Production of Furan Compounds from *Cryptomeria japonica* using Pyridinium Chloride under Various Conditions

Koichi Yoshioka,[a] Tatsuhiko Yamada,[b] Hiroyuki Ohno,[c] and Hisashi Miyafuji [a,]*

Cryptomeria japonica was treated with pyridinium chloride ([Py]Cl)-water mixtures under various conditions to determine the optimum conditions for efficient production of furan compounds, such as 2-hydroxyacetylfuran (2-HAF), 5-hydroxymethylfurfural (5-HMF), and furfural. The maximum total yield of furan compounds, *i.e.*, 9.24 wt.%, was obtained by the treatment of *C. japonica* with a 90% [Py]Cl and 10% water (w/w) solution for 30 min at 120 °C with a sample loading of 6 wt.%. The highest yield of 2-HAF from *C. japonica* was obtained by treatment for 3 min at 160 °C without the addition of water, although the total yield of furan compounds was lower than that obtained under the optimum treatment conditions. Scale-up of this process for efficient production of furan compounds from *C. japonica* was successfully performed under the optimum treatment conditions. In addition, the yields of 2-HAF and 5-HMF increased when ball-milled *C. japonica* containing low-crystallinity cellulose was treated under the optimum conditions.

Keywords: Ionic liquid; Pyridinium chloride; Cryptomeria japonica; 2-Hydroxyacetylfuran; 5-Hydroxymethylfurfural; Cellulose; Hemicellulose; Scale-up; Low crystal cellulose

Contact information: a: Graduate School of Life and Environmental Sciences, Kyoto Prefectural University, Hangi-cho, Shimogamo, Sakyo-ku, Kyoto 606-8522, Japan; b: Center for Advanced Materials, Forestry and Forest Products Research Institute, Matsunosato 1, Tsukuba, Ibaraki 305-8687, Japan; c: Functional Ionic Liquid Laboratories, Graduate School of Engineering, Tokyo University of Agriculture and Technology, 2-24-16 Naka-cho, Koganei, Tokyo 184-8588, Japan;
** Corresponding author: miyafuji@kpu.ac.jp*

INTRODUCTION

Lignocellulosic materials, which are the most abundant renewable organic resources on Earth, have attracted attention as an alternative to fossil fuels in recent years. Lignocellulosics consist mainly of three polymers: cellulose, hemicelluloses, and lignin. The cellulose structure consists of a linear chain of β (1→4)-linked D-glucopyranose units. Hemicelluloses are polysaccharides composed of various hexoses and pentoses, such as D-glucose, D-mannose, D-galactose, D-xylose, L-arabinose, and L-rhamnose. Some hemicelluloses also contain acetyl groups and uronic acid residues. Lignin is a complex polymer and is biosynthesized from phenylpropane *via* oxidative radical coupling of monolignols. These three biopolymers can be converted to value-added compounds through chemical and biological reactions (Ragauskas *et al.* 2006, 2014).

Research on the production of useful compounds from the saccharides in lignocellulosics has been increasing. For example, 5-hydroxymethylfurfural (5-HMF) and furfural (Fig. 1) can be obtained by transformations of hexoses and pentoses in lignocellulosics *via* hydrolysis and dehydration (Van Putten *et al.* 2013; Caes *et al.* 2015). These furan compounds are used as building blocks for polymers, pharmaceuticals, fragrances, and fuels (Van Putten *et al.* 2013; Caes *et al.* 2015). 2,5-Furandicarboxylic acid, which is obtained by oxidation of 5-HMF, and furfuryl alcohol, which is obtained by furfural reduction, are widely used as monomers of functional polymers (Zuo *et al.* 2016). Although numerous methods have been used for the production of furan compounds from lignocellulosics and related compounds, the development of efficient methods for the production of furan compounds is still important for biorefining lignocellulosics and obtaining commercially viable chemicals.

