ORIGINAL ARTICLE

Kei Yoshida · Hisashi Miyafuji · Shiro Saka

Effect of pressure on organic acid production from Japanese beech treated in supercritical water

Abstract The effect of pressure as described by density was studied on organic acid production from Japanese beech (*Fagus crenata*) treated in supercritical water. At a reaction temperature of 380°C, the maximum yield of organic acids was 35% at a pressure of 30 MPa (density of water: 0.53 g/ml) for 1 min in a batch-type system. Furthermore, the yield of organic acids decreased with increasing reaction pressure. It was also found that fragmented products from sugars such as methylglyoxal and glycolaldehyde could be more easily converted to organic acids than dehydrated products such as furfural and 5-hydroxymethyl furfural. This result suggests that organic acids can be mainly derived from fragmented products.

Key words Japanese beech · Supercritical water · Pressure · Organic acid · Reaction pathway

Introduction

Biomass resources will become more important as alternatives to fossil resources in the future, because the latter will become increasingly scarce and eventually exhausted. Among biomass resources, lignocellulosics are one of the most abundant types[1,2] and do not compete with food resources. Thus, efficient utilization of these resources is obligatory for our sustainable future, and some methods such as pyrolysis[3] and acid hydrolysis[4] have been investigated for converting lignocellulosics to useful products. Besides these approaches, supercritical water treatment (>374°C, >22.1 MPa) has been considered to be an attractive alternative technology.[5–16]

On biomass resources, it is reported that various sugars can be obtained from lignocellulosics when treated in supercritical water.[13,14] Furthermore, when the treatment is prolonged, some organic acids can be obtained, as well as dehydrated and fragmented products from sugars.[17,18]

Organic acids such as lactic acid can be converted not only to biodegradable polymers but also to gases such as methane, carbon monoxide, and hydrogen by microorganisms. In addition, organic acids are thought to be one of the intermediates of the gaseous products during supercritical water gasification. Thus, production behavior of organic acids and their identification needs to be studied to obtain useful products and biofuels from lignocellulosics.

It is known that the organic acids such as formic, pyruvic, glycolic, acetic, and lactic acids can be produced from Japanese beech (*Fagus crenata*) in supercritical water. These organic acids are mainly derived from cellulose and hemicellulose, although there was little in production of organic acids from lignin under supercritical water.[18] The propyl side chains in lignin also decompose to organic acids when relatively long treatment is applied.[18]

To optimize the treatment conditions for obtaining organic acids, more detailed production behavior of organic acids during supercritical water treatment should be investigated. In particular, the effect of treatment pressure on organic acids production has not been studied. In this study, therefore, the effect of pressure as described by density was investigated using a biomass conversion system with a batch-type reaction vessel for organic acid production from Japanese beech.

K. Yoshida · H. Miyafuji · S. Saka (✉)
Department of Socio-Environmental Energy Science, Graduate School of Energy Science, Kyoto University, Kyoto 606-8501, Japan
Tel. +81-75-753-4738; Fax +81-75-753-4738
e-mail: saka@energy.kyoto-u.ac.jp

Materials and methods

Samples and chemicals

Wood flour ground to pass 80 mesh screen from Japanese beech (*Fagus crenata* Blume) was used as biomass sample. Methylglyoxal, glycolaldehyde, furfural, 5-hydroxymethyl-furfural (5-HMF), formic acid, glycolic acid, acetic acid, and

lactic acid were purchased from Nakalai Tesque as reagent grade products. For supercritical water treatment, high-performance liquid chromatography (HPLC)-grade water was used. Prior to the supercritical water treatment, Japanese beech was Soxhlet-extracted with a mixture of ethanol and benzene (1:2, v/v) for 12 h.

