Available online at www.sciencedirect.com

ScienceDirect

Carbohydrate Research 343 (2008) 848–854

Carbohydrate
RESEARCH

# Thermochemical transformation of glucose to 1,6-anhydroglucose in high-temperature steam

Masahide Sasaki,[a] Kenji Takahashi,[b] Yui Haneda,[b] Hiroe Satoh,[b] Akiyoshi Sasaki,[a]
Atsushi Narumi,[c] Toshifumi Satoh,[d] Toyoji Kakuchi[d] and Harumi Kaga[a,*]

[a]*National Institute of Advanced Industrial Science and Technology (AIST), Sapporo 062-8517, Japan*
[b]*Graduate School of Natural Science and Technology, Kanazawa University, Kanazawa 920-1192, Japan*
[c]*School of Science and Engineering, Yamagata University, Yonezawa 992-8510, Japan*
[d]*Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan*

Received 18 October 2007; received in revised form 31 January 2008; accepted 4 February 2008
Available online 10 February 2008

---

**Abstract**—An aqueous solution of glucose was reacted at temperatures from 200 to 400 °C under atmospheric pressure using a continuous flow reactor. For reaction temperatures above 300 °C, the liquid product yield was not sensitive to the temperature change; on the other hand, below 300 °C, it decreased rapidly with decreasing temperature. 1,6-Anhydro-β-D-glucopyranose (AGP) and 1,6-anhydro-β-D-glucofuranose (AGF) were the major components in the liquid product. The yields of AGP and AGF were 40% and 19%, respectively, at 360 °C and a feed rate of 0.5 mL/min. The optimum space time to produce AGP and AGF was about 0.2–0.4 s under the present temperature conditions.

*Keywords:* High-temperature steam; Anhydroglucose; Levoglucosan; Glucose; Dehydration; 1,6-Anhydro-β-D-glucopyranose

---

## 1. Introduction

The most typical anhydroglucose is 1,6-an-hydro-β-D-glucopyranose (AGP), also known as levoglucosan, a product that forms when the dehydration reaction occurs between the C-1 and C-6 positions of glucose. This compound is one of the main products from the pyrolysis of cellulosic biomass. With the increasing interest in sustainable development, it is quite important to seek possible applications of anhydroglucose as a chemical or fuel feedstock. AGP has a number of chemical attributes that may make it desirable as a chemical feedstock in the production of biodegradable surfactants,[1] stereoregular polysaccharides,[2] and hyperbranched polysaccharides.[3]

There have been numerous efforts to produce AGP. The classical pyrolysis method uses batch pyrolysis of starch or cellulose under high vacuum.[4,5] Recently, continuous-feed pyrolysis of starch or cellulose into AGP has been reported, which requires a special belt conveyer-type pyrolyzer as well as difficult handling and reaction conditions under moderate vacuum.[6] Chemical synthetic methods[7] for producing AGP from D-glucose require not only several reaction steps but also many chemicals such as protecting groups, leaving groups, and acid or base catalysts. Rapid pyrolysis using microwave-assisted heating has been carried out for the treatment of a cellulose pellet[8] or a large wood block.[9–11] Another procedure is pyrolysis with solvent under supercritical conditions. Köll et al.[12] have performed the pyrolysis of cellulose in supercritical acetone, obtaining yields of AGP comparable to those reported for fast pyrolysis.[4] Kabyemela et al.[13–15] and Sasaki et al.[16,17] reported a systematic study of carbohydrates in supercritical water and proposed reaction pathways for glucose decomposition. At 350 °C and 40 MPa, the main products were glycolaldehyde and erythrose,

---

[*] Corresponding author. Tel.: +81 11 8578921; fax: +81 11 8578988; e-mail: h.kaga@aist.go.jp

0008-6215/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carres.2008.02.005

which are formed via retro-aldol condensation of glucose. Although the decomposition products included AGP, its yield was less than 6%.[17] Those studies did not examine the effect of experimental conditions on the yield of AGP. Recently, we examined the effect of pressure on the formation of AGP in an aqueous glucose solution, and the yield of AGP was found to increase significantly with decreasing pressure.[18] The maximum yield of AGP (32%) was attained at 320 °C and 7 MPa, where water molecules may exist as high-temperature steam rather than high-temperature water.

