Chemical Engineering Journal 153 (2009) 170–174

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Formation kinetics of levoglucosan from glucose in high temperature water

Kenji Takahashi[a,*], Hiroe Satoh[a], Toshifumi Satoh[b], Toyoji Kakuchi[b], Masakatsu Miura[c], Akiyoshi Sasaki[c], Masahide Sasaki[c], Harumi Kaga[c]

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

ARTICLE INFO

Article history:
Received 18 February 2009
Received in revised form 12 June 2009
Accepted 18 June 2009

Keywords:
Glucose
Dehydration
Anhydrosugar
1,6-Anhydro-β-D-glucopyranose
Supercritical water
Hyperbranched polysaccharides

ABSTRACT

The application of high temperature water to produce levoglucosan from glucose was studied. The reactions were performed using a tube reactor, and the kinetics for the decomposition of glucose and levoglucosan in high temperature water was examined. The temperature dependence of the reaction rate of the glucose decomposition was of the Arrhenius type. In contrast, the reaction rates for the decomposition of levoglucosan decreased with the increasing temperature at the constant pressure of 25 MPa. The yields of levoglucosan were examined in the temperature range from 200 to 410 °C and the pressure from 5 to 25 MPa. It was found that the yields of levoglucosan increased with the decreasing pressure.

1. Introduction

It is known that levoglucosan (1,6-anhydro-β-D-glucopyranose) is the main product from the fast pyrolysis of cellulose. Levoglucosan is an important starting material for the synthesis of stereoregular polysaccharides possessing biological activities, such as the anti-human immunodeficiency virus and blood anti-coagulant activities [1]. The derivatives of stereoregular polysaccharides can be used for the chiral stationary phase in high-performance liquid chromatography [2]. We have reported that hyperbranched polysaccharides have been produced by the polymerization of levoglucosan [3,4]. Fig. 1 shows structures of levoglucosan and the hyperbranched polysaccharides. The physical properties of the hyperbranched polysaccharides are quite different from linear polysaccharides. For example, the viscosities of the hyperbranched polysaccharides are much less than that of linear polysaccharides. We have proposed that the hyperbranched polysaccharides might be useful as a drug delivery system [5].

There have been many studies related to the production of levoglucosan from cellulose. Miura et al. reported that levoglucosan was produced with a 3% yield by the microwave heating of a wood block [6]. Recently, Kawamoto et al. demonstrated the conversion of cellulose into levoglucosan in the aprotic polar solvent of sulfolane [7]. Within a 1 min reaction time, levoglucosan was produced with a 34.5% yield, corresponding to an approximate 60% selectivity. Köll and Metzger [8] have described the pyrolysis of cellulose in supercritical acetone, and the yield of levoglucosan was 39%.

In contrast to the studies for cellulose, studies for glucose are limited. Kabeyemela et al. studied glucose decomposition in subcritical and supercritical water [9]. The decomposition products included levoglucosan. However, the yield of levoglucosan was negligible. They did not examine the effect of the experimental conditions on the yield of levoglucosan. Sasaki et al. have also studied the reaction of glucose in supercritical water [10]. Under their conditions (623, 673 and 723 K; 25 and 40 MPa), the yields of levoglucosan were 6.3% at 623 K and 40 MPa, and 5.2% at 623 K and 25 MPa. At higher temperatures, the yield of levoglucosan was only a trace amount.

Supercritical fluids may be useful to dehydration reaction of other sugars. Bicker et al. examined the dehydration of fructose to hydroxymethylfurfural in sub- and supercritical acetone/water mixtures [11]. They also examined the same reaction in sub- and supercritical methanol and acetic acid. The selectivity in supercritical acetone was 77% at a 99% conversion. In methanol and acetic acid, however, the addition of acid catalyst was required, otherwise no hydroxymethylfurfural in pure subcritical acetic acid nor methoxymethylfurfural in pure supercritical methanol was produced.

These studies indicated that there is the possibility that levoglucosan may be produced with a high yield by the dehydration of glucose in high temperature water. We now present a method to produce levoglucosan in a high yield from glucose using high

---

[*] Corresponding author. Tel.: +81 76 234 4828; fax: +81 76 234 4829.
E-mail address: ktkenji@t.kanazawa-u.ac.jp (K. Takahashi).