Supercritical water treatment

Treatments were conducted by using a batch-type system.[13] A sample was slurried at 1% (w/w) by adding water. To control the reaction pressure, the slurry was fed in pre-scribed volume to a 5-ml reaction vessel made of Inconel-625, as specified in Table 1. The reaction vessel was charged with nitrogen and heated by immersion in a molten tin bath preheated at 500°C until the temperature in the reaction vessel reached 380°C. The reaction vessel was removed from the tin bath and allowed to stand for the required reaction time. The vessel was then immersed in a water bath to quench the reaction. During this treatment, the tempera-ture and the pressure in the reaction vessel were monitored by a thermocouple and pressure gauge attached to the reac-tion vessel. In this batch-type system, temperature and pres-sure were both changeable so that the treatment condition was defined by maximum temperature and maximum pres-sure during the experiment. The detail of reaction tempera-ture and pressure profiles was presented in our previous report.[13]

The obtained reaction mixture was filtered with a 0.2-μm membrane filter to separate the water-soluble portion from the water-insoluble residue. The water-insoluble residue was dried at 105°C for 24 h and weighed to obtain the yield. The yield was calculated from the following equation:

$$\text{Yield (\%)} = W_1/W_0 \times 100$$

where W_0 is the amount of charged sample, and W_1 is the weight of water-insoluble residue.

For comparison, the recovery of organic acids from a model mixture of organic acids from the batch-type system was also studied. The sample was also mixed at 1% (w/w) in water. The procedure for supercritical water treatment was the same as described above. The recovery of organic acids after supercritical water treatment was calculated assuming the total organic acid in the untreated mixture was 100%.

$$\text{Recovery (\%)} = W_2/W_3 \times 100$$

where W_3 is the amount of charged organic acid mixture (formic acid, glycolic acid, acetic acid, and lactic acid), and

Table 1. Sample contents with water in reaction vessel for various supercritical water treatments

Pressure	Sample mass (mg)	Water (ml)
25	22.5	2.23
30	26.7	2.6
40	29.8	2.95
60	32.8	3.24
100	50	4.95

W_2 is the recovered organic acids after supercritical water treatment.

Yields of organic acids from model fragmented and dehydrated products after treatment in the batch-type system were also studied. The concentration of the sample was also set at 1% (w/w) by adding water. This solution was fed in prescribed volume to a 5-ml reaction vessel. The mixture was reacted in similar fashion to that described for beech wood. The yield of organic acid was calculated from the following equation:

$$\text{Yield (\%)} = W_4/W_5 \times 100$$

where W_5 is the combined weight of the charged model fragmented and dehydrated compounds (5-HMF, furfural, methylglyoxal, glycolaldehyde), and W_4 is the weight of organic acids obtained by supercritical water treatment.

Analyses

The obtained water-soluble portions were analyzed by HPLC and capillary electrophoresis (CE). HPLC analysis was conducted on a Shimadzu LC-10A equipped with a Shodex Sugar KS-801 (Showa Denko) column and a refrac-tive index detector (RID). Water was used as eluent at a flow rate of 1.0 ml/min. CE analysis was conducted on a HP3D CE systems instrument (Agilent). A fused-silica cap-illary (75 μm i.d., 104 cm total length, 95.5 cm effective length) from Agilent was used. Indirect ultraviolet (UV) detection at 270 nm (reference wavelength 350 nm) was performed using 2,6-pyridine dicarboxylic acid buffer (con-taining 0.5 mM cetyl trimethyl ammonium bromide, pH = 5.6) for organic acid analysis (Agilent). Injection was carried out at 50 mbar for 4 s at the cathodic end. The applied voltage was set at −30 kV, with a capillary temperature of 15°C.

Results and discussion

Figure 1 shows yields of water-insoluble residue, fragmented products, and dehydrated products from Japanese beech after treatment in supercritical water. The yields of frag-mented products and dehydrated products, respectively, corresponded to the total yields of glycol aldehyde/methyl-glyoxal/dihydroxyacetone and levoglucosan/5-HMF/furfu-ral. At the low pressure of 25 MPa at 380°C (Fig. 1a), the yield of water-insoluble residue was found to decrease rapidly to 27% after 5 s of treatment. After 5 s, however, its yield decreased gradually to 12% as the reaction time increased. At the high pressure of 100 MPa at 380°C (Fig. 1b), the yield of residue leveled off at 20% after 5 s of treat-ment. Cellulose and hemicellulose are known to be easily decomposed in supercritical water. In addition, ether link-ages of lignin are preferentially hydrolyzed by supercritical water. Therefore, it is likely that the water-insoluble resi-dues were condensed-type lignin structures from Japanese beech wood.[12,18]