Some ionic liquids (ILs), which are organic salts with melting points at around ambient temperature, can dissolve cellulose and plant biomass (Swatloski *et al.* 2002; Tadesse and Luque 2011; Brandt *et al.* 2013). IL treatment of lignocellulosics and related compounds, with or without catalysts, is being increasingly studied, and various useful low-molecular-weight compounds have been produced (Zakrzewska *et al.* 2010; Dashtban *et al.* 2014; Ito *et al.* 2016; Yokoyama and Miyafuji 2016). In previous studies, 5-HMF, furfural, and 2-hydroxyacetylfuran (2-HAF) (Fig. 1) were identified in the IL-water-soluble fractions after treatment of *Cryptomeria japonica* with IL-water mixtures (Yoshioka *et al.* 2015, 2016). It has been suggested that, in 2-HAF production from D-glucose, the hydroxyl group at the C6 position of the 2,3-endiol, which is the key intermediate formed from glucose, attacks the carbonyl carbon at the C3 position of the intermediate, followed by ring closure and dehydration (Moreau *et al.* 1996; Yang *et al.* 2011). 2-HAF is also an important building block, it is used as the starting material for the chemical synthesis of bioactive compounds (Trost and Yeh 2002) and is a precursor of serine and azasugars (Demir *et al.* 2003). Furthermore, 2-HAF can be converted to α-oxo-2-furanacetic acid *via* oxidation of the primary hydroxyl group in 2-HAF. α-Oxo-2-furanacetic acid is a starting material for the chemical synthesis of cefuroxime axetil (Barry *et al.* 1983), which is an enteral second-generation cephalosporin antibiotic supplied by GlaxoSmithKline plc.

In a previous paper, the reaction of *C. japonica* with a 90% pyridinium chloride ([Py]Cl) and 10% water (w/w) solution was reported. The solution was effective for achieving liquefaction of *C. japonica* and the production of useful low-molecular-weight compounds (Yoshioka *et al.* 2015, 2016). An understanding of the production of furan compounds from lignocellulosics after treatment with [Py]Cl using various treatment conditions is therefore important. Furthermore, identifying the optimum treatment conditions for the production of furan compounds from lignocellulosics is essential for developing industrial processes.

In this study, the production of furan compounds from *C. japonica* by treatment with [Py]Cl, with/without water, was investigated under various conditions. Additionally, scale-up of the process for efficient production of furan compounds from *C. japonica* was conducted under the optimum treatment conditions.

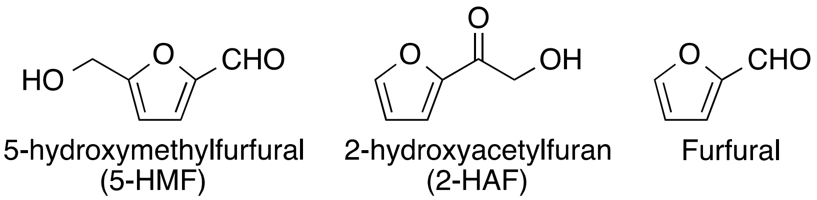

Fig. 1. Chemical structures of furan compounds obtained from saccharides in lignocellulosics

EXPERIMENTAL

Materials

All solvents were analytical grade and purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). [Py]Cl (> 98.0%) was obtained from the Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). 5-HMF and furfural were purchased from Sigma-Aldrich (St. Louis, MO, USA). 2-HAF was prepared as previously described (Yoshioka *et al.* 2015). Milli-Q water was used for IL-water treatments and high-performance liquid chromatography (HPLC). *C. japonica* (Japanese cedar) was ground in a Wiley-mill to a particle size of 90 µm to 180 µm and then extracted with ethanol/benzene (1/2, v/v) for 6 h in a Soxhlet extractor. The extracted wood powder was dried in an oven for 24 h at 105 °C and stored at room temperature under air.

Methods

Treatment of C. japonica with [Py]Cl-water mixtures in glass tube

Treatment with 90% [Py]Cl and 10% water (w/w) solution, and a 6 wt.% sample loading relative to [Py]Cl was performed as follows: Wood powder (0.18 g), [Py]Cl (3.0 g), and Milli-Q water (0.33 g) were added to a 15 mL pressure tube (Ace Glass, Inc., Vuneland, NJ, USA). The mixture was stirred for 4 h at 120 °C in an oil bath. At specified treatment times, the reaction mixture was analyzed using HPLC, as described below.