There have been other studies suggesting that the lower pressure conditions are favorable to produce AGP. Cellulose and lignocellulose were pyrolyzed using a 'cyclone reactor' (a long tubular coil) by transporting the feed through the reactor with superheated steam.[1,19] AGP yields were up to 50% based on cellulose with the best results from corncob lignocellulose. Pyrolysis of cornstarch in steam yielded 12.6% and 32.9% of AGP under atmospheric and sub-atmospheric pressure (i.e., 190 mmHg), respectively. In addition, pyrolysis of acetic acid-pretreated cornstarch in steam yielded up to 44.5% of AGP under sub-atmospheric pressure.[20] These results indicated the possibility that 1,6-anhydroglucose may be produced in good yield through intramolecular dehydration of glucose in high-temperature steam. However, little effort has been directed to a continuous preparation method of 1,6-anhydroglucose from glucose. We present here a simple method to produce 1,6-anhydroglucose by generating high-temperature steam from aqueous solution in a continuous flow reactor under atmospheric pressure.

## 2. Results and discussion

### 2.1. Effect of reaction temperature on liquid product yield

The liquid product yield obtained from total organic carbon (TOC) measurement are plotted against reaction temperature in Figure 1. The liquid product yield reduced gradually to about 70% based on the feed as reaction temperature decreased to 300 °C from 400 °C. This trend seems independent of the feed rate of the reactant. For reaction temperatures below 300 °C, the liquid product yield reduced very rapidly to about 20%. In the following section, we will mainly discuss the reaction behavior at temperatures ranging from 300 to 400 °C, because, in most cases, the liquid product yield was greater than 70% at these temperatures. After separating the liquid product, approximately 10% of water-soluble materials were recovered by washing the reactor with hot water. Thus, the total yield of water-soluble materials including the liquid product was more than 80% based on the feed. The remaining components are probably water-insoluble materials such as a coke precursor and non-condensable gaseous products.

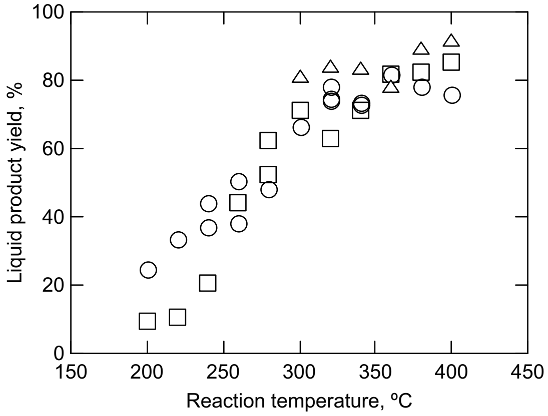

**Figure 1.** Liquid product yield versus reaction temperature at a feed rate of 0.5 and 1.0 mL/min. (○) 0.5 mL/min, (□) 1.0 mL/min, and (△) 1.5 mL/min.

### 2.2. Product distribution and main reaction pathway

Figure 2 shows a typical HPLC chromatogram for the liquid product obtained at 360 °C with a feed rate of 0.5 mL/min. The peaks of glucose (Glc), fructose (Fru), erythrose, glycolaldehyde dimer, 1,6-anhydro-β-D-glucopyranose (AGP), and 5-(hydroxymethyl)furfural (HMF) were identified by comparing their retention times with those of authentic samples. Glycolaldehyde dimer, HMF, AGP, and Glc were also identified by comparing their retention times with those of authentic samples with gas chromatography (GC).[10] AGP and

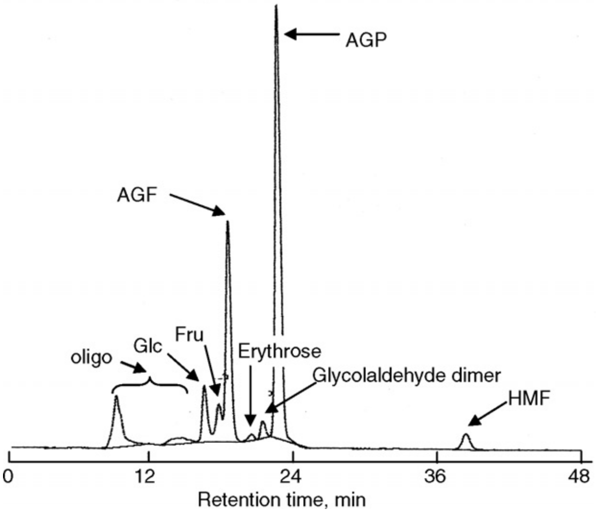

**Figure 2.** Typical HPLC chromatogram for the liquid product: products at 360 °C with a feed rate of 0.5 mL/min. Retention times (min)/yield (%): oligo 9.3–14.8/9; glucose 16.6/5; fructose 17.8/4; AGF 18.6/19; erythrose 20.5/0.6; glycolaldehyde dimer 21.5/1; AGP 22.7/40; and HMF 38.4/2.

