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Glucose reactions within the heating period and the effect of heating rate on the reactions in hot compressed water

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Abstract—Glucose reactions were conducted in hot compressed water (473–773 K, 4–40 MPa) by means of a batch-type reactor. The reactions in the heating period (about for 60 s) were observed. More than 80% of the glucose was consumed in the heating period above 573 K. Gasification of glucose was promoted with increasing temperature. The effect of heating rate (from 4.2 to 15.8 K/s) on glucose conversion was also examined, and gasification of glucose was enhanced with increasing the heating rate. © 2005 Elsevier Ltd. All rights reserved.

Keywords: Glucose; Batch reactor; Hot compressed water; Gasification; Heating period; Heating rate

1. Introduction

Biomass conversion in hot compressed water is one of the candidates for a biomass refinery technique because biomass reactions such as the conversion of cellulose into glucose and its oligomers,^{1,2} the conversion of oligomers and glucose into useful chemicals,³⁻¹³ and the gas-ification of glucose into H_2 and CH_4 ,^{14–35} effectively proceed in the media. For biomass cascade utilization, a compound from biomass has to be transformed into important chemicals. Glucose can be selectively produced from cellulosic biomass, and it becomes the starting material of the biomass refinery because glucose is the monomer unit of cellulose, which is the most abundant organic compound on the earth and is the major component of plant biomass. Thus, the conversion of glucose into chemicals will be an alternative process to petroleum chemistry and is desirable for a sustainable feedstock.

The reaction mechanism of glucose in supercritical water (SCW) was studied by Kabyemela et al.^{3–6} They

used a flow apparatus, almost without a heating period, to evaluate the reaction rate. As a result, the primary reactions of glucose were found to be as follows (Fig. 1): (1) glucose isomerization into fructose via keto-enol tautomerization, (2) glucose dehydration into 1,6-anhydroglucose, and (3) glucose decomposition into aldehyde and ketone via retro-aldol condensation. Further, (4) dehydration of the tautomerization intermediate and fructose produce 5-hydroxymethyl furfural (HMF). This reaction mechanism can typically be applied to the reaction that proceeds in a rapid heat– flow apparatus. Sinag et al.^{10,12} and Dinjus and Kruse³⁶ studied glucose decomposition in SCW. They proposed a relatively simple reaction mechanism for glucose as shown in Figure 2. According to their reaction scheme, glucose converts into furfurals and acids/aldehydes in parallel. Further conversion of furfurals leads to acids/ aldehydes and phenol formation. Acids and aldehydes are precursors of the gaseous compounds. Furfural formed through dehydration is shown in Figures 1 and 2. Further dehydration of furfural gives phenols. In contrast, acids and aldehydes are produced by bond-breaking reactions. This mechanism is quite simple; however, it tells us that the glucose reaction mainly proceeds via dehydration or bond breaking. The predominance of

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Figure 1. Primary reaction pathways of glucose in supercritical water.



Figure 2. Simple reaction pathways of glucose reaction including secondary or higher reactions in supercritical water.

the two pathways (dehydration and bond breaking) can be estimated from the yields of the key compounds such as furfurals, acids, aldehydes, phenols, and gaseous products.

Most of the biomass is solid under ambient conditions. Therefore, understanding biomass reactions in batch and semi-batch reactors is important for the establishment of a biomass refinery process. One of the characteristics for batch and semi-batch systems is that they have a non-steady-state stage, namely heating up (this period is called 'heating period' in this study)