1385-8947/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2009.06.027

Nomenclature

C_{A0}	initial concentration of glucose (mol/L)
C_R	concentration of levoglucosan (mol/L)
F	mass flow rate (kg/m^3)
k_1	reaction rate constant of glucose in Eq. (1) (1/s)
k_2	reaction rate constant of levoglucosan in Eq. (1) (1/s)
P	pressure (Pa)
t	reaction time (s)
T	reaction temperature (K)
V	reactor volume (m^3)

Greek letters

ρ	density of glucose solution (kg/m^3)

temperature water. The effects of temperature and pressure on the yields of levoglucosan will be examined.

2. Experimental

Glucose was obtained from Wako Pure Chemicals Industries Limited. 1,6-anhydro-β-D-glucopyranose was obtained from Tokyo Chemical Industry Limited. All other reagents were used without further purification.

The experimental apparatus is shown in Fig. 2. The reactions were conducted in a high-pressure tube reactor made of Hastelloy C-276. The inside diameter of the reactor is 0.5 mm. Two different reactors, each volume is 19.6 and 58.9 μL, were used. Two HPLC pumps (JASCO, PU980) were used to pump the glucose aqueous solution and water. The water and glucose solutions were continuously purged with ambient pressures argon gas for degassing. The glucose solution was merged with high temperature water at the inlet of the tube reactor. The flow rates of the glucose aqueous solution and water were adjusted so that the concentration of glucose at the inlet of the reactor was 0.05 M. The water was heated using two electric heaters so that the temperature of the merged solution would reach the desired level. An electric heater controlled the temperatures at the inlet and outlet of the reactor so that the both temperatures were identical. The pressure was controlled using a back-pressure regulator and monitored using a pressure transducer. To terminate the reaction, the glucose solution was immediately cooled by a heat exchanger. Estimated cooling times based on the space–time in the heat exchanger are 0.2–5 s, depending on the flow rate. The space–time of the glucose solution was ranged from 0.1 to 15 s. The space–time was calculated by $\tau = V\rho/F$, where F is the mass flow rates, V is the reactor volume, and ρ is the density of the glucose solution. The density of the glucose solution was assumed to be the density of pure water because the sample concentration is very dilute. The employed experimental conditions were over the temperature range of 200–400 °C and the pressure range of 2–25 MPa.

The products were analyzed by the HPLC using a KS-801 (Shodex) column operated at 50 °C with a 1 mL/min water solvent flow. A refractive index detector (Shimadzu, RID-6A) was used. Levoglucosan was quantified by comparison of the sample peak and the peak of a range of standard solutions at known concentrations. Levoglucosan was also analyzed as a trimethylsilyl derivative using gas chromatography (GC: Shimadzu GC14A; column: Shimadzu CBP10, 25 m × 0.32 mm ID × 0.5 μm; column temperature: 110–260 °C; heating rate: 7.5 °C/min; glass capillary column: 25 m; He; FID-detector) [6]. We identified 1,6-anhydro-β-D-glucofuranose as well as 1,6-anhydro-β-D-glucopyranose. However, 1,6-anhydro-β-D-glucofuranose was produced under low-pressure conditions only, and we did not examine its yields.

3. Results and discussion

3.1. Temperature effect on the dehydration of glucose

Fig. 3 shows the concentration of glucose and levoglucosan as a function of the space–time at the constant pressure of 25 MPa. At 250 °C, 8 s is required to achieve an 80% glucose conversion. However, at 320 °C, most of the glucose reacted within 2 s, and the glucose conversion was nearly 90%. As will be discussed later, these results suggest that the reaction rate of the glucose decomposition largely depends on the reaction temperature, and the activation energy of the glucose decomposition rate is 61 kJ/mol (250 °C < T < 370 °C). For the formation of levoglucosan, it is clear that an optimum space–time exists to produce levoglucosan. The maximum concentrations of levoglucosan were obtained at about 6 and 1.0 s at temperatures of 250 and 320 °C, respectively. These results indicate that the formation of levoglucosan may be via a successive reaction. The change on concentration of levoglucosan as a function of time was examined at several different temperatures and the results are shown in Fig. 4. At temperatures except for 370 and 380 °C, the time profile of the levoglucosan concentration is parabolic, suggesting that levoglucosan could be the intermediate product of a successive reaction as follows.

$$\text{Glucose} \xrightarrow{k_1} \text{Levoglucosan} \xrightarrow{k_2} \text{Degradation products} \qquad (1)$$