1,6-anhydro-β-D-glucofuranose (AGF) were isolated from the liquid product by the reported procedure[21] using a cation-exchange column. Broad peaks in the shorter retention time region were defined as 'oligo', which included oligomers and organic acids.[17] The total yield of anhydroglucose was defined as the sum of AGP and AGF, and quantified by the ratio of each peak area.

Figure 3 shows the main reaction pathway of glucose transformation in high-temperature steam based on the product distribution. The glucose transformation proceeds mainly through a dehydration reaction. AGP is produced by the intramolecular dehydration of glucose (i.e., glucopyranose). The formation of AGF can also be rationalized by intramolecular dehydration of the glucofuranose form in thermal equilibrium with glucopyranose. In addition to this, AGF is reported not to be formed from AGP under pyrolysis conditions without catalysts.[22] In contrast to AGP and AGF formation, another dehydration product, that is, HMF, from glucose or fructose, was not predominant. Retro-aldol condensation forming glycolaldehyde and erythrose occurred with very low yield. Isomerization of glucose to fructose was also suppressed. A small amount of oligomers can be produced by glycosidation among glucose, glucofuranose, AGP, and AGF. Organic acids may include levulinic acid as well as formic acid derived from HMF, although every component was not identified.

The effect of temperature and feed rate on the yield of products and the glucose conversion are shown in Figure 4. As shown in Figure 4a, at a feed rate of 0.5 mL/min, the major components in the liquid product are 1,6-anhydroglucoses, that is, AGP and AGF. No significant change in 1,6-anhydroglucose yield is observed as a function of the reaction temperature above 300 °C. Minowa et al.[23] reported that AGP formation from glucose started at less than 220 °C in hot-compressed water. The reaction temperature range for the formation of AGP in the present study is relatively high compared to that in hot-compressed water. The yields of other products such as oligo, fructose, erythrose, glycolaldehyde dimer, and HMF were less than 10%, 6%, 3%, 6%, and 5%, respectively, in all of the reaction conditions employed (Figs. 2 and 4).

AGP and AGF were obtained in good yields at temperatures ranging from 300 to 400 °C with a feed rate of 0.5 mL/min (Fig. 4a). For example, the yield of AGP and AGF at 360 °C was 40% and 19%, respectively. The average yield of AGP and AGF in Figure 4a was 35% and 17%, respectively, at temperatures ranging from 300 to 400 °C. Therefore, the yield of 1,6-anhydroglucose observed at these temperatures in the present study was much higher than the previously reported yield at 350 °C and 40 MPa (6.3%) in supercritical water.[17] The result clearly indicates that the intramolecular dehydration of glucose proceeds predominantly in high-temperature steam under atmospheric pressure. Therefore, the thermochemical transformation in high-temperature steam under atmospheric pressure is appropriate for the production of 1,6-anhydroglucose compared with that under high pressure.

