-1}]	ΔE [kJ/mol]	n
Kg	0	-	-
Kf	1.35E+06	61.1	1.35
Kgf	3.16E+07	95.7	0.90
Kga	6.28E+08	114.5	1.13
Kge	2.37E+11	142.3	0.81
Kggl	3.02E+09	129.4	0.77
Kg5	7.34E+06	96.0	1.01
Kfe	4.61E+06	111.1	0.22
Kfgl	8.84E+07	286.0	1.43
Kf5	9.38E+07	259.4	1.12
Ka	6.60E+05	81.7	1.12
Ke	8.78E+09	119.6	1.11
Kgl	0	-	-
K5	1.22E+45	573.2	1.05

Estimation of 5-HMF Production during Heating Process

5-HMF (5-hydroxymethylfurfural) is expected to be decomposed or polymerized into tarry material in SCWG process. Therefore, we think estimation of the effect of glucose concentration on 5-HMF production is valuable. Figure 5 shows the calculated yield of 5-HMF from glucose during heating up process (heating rate: 5 K/s, heating from 373 K up to 673 K at 25 MPa) at different glucose concentration using the reaction rate parameters in Tables 3 and 4. At lower concentration, the yield increased rapidly and at higher concentration than 0.4 M, the yield remained rather stable along the concentration. Taking into account that 5-HMF may polymerize into tarry material, this result shows that our reaction mechanism and reaction rate parameters can explain the increase of tarry material with increase of glucose concentration in SCWG.

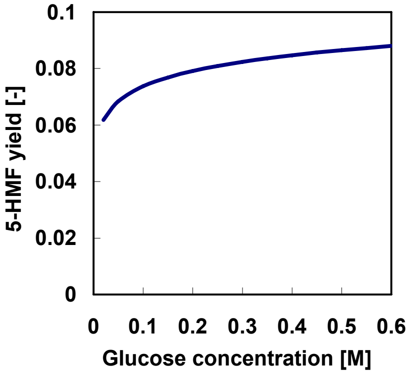

Figure 5 Glucose concentration effect on estimated yield of 5-hydroxymethylfurfral (heating rate: 5 K/s, heating from 373 K up to 673 K at 25 MPa)

Conclusions

Reaction rate for glucose decomposition in water under 25 MPa was determined in the temperature range of 448 – 673 K. The reaction order decreased with temperature from values around unity at 448 K to 0.7 at 673 K. Moreover reaction rate parameters for each reaction of detailed glucose decomposition mechanism were also determined. The production of 5-hydroxymethylfurfural calculated using reaction rate parameters we obtained, which implies higher glucose concentration can increase 5-HMF product amount.

References

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