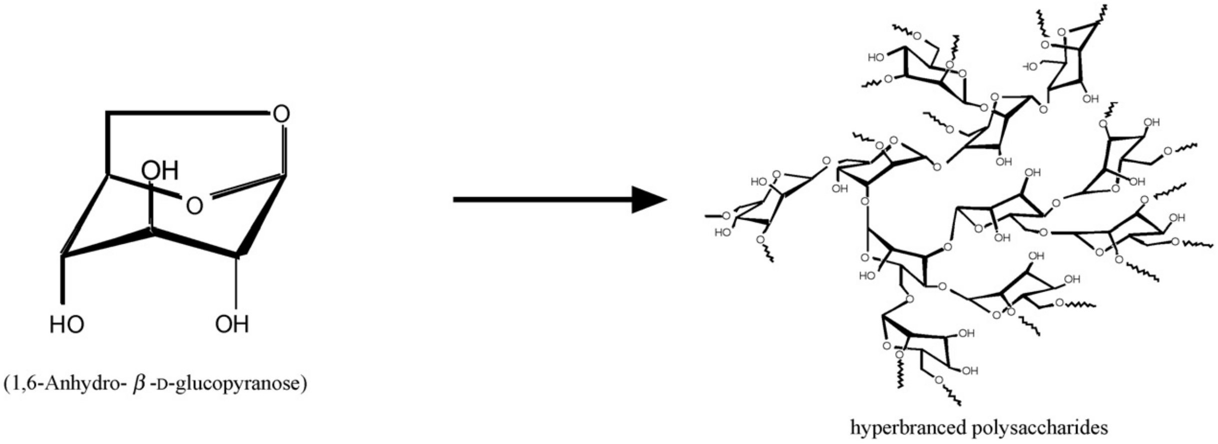

Fig. 1. Structures of levoglucosan (1,6-anhydro-β-D-glucopyranose) and hyperbranched polysaccharides.

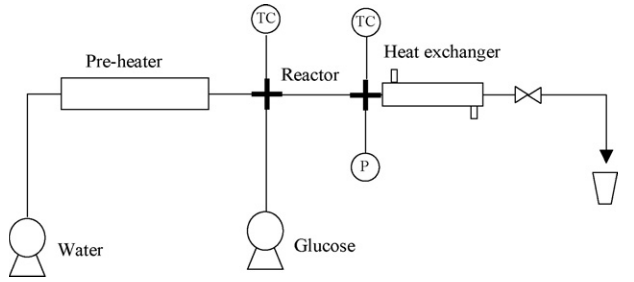

Fig. 2. Experimental apparatus used for high temperature water reaction system.

We measured the decomposition of levoglucosan in high temperature water at 25 MPa to examine the above reaction scheme. The decomposition of levoglucosan was assumed to be a first-order reaction. In Fig. 5, the temperature dependence of the first-order reaction rates for the decomposition of glucose and levoglucosan, k_1 and k_2, respectively, were plotted. As can be seen in the figure, the decomposition rate of levoglucosan decreased with the increasing temperature. In the kinetic analysis, we simply assumed the first-order reaction for the decomposition of levoglucosan. However, the