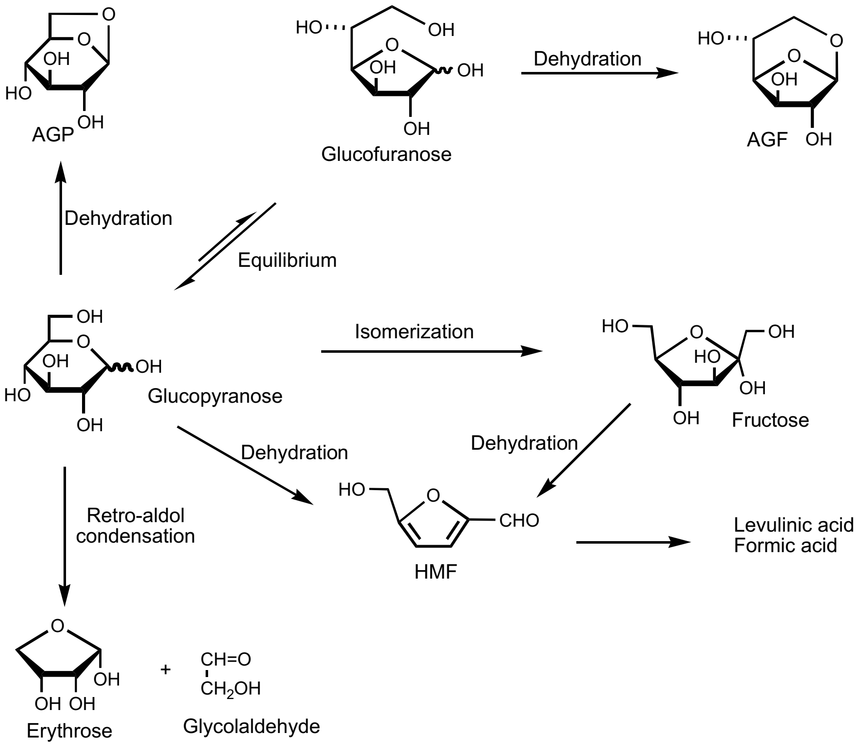

**Figure 3.** Main reaction pathway of glucose transformation in high-temperature steam.

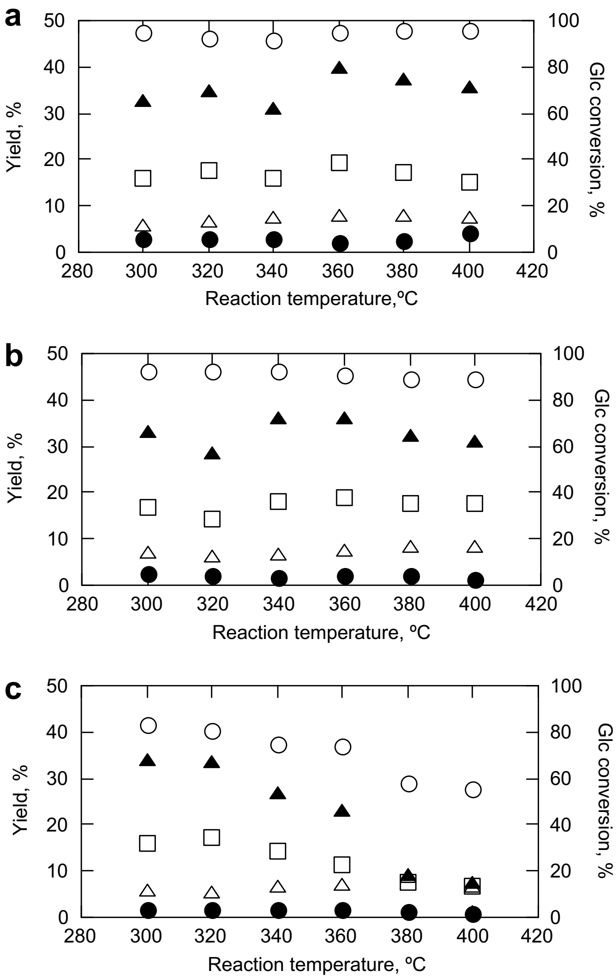

**Figure 4.** Effects of temperature on product yields and glucose conversion. A feed rate of (a) 0.5, (b) 1.0, and (c) 1.5 mL/min. (○) Glucose conversion, (▲) AGP yield, (□) AGF yield, (●) HMF yield, and (△) oligo yield.

The results for a feed rate of 1.0 mL/min are illustrated in Figure 4b. The temperature effect on the distribution of the liquid product at 1.0 mL/min was very similar to that at 0.5 mL/min as shown in Figure 4a. At 360 °C with a feed rate of 1.0 mL/min, the yield of AGP and AGF was 36% and 19%, respectively. The average yields of AGP and AGF were 33% and 17%, respectively, at temperatures ranging from 300 to 400 °C. Thus, the yields of 1,6-anhydroglucose at 1.0 mL/min were reduced slightly compared to those obtained with a feed rate of 0.5 mL/min, for example, from 59% to 55% at 360 °C. The glucose conversion decreased slightly with increasing feed rate.