Fig. 1a,b. Yield of water-insoluble residue, fragmented products, and dehydrated products from Japanese beech treated in supercritical water at **a** 25 MPa (density of water 0.45 g/ml) and 380°C and **b** 100 MPa (0.72 g/ml) and 380°C in a batch-type system. Yields of fragmented products and dehydrated products correspond to the total yield of glycolaldehyde/methylglyoxal/dihydroxyacetone and levoglucosan/5-hydroxymethyl furfural/furfural, respectively
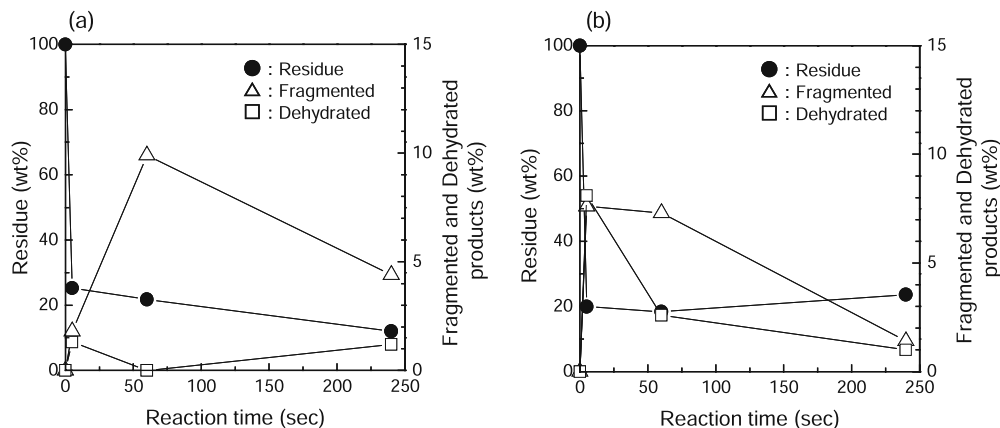
Fig. 2a,b. Changes of yield for organic acids from Japanese beech treated in supercritical water at **a** 25 MPa (density of water 0.45 g/ml) and 380°C and **b** 100 MPa (0.72 g/ml) and 380°C in a batch-type system
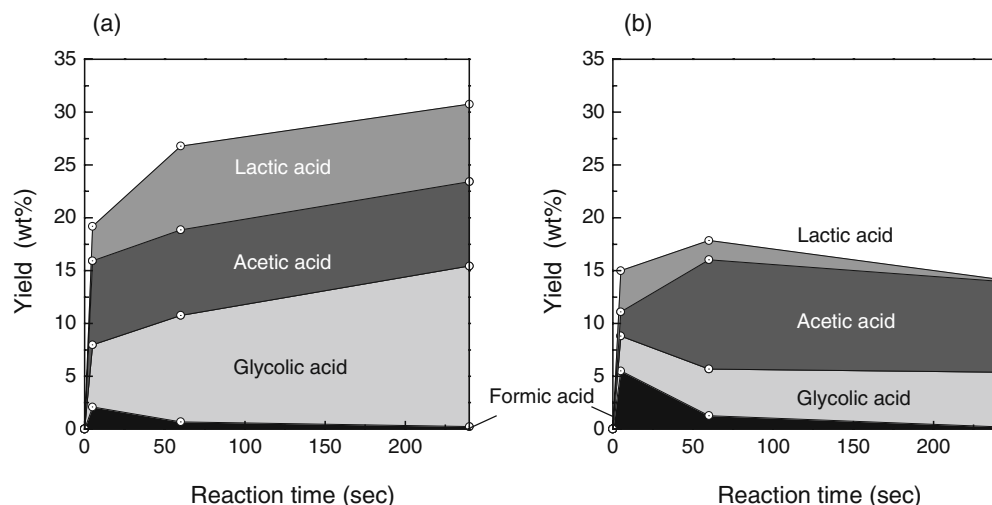
The yield of fragmented products at 25 MPa and 380°C (Fig. 1a) was higher than that at 100 MPa and 380°C (Fig. 1b) for 60-s treatment. However, the yield of dehydrated products was very low under conditions of 25 MPa and 380°C (Fig. 1a) and various reaction times, while the yield at 100 MPa and 380°C was about 8% for 5 s of treatment. These results are in good agreement with those from our previous studies in which dehydrated products were preferentially produced in high-pressure reactions due to higher density and higher concentration of ionic product of water.[13]