Normal- and large-scale treatments of C. japonica under reflux

In the large-scale treatment, wood powder (1.8 g), [Py]Cl (30 g), and Milli-Q water (3.3 g) were added to a 100 mL three-necked round-bottomed flask. The mixture was stirred for 4 h at 120 °C under reflux. In the normal-scale treatment, wood powder that had been stored under air as described in the materials section (0.18 g), [Py]Cl (3.0 g), and Milli-Q water (0.33 g) were added to a 5 mL two-necked round-bottomed flask. The mixture was stirred for 4 h at 120 °C under reflux. At specified treatment times, the reaction mixture was analyzed using HPLC, as described below.

Treatment of C. japonica with [Py]Cl without water addition

[Py]Cl (3.33 g) in a 15 mL pressure tube was heated at 140 °C, 160 °C, or 180 °C in an oil bath. Wood powder (0.18 g) was added, and the mixture was stirred for 4 h. At specified treatment times, the reaction mixture was analyzed using HPLC, as described below.

Treatment of ball-milled C. japonica in glass tube

Ball-milled *C. japonica* was prepared from wood powder stored under air (as described in the materials section), using the procedure described in a previous paper (Ogawa and Miyafuji 2015). The ball-milled *C. japonica* (0.18 g), [Py]Cl (3.0 g), and Milli-Q water (0.33 g) were added to a 15 mL pressure tube. The mixture was stirred for 4 h at 120 °C in an oil bath. At specified treatment times, the reaction mixture was analyzed using HPLC, as described below.

HPLC analysis of reaction mixture

HPLC was performed using a Shimadzu Prominence system (Shimadzu Co., Ltd, Kyoto, Japan) equipped with an LC-20AD pump, a CTO-20A column oven, and an SPD-M20A photodiode array. The HPLC conditions were as follows: an Aminex HPX-87H column (Bio-Rad Laboratories, Inc., Hercules, CA, USA), a flow rate of 0.6 mL/min, 5 mM H_2SO_4 as the mobile phase, a column temperature of 45 °C, and sample detection based on UV absorbance at 280 nm.

The samples for HPLC analysis were prepared by diluting the reaction mixture 10 times with Milli-Q water. The diluted reaction mixture was shaken and filtered through a 0.45 µm syringe filter. The filtrate (10 µL) was analyzed using HPLC. The yield of each furan compound was calculated based on the dry weight of *C. japonica* after Soxhlet extraction.

RESULTS AND DISCUSSION

Optimization of Water:[Py]Cl Ratio

Figure 2 shows the yields of furan compounds from *C. japonica* obtained by treatment with [Py]Cl-water mixtures with various water contents for 4 h at 120 °C. In addition, HCl aq. was also used for the treatment of *C. japonica*; the results were compared with those achieved using [Py]Cl-water mixtures.