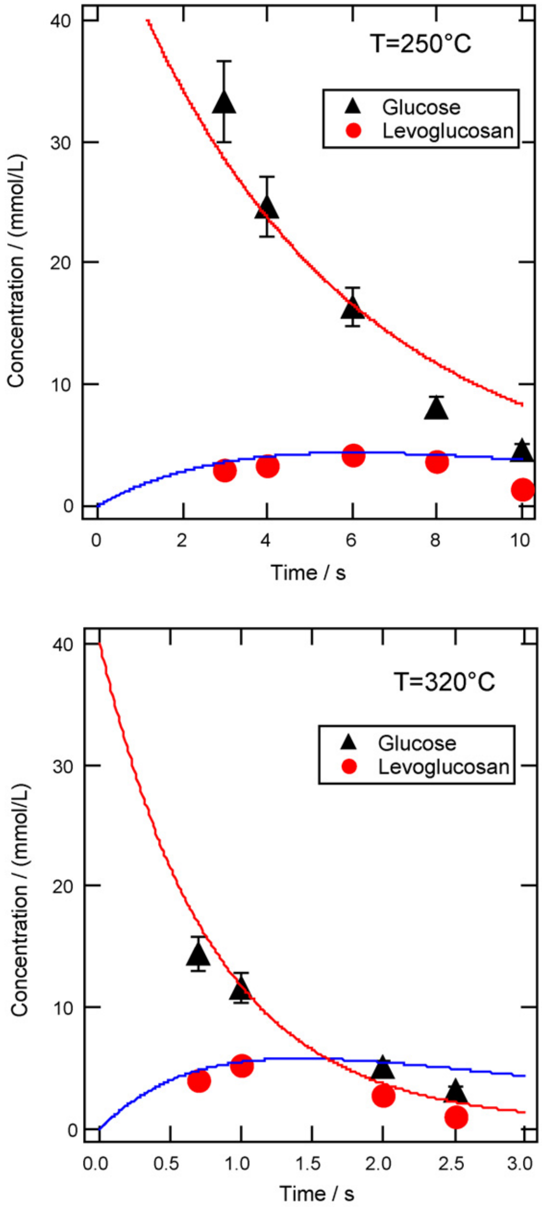

Fig. 3. Concentrations of glucose and levoglucosan as a function of space–time at 250 and 320 °C. Lines visualize the trend of the measured values.

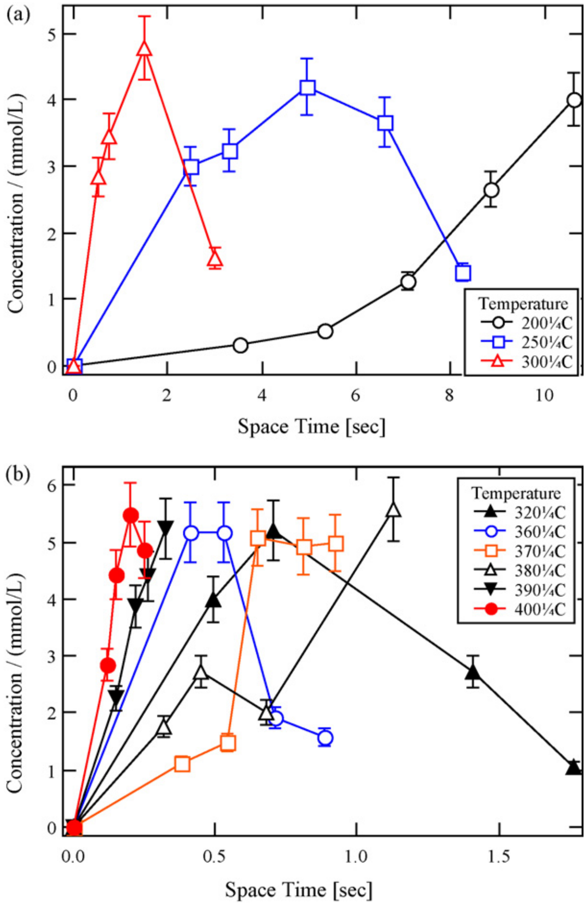

Fig. 4. Concentration of levoglucosan as a function of time at various temperatures and constant pressure of 25 MPa.

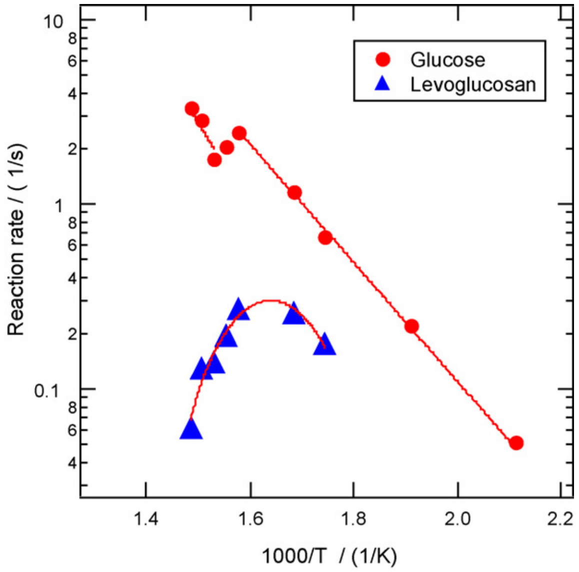

Fig. 5. Arrhenius plot of reaction rate constants for decomposition of glucose and levoglucosan in high temperature water at 25 MPa. Lines visualize the trend of the measured values.

result for levoglucosan decomposition suggests that proton could play a role in the reaction because it is known that proton initiates the ring opening of levoglucosan [3], and that, under a constant pressure condition, the concentration of proton decreases with increasing temperature when temperature is higher than 300 °C.