In contrast to the above results, significant changes in the yield of AGP and the conversion of glucose were observed at a feed rate of 1.5 mL/min as shown in Figure 4c. The yield of 1,6-anhydroglucose and the glucose conversion decreased drastically with increasing temperature. This tendency was most significant for AGP. Furthermore, the yield of anhydroglucose dropped sharply from 59% to 34% at 360 °C when changing the feed rate from 0.5 to 1.5 mL/min (Figs. 4a and c). Under the present reaction condition at 360 °C and a feed rate of 1.5 mL/min, the yields of AGP and AGF were 23% and 11%, respectively. The low yields of AGP observed at high reaction temperature (>380 °C) are probably due to decrease in glucose conversion.

**Table 1.** Thermochemical transformation of AGP at 400 °C

| Feed rate (mL/min) | AGP conversion (%) | Glucose yield (%) |
|---|---|---|
| 0.5 | 27 | 3 |
| 1.5 | 3 | 1 |

There seems to be a few reasons for the decrease in glucose conversion at high reaction temperatures with a feed rate of 1.5 mL/min (Fig. 4c). One is the progress of the reverse reaction, that is, hydrolysis of AGP to glucose, and the other is accumulation of unreacted glucose. To clarify the progress of the reverse reaction of AGP, the thermochemical transformation of AGP in high-temperature steam under atmospheric pressure was carried out at 400 °C. The thermochemical reaction of AGP is summarized in Table 1. At a feed rate of 0.5 mL/min, AGP conversion and glucose yield were 27% and 3%, respectively. In this case, the yield of the liquid product was 88%, and the other components in the liquid product were AGF (3%), HMF (3%), oligo (4%), and unknown (2%). In contrast, at a feed rate of 1.5 mL/min, AGP conversion and glucose yield were only 3% and 1%, respectively. From this result, it was found that the reverse reaction of AGP to glucose hardly proceeds at 400 °C.

## 2.3. Effect of space time on anhydroglucose yield

The plot of yields of 1,6-anhydroglucoses, AGP and AGF, against the space time is shown in Figure 5 at two different reaction temperatures, 300 and 360 °C, respectively. Space times of 0.13 s, 0.19 s, 0.39 s, and 0.78 s are corresponding to a feed rate of 1.5 mL/min, 1.0 mL/min, 0.5 mL/min, and 0.25 mL/min, respectively, at 300 °C. Glucose conversion is also plotted in this figure. The glucose conversion increases with an increase in space time for both reaction temperatures. As shown in Figure 5a, at 300 °C, a long space time was an unfavorable condition for the production of 1,6-anhydroglucose, although glucose conversion was almost 100%. This result suggested that the selectivity of 1,6-anhydroglucose formation from glucose reduced at a long space time (>0.7 s). This effect, however, was not significant at 360 °C. On the other hand, the 1,6-anhydroglucose yield at 360 °C rapidly decreased with decreasing space time (i.e., increasing feed rate), as shown in Figure 5b. This is probably due to the insufficient reaction time to produce 1,6-anhydroglucose rather than the decrease in the selectivity. Therefore, the optimum space

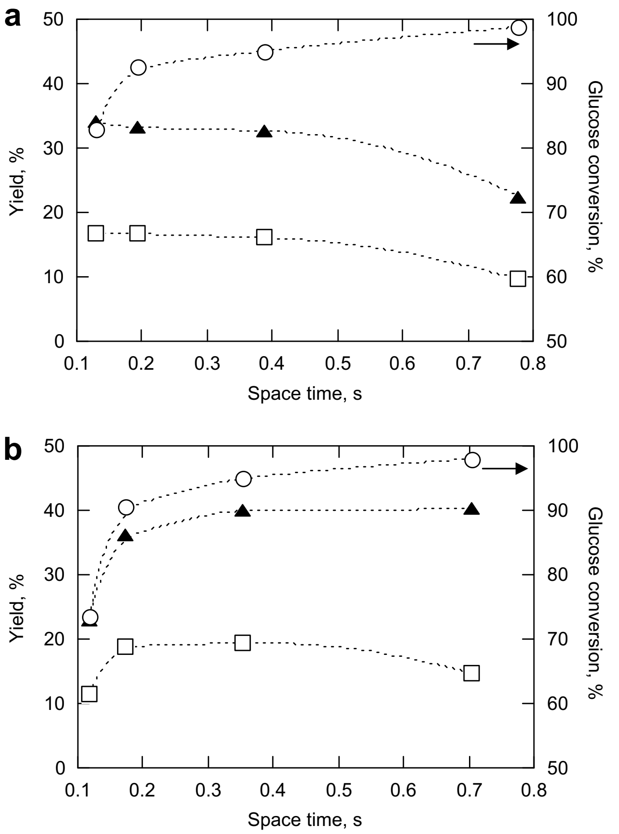

**Figure 5.** Yields of anhydroglucose versus space time. (a) reaction temperature of 300 °C, (b) reaction temperature of 360 °C. (○) Glucose conversion, (▲) AGP yield, and (☐) AGF yield.

time for the production of 1,6-anhydroglucose is in the range of about 0.2–0.4 s.