and cool down of the reactor. There are several studies on the effect of this non-steady-state stage on the glucose and cellulose reactions. 2,13,37 Ehara and Saka² conducted the experiments of cellulose conversion in supercritical water with a batch and a flow apparatus. In the batch system, the heating period was only 10 s from room temperature to 653 K, and the reaction time was 2-8 s. Even at the shortest reaction time, they obtained a lot of decomposition products such as dihydroxyacetone, glycolaldehyde, levoglucosan, and so on. This means glucose reactions rapidly proceed at 653 K. They also confirmed the rapid reaction of cellulose and glucose using the flow apparatus at the reaction time below 0.5 s. From this study, the effect of the heating period on glucose reaction was not clear. Matsumura et al.³⁷ investigated the reaction within the heating period. They focused on the effect of heating rate (how fast the temperature of the reaction mixture increased) on gasification of glucose in supercritical water. They confirmed that higher heating rates brought higher gasification and higher cold gas efficiency. In this report, they only focused on gasification, and thus the effect of the heating period on the other glucose reactions was not shown. Sinag et al.¹³ observed the effect of heating rate on the product distribution of glucose reaction in supercritical water. They conducted experiments at 1 K/min (0.0167 K/s) and 3 K/min (0.05 K/s) and reported that the acids production and gasification were enhanced by rapid heating, while dehydration to furan was suppressed by rapid heating. The final temperature of the studies by Sinag et al.¹³ was 773 K. Since the glucose reaction was quite fast even at 653 K, this temperature (773 K) was too high to know the effect of heating rate on the primary reactions of glucose. In order to develop a biomass refinery batch or semi-batch process for real biomass, the effect of the heating period and heating rate on the reaction must be investigated in more detail at various temperatures and heating rates. Therefore, in this study, glucose conversion in a batch-type reactor was conducted focusing on the effect of heating period and heating rate.

2. Experimental

Glucose was obtained from Wako Pure Chemical Co. and used as received. Pure water, which was distilled after deionization, was obtained with a water distillation apparatus (Yamato Co., model WG-220).

The reaction was carried out in a SS 316 stainless steel tube bomb reactor with an inner volume of 6 cm^3 . The loaded amount of glucose was 0.1 g and that of water was 1.0 g. Ar gas was loaded at 2.5 MPa to ease recovery of the gaseous product after the reaction. After the loading, the reactor was submerged into the heating bath. The set-point of the sand bath where the reactor was submerged was from 473 K to 773 K. A tin bath was also used to change the heating rate inside the reactor at 673 K or 773 K. The reaction was stopped by quenching the reactor in a water bath. Table 1 lists the heating bath and the reaction time of each experiment. Reaction time ranged from 30 to 90 s.

The product gas was recovered in gas samplers connected with GC–TCD to analyze its composition and a syringe to measure the product volume. Among the gaseous products, small hydrocarbons, namely CH₄, C_2H_4 , C_2H_6 , C_3H_6 , C_3H_8 , and so on, were also detected at higher temperatures. However, the total yields of these hydrocarbons were always below 1 mol %. In this study, because hydrocarbon formation was not discussed, the yields of the hydrocarbons are not shown. After collecting the gas samples, the reactor was opened and washed with pure water to recover the liquid samples. Sometimes char formation was observed; however, the amount of char was quite small and not analyzed further.

The identification and quantification of the gaseous products was conducted by GC–TCD (Shimadzu, model GC-7A, and Hitachi, model GC163). The amount of carbon in the water solution was evaluated using TOC (total organic carbon detector, Shimadzu, model TOC-5000A). The liquid products in the recovered solution were analyzed by HPLC–RI and to UV (JASCO) using a KS-802 column (Shodex).

Table 1. Experimental conditions

Run no.	Heating bath	Temperature of the bath, K	Reaction time, s	
1	Sand bath ^a	473	60	
2	Sand bath ^a	573	60	
3	Sand bath ^a	623	60	
4	Sand bath ^a	673	60	
5	Sand bath ^a	723	60	
6	Sand bath ^a	773	60	
7	Sand bath ^a	673	30	
8	Sand bath ^a	673	45	
9	Sand bath ^a	673	70	
10	Sand bath ^a	673	90	
11	Tin bath	673	30	
12	Sand bath ^b	673	90	
13	Tin bath	773	30	

^a With shaking.

^b Without shaking.

Product yield (mol %) of carbon compound was evaluated from carbon base as shown below:

Product yield [mol %]

_	amount of carbon atom in a product				
	amount of carbon atom in the loaded glucose				
	$\times 100$	(1)			

Hydrogen yield (H₂ yield, mol %) was evaluated from hydrogen base of a loaded amount of samples as follows:

H_2	field [mol %]	
_	amount of hydrogen atom in H ₂ produced	
_	amount of hydrogen atom in the loaded glucose	
	× 100 (2	2)