If the formation of levoglucosan is a simple successive reaction, the concentration of levoglucosan may be expressed as follows [12].

$$C_R = \frac{k_1 C_{A0}}{k_2 - k_1}(e^{-k_1 t} - e^{-k_2 t}) \tag{2}$$

where C_R is concentration of levoglucosan, C_{A0} is the glucose initial concentration, and k_1 and k_2 refer to the reaction rate constants defined in Eq. (1), respectively. Therefore, the reaction time that will give the maximum concentration of levoglucosan may be expressed by

$$t_{max} = \frac{\ln(k_2/k_1)}{k_2 - k_1} \tag{3}$$

The calculated reaction times t_{max} from the experimental rate constants k_1 and k_2 using Eq. (3) are 2.7, 1.6, 1.0, 1.3, 1.6, 1.14 and 1.2 s for the temperatures of 300, 320, 360, 370, 380, 390 and 400 °C, respectively. A comparison with experimental data in Fig. 4 revealed that the agreements between the calculations from the simple model and the experimental values are not very good. These discrepancies are probably due to the adopted simple reaction model. Furthermore, although we assumed that glucose decays by first-order reaction kinetics, glucose molecules decompose via several different paths. Sasaki et al. suggested that there might be seven decomposition paths [10]. These are the reaction paths for fructose, glyceraldehydes, erythrose, dihydroxy acetone, glycolaldehyde, 5-hydroxymethyl-furfural and levoglucosan. In contrast, Matsumura et al. reported that by considering changes in the reaction field from ionic to radical as the temperature increases, the reaction order for the glucose decomposition depends on the reaction temperature [13]. They proposed that the reaction order might be less than unity at high temperature ($T > 500$ K). Hence, by considering these previous studies, Eq. (2) may be too simple to predict the optimum reaction time to produce levoglucosan.

3.2. *Pressure effect on glucose dehydration*

In most of the previous studies regarding the decomposition of glucose in high temperature water, the reactions were usually examined at pressures that are higher than the critical pressure of water. Under these high-pressure conditions, the yields of levoglucosan were not as high as already mentioned. For instance, Kabyemela et al. reported that at a pressure of 30 MPa, the amount of produced levoglucosan was negligible [9]. As the formation reaction of levoglucosan from glucose is a dehydration reaction, a low concentration of water or low pressure of water would be a suitable condition to produce levoglucosan. Hence, we examined the pressure effect on the decomposition of glucose and the yield of levoglucosan.

Fig. 6 shows the effect of pressure on the formation of levoglucosan. The reactions were performed under constant space–time conditions (2 s). At high-pressure conditions ($P > 15$ MPa), the yields of levoglucosan are about 10–17 mol.% within the temperatures examined. However, under lower pressure conditions ($P < 10$ MPa), the yields of levoglucosan significantly increased with the decreasing pressure. The maximum yield of 32 mol.% was obtained at the pressure of 7 MPa and 320 °C under the present experimental conditions. A further decrease in pressure may increase the yield of levoglucosan, however, at a lower pressure, the reaction system was unstable in the present experiment. In previous related studies for the formation of levoglucosan from glucose in high temperature water, the yields are quite low. For example, the yield has been reported to be 6.3% at 623 K and 40 MPa, and 5.2% at 623 K and 25 MPa [10]. One reason for the low yield could be their long space–time (1.02 and 0.92 s for 6.3% and 5.2% yield, respectively).

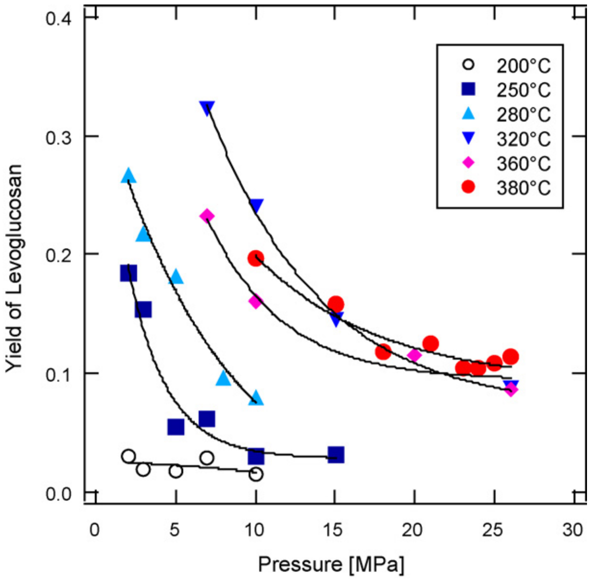

Fig. 6. Yields of levoglucosan as a function of pressure at various temperatures. Lines visualize the trend of the measured values.