From CE analysis, beech wood was found to decompose to formic acid, glycolic acid, acetic acid, and lactic acid by supercritical water treatment as reported previously.[15,18] Figure 2 shows the changes of the yield for organic acids from Japanese beech when treated in supercritical water at a low pressure of 25 MPa and a high pressure of 100 MPa.

At low pressure, although the yield of glycolic acid and lactic acid increased as the reaction proceeded, that of formic acid showed a maximum at 5 s of reaction time. Significant change was not observed in the yield of acetic acid. The total yield of these organic acids was found to increase as reaction time increased.

At high pressure, more glycolic acid was formed with longer reaction time. However, lactic, acetic, and formic acids showed maximal yields at 5 s, 60 s, and 5 s, respectively. The total yield of these organic acids was around 17% at any reaction time.

The yield of organic acid at low pressure was higher than that obtained at high pressure. The maximum yield of total organic acids was 30.8% for 240 s of treatment at 25 MPa.

To investigate the effect of reaction pressure on production of organic acids in supercritical water, beech wood was treated at 380°C at various pressures (densities) for 60 s or 240 s as shown in Fig. 3. For the 60-s treatment, maximum production of total organic acid was 35% at 30 MPa. The yield of total organic acid decreased below 20% at the higher pressure of 100 MPa. A similar trend was observed for the 240-s treatment. However, the decrease at higher pressure was significant, returning a yield below 15%.

These results shown in Figs. 2 and 3 suggest that treatment under low pressure can produce organic acids more efficiently than under 100 MPa at 380°C. To elucidate the difference between organic acid production at high and low pressure, the stability of each organic acid in supercritical water was studied. A mixture of lactic, acetic, glycolic, and formic acids was treated with supercritical water at 25 MPa or 100 MPa. Figure 4 shows the changes of the recovery for these organic acids after supercritical water treatment assuming the total organic acid in the untreated

(a) 60 sec

(b) 240 sec
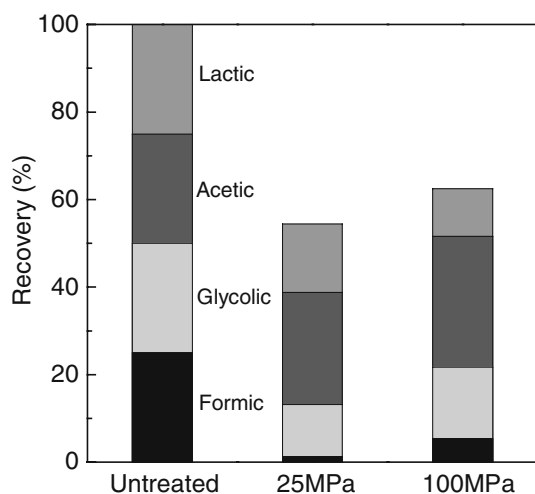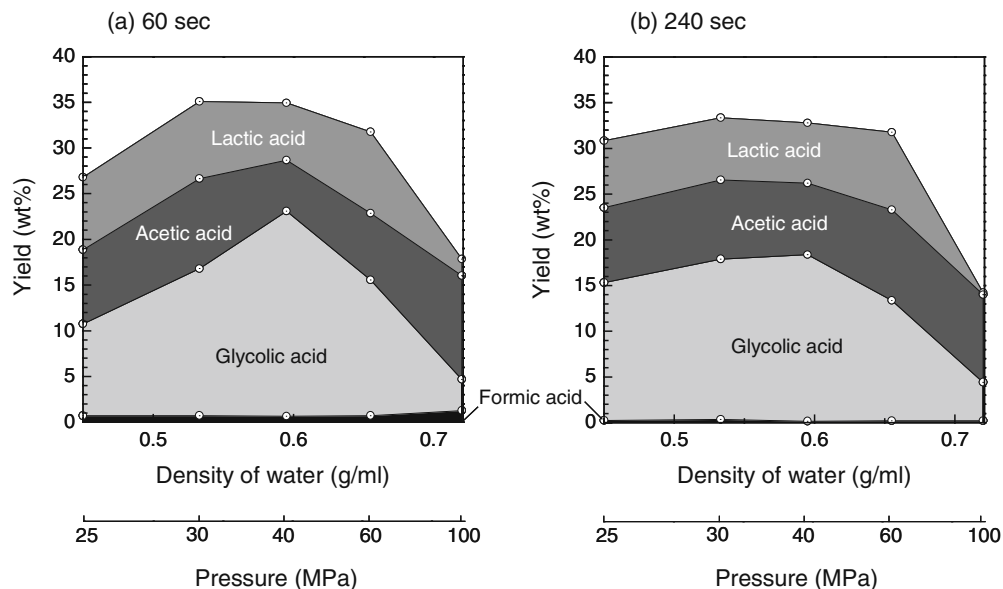
Fig. 4. Recovery of organic acids treated with supercritical water at 25 MPa or 100 MPa for 240 s at 380°C