3. Results and discussion

Before conducting experiments of glucose conversion, the temperature profile inside the batch-type reactor was measured. Water (1.0 g) was loaded into the reactor and then sealed with a thermocouple to monitor the temperature. Then, the batch reactor was shaken inside the fluidized sand bath previously set at 573, 673, and 773 K. The heating profiles under these conditions are shown in Figure 3. In this case, it took almost 60 s to reach the desired temperature inside the reactor. Cooling the reactor down below 373 K was achieved within 30 s for all three conditions. Next, we also employed a tin bath in addition to the fluidized sand bath as the heating media. In order to compare the temperature profile in the tin bath with that in the sand bath, we measured the temperature inside the reactor in the tin bath and the fluidized sand bath. In the sand bath, the temperatures inside the reactor were measured with and without shaking the reactor. The temperature of



Figure 3. Temperature profiles inside the reactor (in the fluidized sand bath with shaking the reactor).

the tin bath was 673 K. The results are shown in Figure 4. As shown in Figure 4, it took about 30 s to reach 673 K with the tin bath. In the case of the fluidized sand bath, it took 90 s to reach 673 K without shaking the reactor. On the other hand, it took about 60 s to reach the same temperature when the reactor was shaken during heating. In summary, we found as follows: (1) in the sand bath, it took 90 s to reach the temperature inside the reactor without shaking the reactor, (2) in the sand



Figure 4. Temperature profiles inside the reactor.

Table	2.	Experimental	resul	ts
1 ante	<i>.</i>	Experimental	resu	

bath, with shaking, it took 60 s to reach the temperature, and (3) using tin bath, it took only 30 s to reach the temperature.

All experimental results of glucose reactions are listed in Table 2.

First, we examined glucose reactions within the heating process at various temperatures using the fluidized sand bath. In this examination, the reactor was shaken in the bath (i.e., it took 60 s to reach the temperature, as shown in Fig. 3). The identified and quantified products in the recovered aqueous solution were glucose, anhydroglucose (AHG), HMF, and furfural. Figure 5 shows the yield of these water-soluble products and the TOC. The difference between the TOC value and the sum of the quantified products indicates that the other products that could not be identified were also produced. For gaseous products, H₂, CO, and CO₂ were obtained. Water-insoluble products such as char was obtained in all the experiments. The amount of char was small, and therefore no further investigation was done. Most of the glucose remained during the heating period to 473 K. On the other hand, 20% of the glucose was mainly converted into dehydrogenated products during the heating to 573 K. Above 623 K the glucose was completely consumed within the heating period. Beyond 673 K the yields of the dehydration products (AHG, HMF, and furfural) and TOC values did not significantly change with the temperature.

Figure 6 shows the gaseous products of the glucose reaction within the heating period at the various temperatures. With increasing temperature, the yield of gaseous products increased. According to the mechanism proposed by Sinag et al.,¹³ the increase of the gaseous products at higher temperature indicates that the bondbreaking reaction is predominant. Figure 7 shows the CO/CO_2 ratio in the gaseous products. As shown in this graph, the CO/CO_2 ratio increased with increasing temperature. This indicates that CO formation is favored at higher temperature. The yield of H₂ increased with increasing temperature as shown in Figure 6. There

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Run no.	TOC, mol %	Glucose, mol %	AHG, mol $\%$	HMF, mol $\%$	Furfural, mol %	H ₂ , mol %	CO, mol %	$\rm CO_2, mol \%$	CO/CO ₂
1	102.8	87.2	0	0	0	0	0	0	0
2	106.4	64.5	17.4	6.28	0.77	0.008	0.008	0.21	0.04
3	79.4	1.25	9.56	16.2	6.56	0.016	0.611	2.26	0.27
4	62.6	0	6.94	11.1	6	0.18	1.32	3.82	0.35
5	60.6	0	6.59	9.67	4.85	0.68	3.56	4.6	0.77
6	61.6	0	4.71	8.07	4.75	1.37	4.12	6.58	1.06
7	99.2	51.7	16.3	7.15	2.02	0	0	0.29	0
8	90.9	0	13.4	14.2	6.43	0.023	0.49	1.76	0.28
9	66.3	0	5.75	10.8	4.9	0.33	1.12	2.9	0.39
10	58.6	0	1.83	8.15	3.29	1.08	1.42	3.73	0.38
11	69.3	0	12.9	8.05	4.21	0.46	1.73	4.85	0.36
12	59	0	3.3	8.9	5.92	0.21	1.12	3.98	0.28
13	63	0	7.151	2.98	2.06	4.36	12	8.35	1.44



Figure 5. Liquid products of glucose reactions within heating period.



Figure 6. Gaseous products of glucose reactions within the heating period.