In conclusion, we report a simple method that can be used to produce 1,6-anhydroglucose in high-temperature steam generated from an aqueous glucose solution in a continuous flow reactor under atmospheric pressure. Yields of AGP and AGF were 40% and 19%, respectively, at 360 °C and a feed rate of 0.5 mL/min. In addition, a suitable residence time is required for production of 1,6-anhydroglucose using a continuous flow reactor. In this study, the optimum space time was in the range of about 0.2–0.4 s.

## 3. Experimental

### 3.1. Materials

(+)-D-Glucose (98%) and 1,6-anhydro-β-D-glucopyranose (AGP, 99%) were obtained from Wako Pure Chemical Industries Ltd and Glycon Biochemicals GmbH, respectively. The reagents used for HPLC analysis were as follows: (−)-D-fructose (99%), (−)-D-erythrose (85%) (Acros Organics); Glycolaldehyde dimer (crystalline), and 5-(hydroxymethyl)furfural (HMF) (99%) (Aldrich Inc.). These reagents were used without further purification. Column chromatography and thin-layer chromatography were performed on silica gel (Merck Art. 9025 and 5715, respectively).

### 3.2. Apparatus and procedure

A continuous flow-type reactor was used for thermochemical transformation of glucose in high-temperature steam at 200–400 °C under atmospheric pressure. Figure 6 shows a schematic diagram of the reactor used in the present study. The reactor was divided into three parts, a preheating section, reactor, and cooling section. The preheating section was made of a 3/8-in. stainless steel tube, having an internal diameter of 7.15 mm and a length of 105 mm. Thermocouples were located inside, TC-2, and outside, TC-1, of the preheating section. The preheating section was wound with a tape heater (400 W, 25 × 1000 mm), and was covered with insulating material. Similarly, the reactor was made of the same parts as the preheater, including stainless tube, thermocouples, and a tape heater, etc. The temperature of the preheating section and the reactor was controlled by TC-2 and TC-4, respectively. These thermocouples were located in the center of the stainless steel tube. The temperature of the preheating section was set 20 °C below that of the reactor. The reaction temperatures examined in this work were from 200 to 400 °C. The temperature of the outside of the reactor was always higher than the

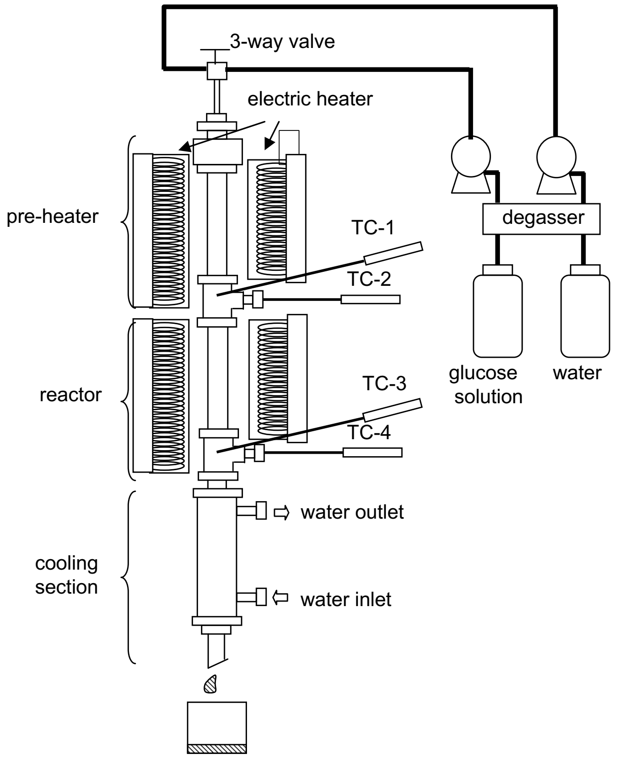

**Figure 6.** Schematic diagram of a continuous flow-type reactor.

inside of the reactor. The temperature difference between the inside and the outside of the reactor was closely related to the feed rate and the reaction temperature. At a feed rate of 0.5 mL/min, the difference ranged from 7 to 9 °C. The maximum difference was 28 °C, which was observed at 400 °C with a feed rate of 1.5 mL/min.