mixture is 100%. The recoveries of total organic acid after supercritical water treatment at 25 MPa and 100 MPa were 54.4% and 62.5%, respectively. This result shows no significant difference between treatments at 25 MPa and 100 MPa at 380°C, indicating that the stability of the organic acids in supercritical water at the lower pressure is almost the same as that at 100 MPa. This does not explain the difference of organic acid production between high and low pressure.

The decomposition pathway of wood in supercritical water has been studied. Kabyemela et al.[19] proposed that cellulose could be decomposed by hydrolysis, dehydration, and fragmentation when treated in supercritical water. However, the production of organic acids from fragmented and dehydrated products has not been studied. Therefore, to examine the yield of organic acids from fragmented or dehydrated products, model compounds of fragmented or dehydrated products were treated in supercritical water.

Methylglyoxal and glycolaldehyde were used as model compounds for fragmented products, while furfural and 5-HMF were used as models for dehydrated products.

Figure 5 shows the yield of organic acids from the model compounds treated in supercritical water. For treatment at both 25 MPa and 100 MPa at 380°C for 240 s, the yields of organic acids from dehydrated products (furfural and 5-HMF) were negligible, while the yields from fragmented products (methylglyoxal and glycolaldehyde) were found to be much higher. As shown in Fig. 2, the total yields of organic acids showed the same tendency for 25-MPa and 100-MPa treatments, and the result of the 240-s treatment was similar to those with other treatment times. These results reveal that organic acids can be produced mainly from fragmented products but not from dehydrated products in supercritical water.

As reported previously,[13] fragmented products are preferentially produced in treatments at pressures lower than 100 MPa. Organic acids can be easily produced from fragmented products rather than dehydrated products, as shown in Fig. 5. Therefore, yields of organic acids treated in supercritical water at lower pressure were higher than those for treatments at 100 MPa. This explains why organic acid production from wood is much greater at low-pressure treatments in supercritical water than in treatments at 100 MPa.

Based on this line of evidence, it is reasonable to suggest that organic acids are efficiently produced from carbohydrate (cellulose and hemicellulose) in low pressure conditions in supercritical water through fragmented products. However, these products may be decomposed further to gases with prolonged treatment.[15] On the other hand, we found that the production of organic acids from lignin is due to decomposition of the propyl side chains of the phenyl propane units and not from the aromatic moiety in lignin.[18] From this finding, we propose a scheme in Fig. 6 for the pathway of lignocellulosic decomposition in supercritical water to organic acids.