4. Conclusion

The formation of levoglucosan from glucose was studied in high temperature water. The kinetics for the decomposition of glucose and levoglucosan in high temperature water were examined. The temperature dependence of the reaction rate of the glucose decomposition was of the Arrhenius type. In contrast, the reaction rates for the decomposition of levoglucosan decreased with the increasing temperature at the constant pressure of 25 MPa. It was found that the yields of levoglucosan increased significantly with the decreasing pressure. The maximum yield of 32 mol.% was obtained at 320 °C and 7 MPa.

Acknowledgments

The authors wish to thank the Hokuriku Industrial Advancement Center (Kanazawa, Japan) for the financial support. This study was also supported by the Industrial Technology Research Grant Program in 2006 from the New Energy and Industrial Technology Development Organization (NEDO) of Japan.

References

[1] K. Hattori, T. Yoshida, H. Nakashima, M. Premanathan, R.R. Aragaki, T. Mimura, Y. Kaneko, N. Yamamoto, T. Uryu, Synthesis of sulfonated amino-polysaccharides having anti-HIV and blood anticoagulant activities, Carbohydr. Res. 312 (1998) 1–8.
[2] A. Kusuno, M. Mori, T. Sato, M. Miura, H. Kaga, T. Kakuchi, Enantioseparation properties of (1 → 6)-α-D-glucopyranan and (1 → 6)-α-D-mannopyranan tris(phenylcarbamate)s as chiral stationary phase in HPLC, Chirality 14 (2002) 498–502.
[3] T. Satoh, T. Imai, H. Ishihara, T. Maeda, Y. Kitajyo, A. Narumi, H. Kaga, N. Kaneko, T. Kakuchi, Synthesis of hyperbranched polysaccharide by thermally induced cationic polymerization of 1,6-Anhydro-β-D-mannopyranose, Macromolecules 36 (2003) 6364–6370.
[4] T. Satoh, T. Imai, H. Ishihara, T. Maeda, Y. Kitajyo, Y. Sakai, H. Kaga, N. Kaneko, F. Ishii, T. Kakuchi, Synthesis, branched structure, and solution property of hyperbranched D-glucan and D-galactan, Macromolecules 38 (2005) 4202–4210.
[5] Y. Kitajyo, T. Imai, Y. Sakai, M. Tamaki, H. Tani, K. Takahashi, A. Narumi, H. Kaga, N. Kaneko, T. Satoh, T. Kakuchi, Encapsulation–release property of amphiphilic hyperbranched D-glucan as a unimolecular reverse micelle, Polymer 48 (2007) 1237–1244.

[6] M. Miura, H. Kaga, A. Sakurai, T. Kakuchi, K. Takahashi, Rapid pyrolysis of wood block by microwave heating, J. Anal. Appl. Pyrolysis 71 (2004) 187–199.

[7] H. Kawamoto, W. Hatanaka, S. Saka, Thermochemical conversion of cellulose in polar solvent (sulfolane) into levoglucosan and other low molecular-weight substances, J. Anal. Appl. Pyrolysis 70 (2003) 303–313.

[8] P. Köll, J. Metzger, Thermischer Abbau von Cellulose und Chitin in überkritischem Aceton, Angewandt Chemie 90 (1978) 802–803.

[9] B.M. Kabyemela, T. Adschiri, R.M. Malaluan, K. Arai, Kinetics of glucose epimerization and decomposition in subcritical and supercritical water, Ind. Eng. Chem. Res. 36 (1997) 1552–1558.

[10] M. Sasaki, K. Goto, K. Tajima, T. Adschiri, K. Arai, Rapid and selective retro-aldol condensation of glucose to glycolaldehyde in supercritical water, Green Chem. 4 (2002) 285–287.

[11] M. Bicker, D. Kaiser, L. Ott, H. Vogl, Dehydration of D-fructose to hydroxymethylfurfural in sub- and supercritical fluids, J. Supercrit. Fluids 36 (2005) 118–126.

[12] O. Levenspiel, Chemical Reaction Engineering, 3rd ed., John Wiley & Sons, New York, 1999.

[13] Y. Matsumura, S. Yanachi, T. Yoshida, Glucose decomposition kinetics in water at 25 MPa in the temperature range of 448–673 K, Ind. Eng. Chem. Res. 45 (2006) 1875–1879.