A 0.05 M (0.9 wt%) glucose aqueous solution was fed into the reactor by a high performance liquid chromatograph pump (PU-2080 Plus, Jasco). The feed rate of glucose solution ranged from 0.25 to 1.5 mL/min. Another feeding system was installed for washing away any water-soluble residue in the reactor. The reactor volume and the feed rates of glucose solution are known, and therefore, the space time in the reactor, $\tau$ (s) can be calculated by the following equation, $\tau = (V/Q)(\rho/\rho_0)$, where $V$ (mL) is the reactor volume including the preheating section, $Q$ (mL/s) is the flow rate of glucose aqueous solution introduced, $\rho$ (g/mL) is the density of the reaction mixture at the reaction temperature, and $\rho_0$ (g/mL) is the density of glucose aqueous solution at the ambient temperature and pressure. Both densities were assumed to be equal to the density of pure water under same conditions because glucose concentration was very low.

Prior to the thermochemical transformation of glucose, water was fed into the preheater and heated very rapidly to a preset temperature at which liquid water changes into high-temperature steam. At a preset temperature, the feed solution was changed from water to glucose solution. The reaction products with high vapor pressure were vaporized in the preheater and/or reactor, and transferred to the cooling section through the high-temperature steam. The steam containing the vaporized products was cooled rapidly and condensed in a collection bottle. The condensed product was defined as ‘liquid product’. When the temperatures of the preheating section and reactor reached steady state conditions, the liquid product was collected in a collection bottle for 40 min. After the sampling, the feed solution was changed to water with a feed rate of 5.0 mL/min for 15 min to terminate glucose transformation by rapidly decreasing the temperature. During this procedure, the preheating section and reactor were flushed out with hot water until all residual water-soluble materials in non-vaporized products had been displaced.

### 3.3. Liquid product analysis

The liquid product collected was analyzed for total organic carbon (TOC) using a TOC 5000A (Shimadzu). The liquid product yield (carbon wt%) was evaluated from the results of TOC analyses by the following equation:

$$\text{Liquid product yield} = \frac{\text{TOC value of liquid product}}{\text{TOC value of feed solution}} \times 100$$

The reaction products in the liquid product were also analyzed using an HPLC (Gilson HPLC system) with a Shodex KS-801 column. The column oven temperature was 80 °C. The eluent was water at a flow rate of 0.5 mL/min. A refractive index (RI) detector (Shimadzu RID-10A) provided quantitative analysis.

### 3.4. Isolation of AGP and AGF

A 0.05 M (0.9 wt%) glucose aqueous solution was continuously fed to the reactor for 8 h at 360 °C with a feed rate of 1.0 mL/min. The liquid product obtained (482 g) was frozen and then lyophilized to obtain a residue (3.648 g). The ratio of AGP/AGF in the liquid product was 2.1, determined using a HPLC (Gilson HPLC system) with a KS-801 (Shodex) column. The residue was purified twice by flash column chromatography on silica gel (80 g; eluted with 2% MeOH/EtOAc, 5% MeOH/EtOAc, and finally 10% MeOH/EtOAc) to afford crude anhydroglucose mixture (2.271 g, 58.4%), that is, AGP and AGF, as a pale brown syrup. The syrup was recrystallized from *i*-propyl alcohol/EtOAc to yield pure AGP (1.057 g, 27.2%) as colorless crystals and the mother liquor (1.004 g, 25.8%, AGP/AGF (0.47:1)) as a pale brown syrup. AGF and AGP in the mother liquor were separated by a procedure[21] involving the use of a cation-exchange column in the calcium form. AGF was obtained as the first eluting component as a pale yellow syrup (0.663 g, 17.1% yield), and the second eluting component contained AGP as a solid (0.298 g, 7.7%). The combined AGP (1.355 g, 34.9%) was identical with the authentic sample in all respects. $^1$H NMR and $^{13}$C NMR spectral data of AGF were essentially identical with those reported.[24]

## Acknowledgments

The author, K.T., thanks the Hokuriku Industrial Advancement Center (Kanazawa, Japan) for partial financial support. Part of this study was supported by the Industrial Technology Research Grant Program in 2006 from the New Energy and Industrial Technology Development Organization (NEDO) of Japan.