Fig. 5. Yield of organic acids from model compounds of dehydrated products [furfural and 5-hydroxymethyl furfural (*5-HMF*)] and fragmented products (methylglyoxal and glycolaldehyde) treated in supercritical water in a batch-type system at 25 MPa (density of water: 0.45 g/ml) at 380°C for 240 s, and at 100 MPa (0.72 g/ml) at 380°C for 240 s
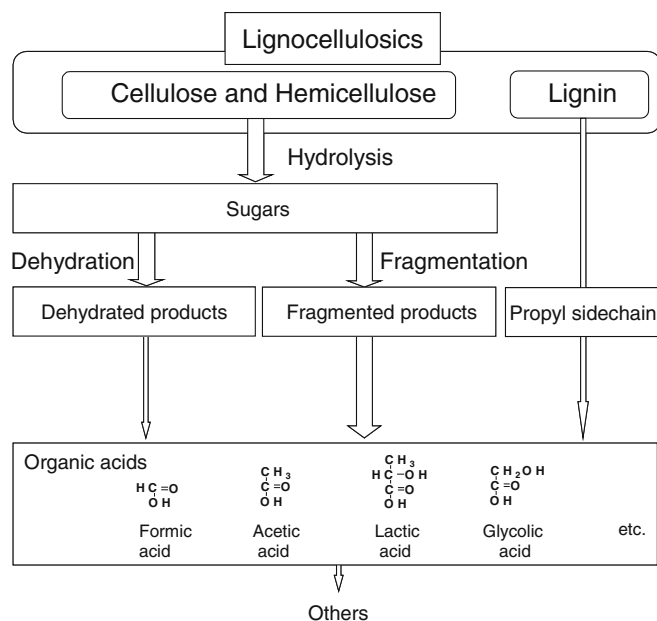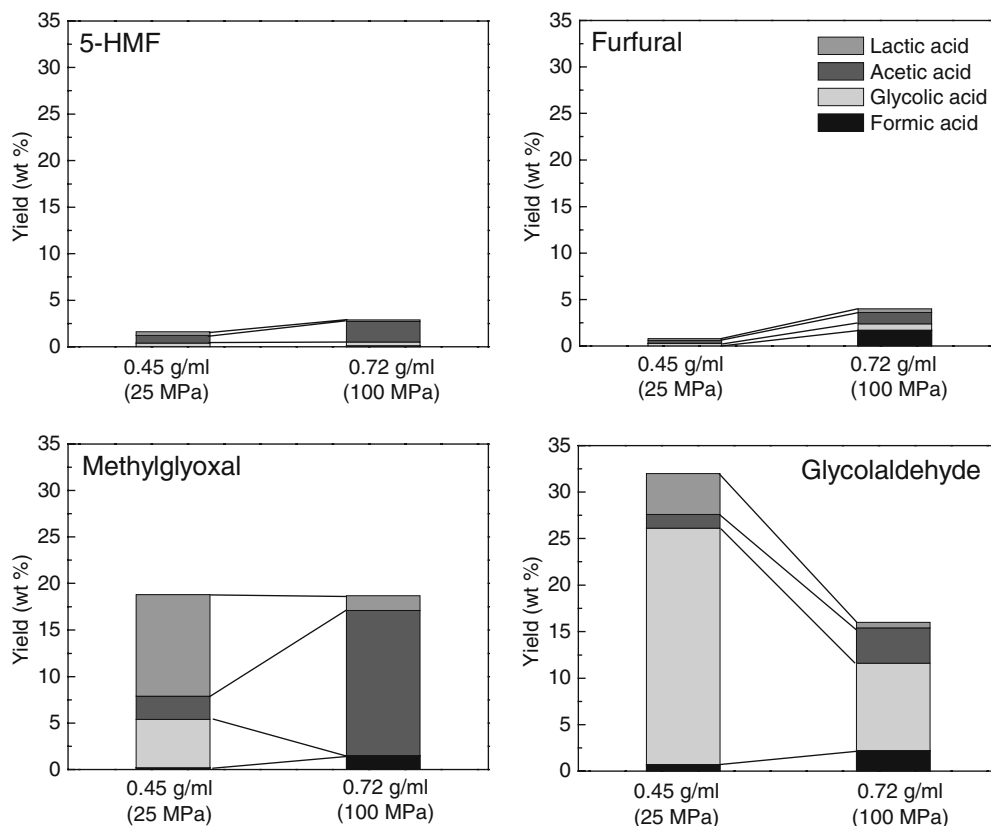
Fig. 6. Scheme of lignocellulosic decomposition in supercritical water. *Wide arrows* show major pathways; *narrow arrows* show minor pathways