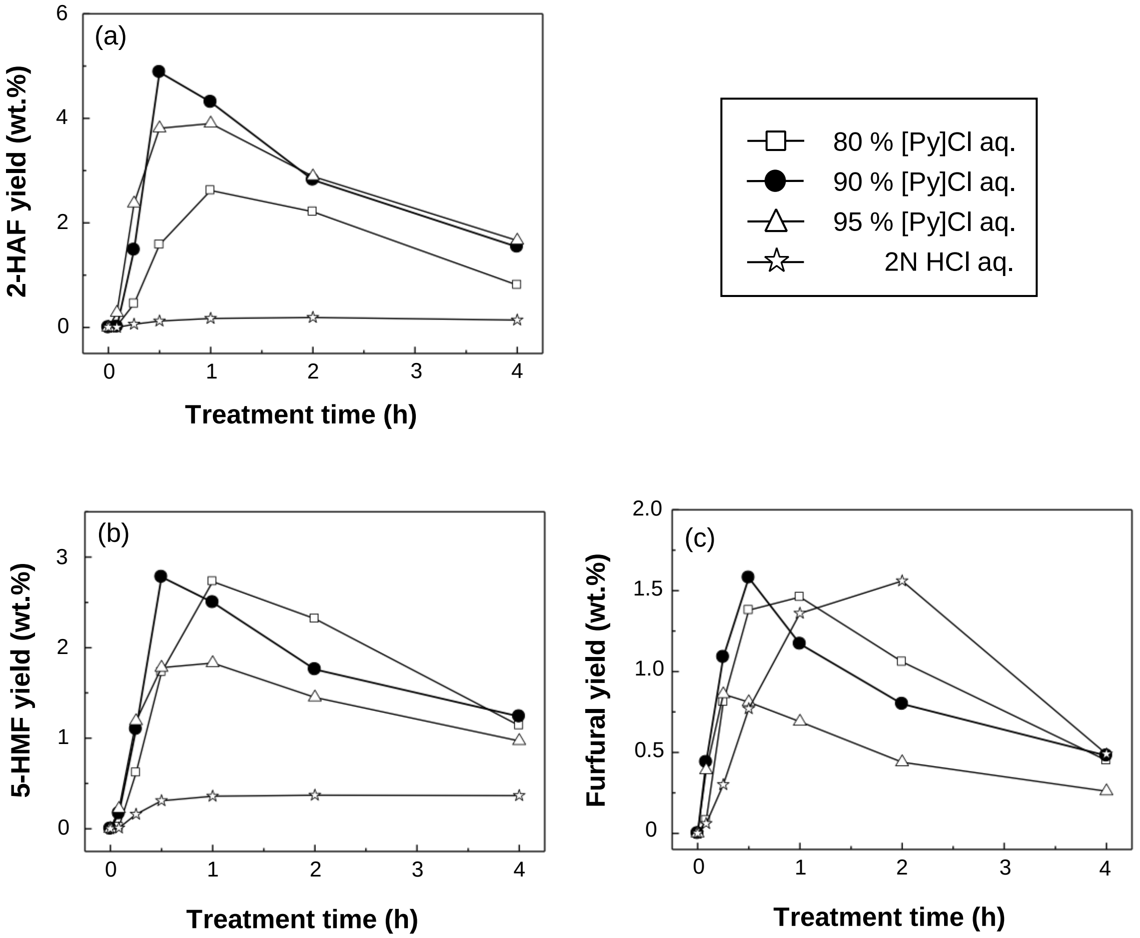

Fig. 2. Yields of (a) 2-HAF, (b) 5-HMF, and (c) furfural obtained by treatment of *C. japonica* with [Py]Cl-water mixtures with various water contents, and by treatment with 2N HCl aq

The highest yields of 2-HAF, 5-HMF, and furfural, *i.e.*, 4.88 wt.%, 2.78 wt.%, and 1.58 wt.%, respectively, were obtained by treatment with 90% [Py]Cl and 10% water (w/w) solution for 30 min. In contrast, the maximum yields of 2-HAF and 5-HMF obtained by treatment of *C. japonica* with 2N HCl aq. were lower than 0.5 wt.%. The maximum yield of furfural obtained by treating *C. japonica* with 2 N HCl aq. was almost the same as that obtained using 90% [Py]Cl and 10% water (w/w) solution. However, the time needed to achieve the maximum yield was 2 h longer with 2N HCl aq. These results showed that the treatment with 90% [Py]Cl and 10% water (w/w) solution gave the highest yields of furan compounds from *C. japonica*.

Optimization of Temperature

Figure 3 shows the yields of furan compounds obtained by treatment of *C. japonica* with 90% [Py]Cl and 10% water (w/w) solution at 80 °C, 100 °C, 120 °C, and 140 °C.