## References

1. Radlein, D. In *Fast pyrolysis of Biomass: A Handbook*; Bridgwater, A. V., Ed.; CPL Press: Newbury, UK, 2002; Vol. 2, pp 205–241.

2. Kakuchi, T.; Kusuno, A.; Miura, M.; Kaga, H. *Macromol. Rapid Commun.* **2000**, *21*, 1003–1006.
3. Satoh, T.; Imai, T.; Ishihara, H.; Maeda, T.; Kitajyo, Y.; Sakai, Y.; Kaga, H.; Kaneko, N.; Ishii, F.; Kakuchi, T. *Macromolecules* **2005**, *38*, 4202–4210.
4. Shafizadeh, F.; Fu, Y. L. *Carbohydr. Res.* **1973**, *29*, 113–122.
5. Kwon, G.-J.; Kuga, S.; Hori, K.; Yatagai, M.; Ando, K.; Hattori, N. *J. Wood Sci.* **2006**, *52*, 461–465 and references cited therein.
6. Kwon, G.-J.; Kim, D.-Y.; Kimura, S.; Kuga, S. *J. Anal. Appl. Pyrol.* **2007**, *80*, 1–5.
7. Zottola, M. A.; Alonso, R.; Vite, G. D.; Fraser-Reid, B. *J. Org. Chem.* **1989**, *54*, 6123–6125 and references cited therein.
8. Allan, G. G.; Krieger, B. B.; Work, D. W. *J. Appl. Polym. Sci.* **1980**, *25*, 1839–1859.
9. Miura, M.; Kaga, H.; Tanaka, S.; Takahashi, K.; Ando, K. *J. Chem. Eng. Jpn.* **2000**, *33*, 299–302.
10. Miura, M.; Kaga, H.; Yoshida, T.; Ando, K. *J. Wood Sci.* **2001**, *47*, 502–506.
11. Miura, M.; Kaga, H.; Sakurai, A.; Kakuchi, T.; Takahashi, K. *J. Anal. Appl. Pyrol.* **2004**, *71*, 187–199.
12. Köll, P.; Borchers, G.; Metzger, J. O. *J. Anal. Appl. Pyrol.* **1991**, *19*, 119–129.
13. Kabyemela, B. M.; Adschiri, T.; Malaluan, R. M.; Arai, K. *Ind. Eng. Chem. Res.* **1997**, *36*, 1552–1558.
14. Kabyemela, B. M.; Adschiri, T.; Malaluan, R. M.; Arai, K.; Ohzeki, H. *Ind. Eng. Chem. Res.* **1997**, *36*, 5063–5067.
15. Kabyemela, B. M.; Adschiri, T.; Malaluan, R. M.; Arai, K. *Ind. Eng. Chem. Res.* **1999**, *38*, 2888–2895.
16. Sasaki, M.; Fang, Z.; Fukushima, Y.; Adschiri, T.; Arai, K. *Ind. Eng. Chem. Res.* **2000**, *39*, 2883–2890.
17. Sasaki, M.; Goto, K.; Tajima, K.; Adschiri, T.; Arai, K. *Green Chem.* **2002**, *4*, 285–287.
18. Satoh, H.; Takahashi, K.; Kaga, H. *Abstracts of* Papers (in CD-ROM), 10th Asian Pacific Confederation of Chemical Engineering (APCChE) Congress, Kokura, Japan, October 2004; 3P-03-018.
19. Carson, L. J. U.S. Patent 3,235,541, 1966.
20. Lakshmanan, C. M.; Hoelscher, H. *Ind. Eng. Chem. Prod. Res. Develop.* **1970**, *9*, 57–59.
21. Angyal, S. J.; Beveridge, R. J. *Aust. J. Chem.* **1978**, *31*, 1151–1155.
22. Kawamoto, H.; Saito, S.; Hatanaka, W.; Saka, S. *J. Wood Sci.* **2007**, *53*, 127–133.
23. Minowa, T.; Fang, Z.; Ogi, T.; Varegyi, G. *J. Chem. Eng. Jpn.* **1998**, *31*, 131–134.
24. Köll, P.; Angyal, S. J. *Carbohydr. Res.* **1988**, *179*, 1–5.