Figure 7. CO/CO_2 ratios within the heating period.

are a lot of possibilities for the formation of H_2 with the glucose reaction, for example, the dehydrogenation of the substances that have a hydroxyl group, decomposition of small compounds, among others. However, H_2 formation was assumed to relate to the water–gas shift reaction here. That is, if all the H_2 formation was caused by the water–gas shift reaction, the H_2 originated from CO. In Figure 6, the CO/CO₂ ratio with correction of the contribution of the water–gas shift reaction on CO and CO₂ formations is also shown. From this figure, the contribution of the water–gas shift reaction

increased with increasing temperature. At lower temperatures, CO_2 formation was favored, while CO formation was enhanced with temperature. These results show that the decarboxylation of acids is assumed to be the main pathway of gas formation, at lower temperature and the C–C bond breaking of an organic compound (glucose, aldehydes, and so on) to form CO is enhanced at higher temperature.

The reaction time dependence on glucose reactions was also observed at 673 K. As shown in Figures 3 and 4, in the case of the temperature of the sand bath at 673 K the temperature inside the reactor was about 573 K at 30 s. At 45 s, the temperature inside the reactor was 653 K. After 45 s, the temperature inside the reactor was constant at 673 K.

Figure 8 shows the liquid products of the glucose reaction when the sand bath was set to 673 K. At 30 s of reaction time (573 K inside the reactor), half of the loaded glucose was mainly converted into liquid products. After 45 s glucose completely disappeared. The yield of dehydrogenated products and the values of TOC decreased with time. Figure 9 shows the gaseous products. CO and H₂ formation increased with increasing reaction time. As well as the case of the effect of temperature (Figs. 6 and 7), we consider that all the H₂ formation was due to the water-gas shift reaction. The CO/CO_2 ratio implies the gas formation pathway. Figure 10 shows the CO/CO_2 ratio. At the earlier reaction time (namely, below 673 K), CO₂ formation was dominant, and this implies decarboxylation was favored at a lower temperature as same as the results in Figure 7. With increasing reaction time, CO formation linearly increased after 60 s (i.e., the reaction at 673 K). In this region (after 60 s), glucose completely disappeared. Thus, the product of glucose decomposed further into CO by breaking C-C bonds. Considering Figure 2, the precursor of the gaseous compounds are acids or aldehydes. As shown in Figures 7 and 10, at the lower temperatures, CO₂ formation was preferred and this implies that the formation of acids occurs with ease. In contrast, CO formation became dominant at higher



Figure 8. Liquid products of glucose reactions at 673 K including the heating period.



Figure 9. Gaseous products of glucose reactions at 673 K including the heating period.



Figure 10. CO/CO₂ ratios at 673 K including the heating period.

temperature and longer reaction time at 673 K. These indicate that aldehyde was preferentially formed. Goto et al.³⁸ conducted experiments of glucose conversion using a flow apparatus at various temperatures and pressures. They confirmed that the retro-aldol condensation to form aldehydes mainly proceeded at higher temperature and lower pressure. Sasaki et al.⁸ also confirmed this phenomenon. As a consequence, at higher temperature, the formation of aldehyde resulted in CO formation. At 673 K the retro-aldol condensation also proceeded, and the product aldehydes gradually converted into CO; thus CO formation was dominant at longer reaction time. For confirmation of these speculations, the yields of acids and aldehydes must be measured and are now being identified and quantified.

As mentioned in the Introduction, Matsumura et al.³⁷ and Sinag et al.¹³ reported that higher heating rates lead to higher gasification efficiency. Therefore, finally, we also examined the effect of heating rate on the glucose reactions.

Figure 11 shows the effect of the heating rate on the yield of the liquid products and the TOC value. The

temperature profiles at the different heating procedures are shown in Figure 4. In the case of the immersion of the reactor into the tin bath, the heating rate inside the reactor was 12.5 K/s. The slowest heat-up procedure was obtained by use of the fluidized sand bath without shaking the reactor. In this case, it takes 90 s to reach 673 K, which means that the heating rate was 4.2 K/s. The heating rate was 6.3 K/s in the sand bath with shaking the reactor. As shown in Figure 11, the shortest reaction time (highest heating rate in the tin bath) showed the highest yield of water-soluble products (TOC and the dehydration products). Figure 12 shows the gaseous products at the different heating times. The total yield of gaseous products was not significantly different; however, yields of CO and H₂ at the highest heating rate were the highest among all three experimental results. The heating rate also affected the gas formation reaction. Figure 13 shows the CO/CO₂ ratio with and without correction of the water-gas shift reaction. Although the maximum temperature was the same at 673 K for all the experimental results in Figure 13, the CO yield increased with increasing the heating rate. This result



Figure 11. Effect of heating rate on the liquid products of glucose reactions at 673 K.