References

1. Minami E, Saka S (2001) Biomass resources in Japan. In: Saka S (ed) Biomass Energy Environment (in Japanese). Industrial, Tokyo, pp 61–103
2. Minami E, Saka S (2002) Survey on the virgin biomass and its unused and waste portions in Japan in their available quantity (in Japanese). Energ Resour 23:219–223
3. Bridgwater AV, Peacocke GVC (1999) Fast pyrolysis processes for biomass. Renew Sustain Energ Rev 4:1–73
4. Ehara K, Saka S (2001) Acid hydrolysis. In: Saka S (ed) Biomass Energy Environment (in Japanese). Industrial, Tokyo, pp 251–260
5. Bobleter O (1994) Hydrothermal degradation of polymers derived from plants. Prog Polym Sci 19:797–841
6. Sakaki T, Shibata M, Miki T, Hirosue H, Hayashi N (1996) Decomposition of cellulose in near-critical water and fermentability of the products. Energ Fuel 10:684–688
7. Sakaki T, Shibata M, Miki T, Hirosue H, Hayashi N (1996) Reaction model of cellulose decomposition in near-critical water and fermentation of products. Bioresour Technol 58:197–202
8. Sakaki T, Shibata M, Sumi T, Yasuda S (2002) Saccharification of cellulose using a hot-compressed water-flow reactor. Ind Eng Chem Res 41:661–665
9. Sasaki M, Fang Z, Fukushima Y, Adschiri T, Arai K (2000) Dissolution and hydrolysis of cellulose in subcritical and supercritical water. Ind Eng Chem Res 30:2883–2890
10. Sasaki M, Iwasaki K, Hamatani T, Adschiri T, Arai K (2001) Super-rapid enzymatic hydrolysis of cellulose with supercritical water solubilization pretreatment (in Japanese). Kobunshi Ronbunshu 58:527–532

Although more quantitative and comprehensive studies are necessary to propose the production mechanisms of organic acids, the results of this study are sufficient to demonstrate that the production of organic acids in supercritical water may be manipulated by controlling the pressure (density) of supercritical water.

208

11. Saka S, Ueno T (1999) Chemical conversion of various celluloses to glucose and its derivatives in supercritical water. Cellulose 6:177–191
12. Ehara K, Saka S, Kawamoto H (2002) Characterization of the lignin-derived products from wood as treated in supercritical water. J Wood Sci 48:320–325
13. Ehara K, Saka S (2002) A comparative study on chemical conversion of cellulose between the batch-type and flow-type systems in supercritical water. Cellulose 9:301–311
14. Sasaki M, Furukawa M, Minami K, Adschiri T, Arai K (2002) Kinetics and mechanism of cellobiose hydrolysis and retro-aldol condensation in subcritical and supercritical water. Ind Eng Chem Res 41:6642–6649
15. Antal MJ, Mok WSL, Richards GN (1990) Kinetic studies of the reactions of ketoses and aldoses in water at high temperature. Carbohydr Res 199:91–109
16. Yoshida H, Tavakoli O (2004) Sub-critical water hydrolysis treatment for waste squid entrails and production of amino acids, organic acids, and fatty acids. J Chem Eng Jpn 37:253–260
17. Kim K, Fujita M, Daimon H, Fujie K (2004) Change of monochloroacetic acid to biodegradable organic acids by hydrothermal reaction. J Hazard Mater 108:133–139
18. Yoshida K, Kusaki J, Ehara K, Saka S (2005) Characterization of low molecular weight organic acids from beech wood treated in supercritical water. Appl Biochem Biotechnol 121–124:794–806
19. Kabyemela B, Adschiri T, Malaluan R, Arai K (1999) Glucose and fructose decomposition in subcritical and supercritical water: detailed reaction pathway, mechanisms, and kinetics. Ind Eng Chem Res 38:2888–2895