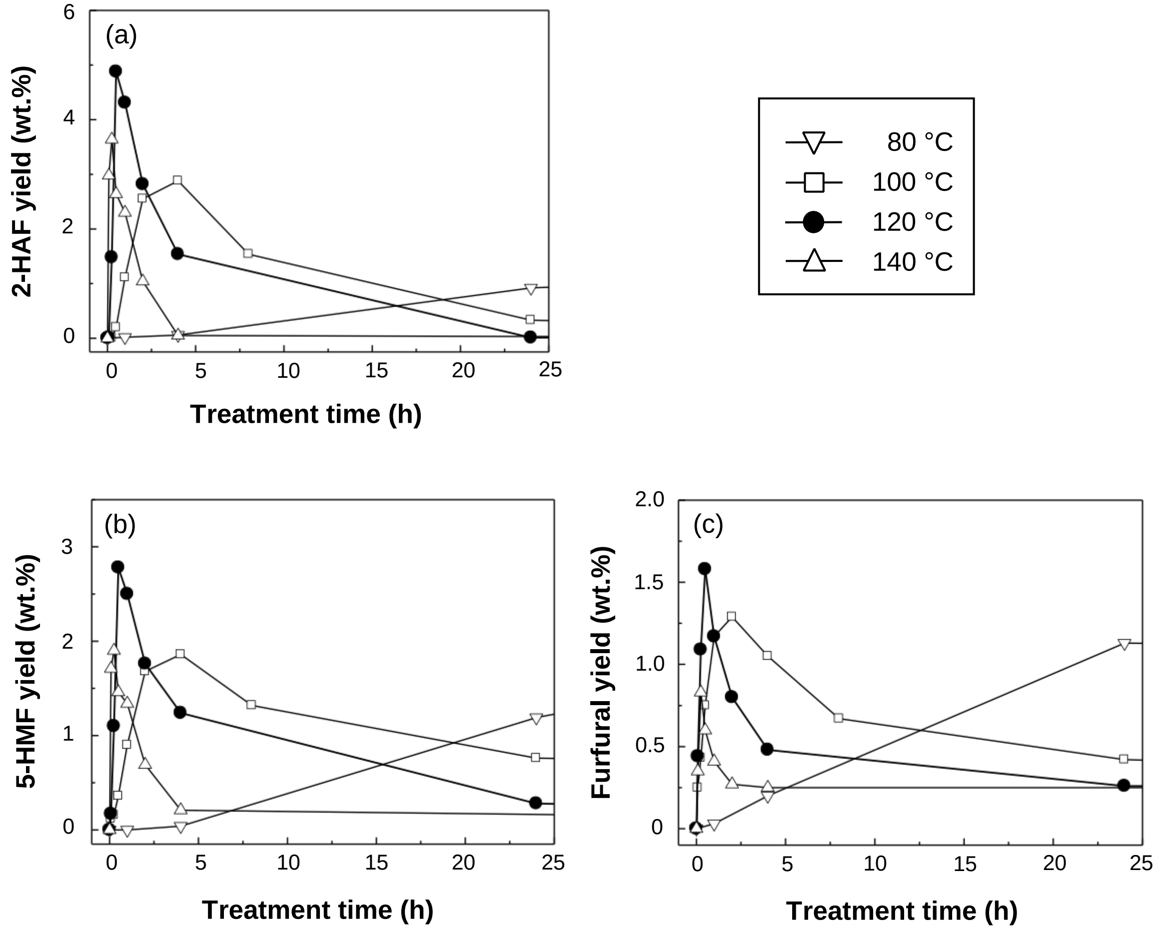

Fig. 3. Yields of (a) 2-HAF, (b) 5-HMF, and (c) furfural obtained by treatment of *C. japonica* with 90% [Py]Cl and 10% water (w/w) solution at various temperatures

The maximum yields of furan compounds were obtained at 120 °C and 140 °C within 1 h. The yields of 2-HAF and 5-HMF achieved by treatment at 100 °C reached a maximum at 4 h. The maximum yields of 2-HAF, 5-HMF, and furfural at 80 °C were obtained after 24 h (data not shown). The maximum yield of each furan compound obtained at 120 °C was higher than those at 80 °C, 100 °C, and 140 °C. These results showed that

120 °C was the optimum temperature for producing furan compounds from *C. japonica* using 90% [Py]Cl and 10% water (w/w) solution.