Figure 12. Effect of heating rate on gaseous products of glucose reactions at 673 K.



Figure 13. Effect of heating rate on CO/CO₂ ratios at 673 K.

suggests that the longer time at lower temperature resulted in inhibition of gas formation, in particular CO formation.

We also investigated the effect of heating rate on gas formation at a higher temperature (at 773 K). The experiments at 773 K were also conducted by use of the tin bath and the fluidized sand bath (with shaking). The heating time required to achieve 773 K and 673 K in the tin bath was same, namely both 30 s. Figure 14 shows the yield of the liquid products and the TOC values. Increasing the heating rate suppressed HMF and increased anhydroglucose formation. The TOC value and furfural yield was not affected by this change in heating rate. Figure 15 shows the effect of the heating rate on the gaseous product yield at 773 K. Experiments using the tin bath significantly increased the gaseous yield. Figure 16 shows the CO/CO₂ ratio at different heating rates. For comparison, the results obtained at 673 K are also shown in this figure. The maximum ratio was about 0.5 at 673 K, where it reached up to 4.5 at 773 K. The



Figure 14. Effect of heating rate on liquid products of glucose reactions at 773 K.



Figure 15. Effect of heating rate on gaseous products of glucose reactions at 773 K.



Figure 16. Effect of heating rate on CO/CO₂ ratios at 773 K.

heating rate in the tin bath (15.8 K/s) was almost twice as high than that in the sand bath (7.9 K/s). With twice the increase of heating rate, the CO/CO₂ ratio increased four times. Thus, heating has a great influence for gasification of glucose at higher temperatures, as suggested by Matsumura et al.³⁷ and Sinag et al.¹³

Through this study, we observed the effect of heating period and rate on glucose conversions in hot compressed water. The concentration of glucose was always constant in this study. Chemical reactions are affected by concentration of a reacting species. Naturally, the effect of heating on the glucose reaction is also changed by the concentration of glucose. Also, the ratio of glucose to water is an interesting topic for glucose refinery in hot compressed water. The amount of water is closely related to the pressure and the concentration of water as a reactant. The next step for developing the batch and semi-batch biomass refinery process by use of hot compressed water will be studied on the effect of the factors listed above.

4. Conclusions

Glucose conversions using a small batch reactor were performed. Different types of heating bath were employed: the fluidized sand bath, the fluidized sand bath with shaking the reactor, and the tin bath. The heating periods were 90 s, 60 s, and 30 s in the fluidized sand bath, the fluidized sand bath with shaking the reactor, and the tin bath, respectively.

Within the heating period the fluidized sand bath with shake (60 s), almost all the glucose disappeared above 623 K. The yields of TOC and the dehydration products became lower at higher temperature and plateaued at higher temperature; that is, almost 60 mol % of TOC and 20 mol % of the dehydration products still exited at 673 K, 723 K, and 773 K. On the other hand, gasification significantly enhanced at higher temperature. Among the gas products, CO formation was preferred at the higher temperature.

At 673 K, the time dependence of the glucose reaction was measured. The glucose was completely consumed at 45 s, namely before reaching 673 K. The yields of TOC and the dehydration products gradually decreased with the reaction time. The gas formation, in particular, CO formation continued to increase with time.

The effects of heating rate on the glucose reaction were examined at 673 K and 773 K of the heating bath. The heating rates at 673 K were 4.2 K/s, 6.3 K/s, and 12.5 K/s in the fluidized sand bath, the fluidized sand bath with shaking the reactor, and the tin bath, respectively. At 773 K, the heating rates were 7.9 K/s and 15.8 K/s in the fluidized sand bath with shake and the tin bath, respectively. The effect of the heating rate on the TOC and dehydration products were not observed at 673 K and 773 K. In contrast, the gas production was significantly affected by the heating rate. In particular, CO formation was promoted by rapid heating. The 20 mol % of carbon in glucose could be gasified by the quick heating at 773 K. In this case, the formation of CO was yielded four times higher than that of CO₂.

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