Optimization of Sample Loading

Figure 4 shows the yields of furan compounds obtained by treating *C. japonica* with 90% [Py]Cl and 10% water (w/w) solution at 120 °C at various sample loadings. All the treatments described above were conducted at sample loadings of 6 wt.%. Therefore, the yields of the furan compounds obtained at sample loadings of 0.1 wt.%, 2 wt.%, and 10 wt.% were investigated. The maximum yields of furan compounds were all obtained within 1 h. For the sample loading of 0.1 wt.%, the time needed to achieve the maximum yields of furan compounds was longer than in the other cases. The maximum yield of each furan compound obtained at a sample loading of 10 wt.% was significantly lower than those obtained using other sample loadings.

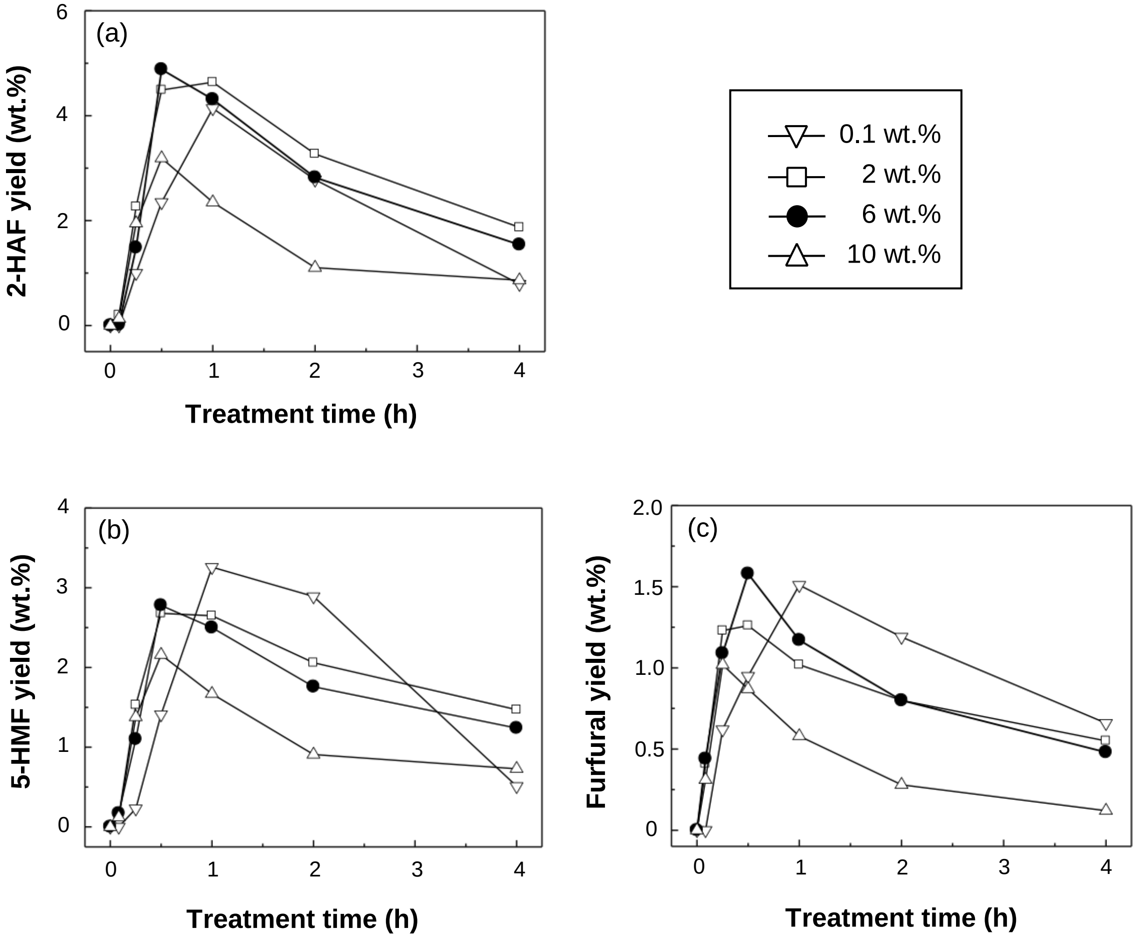

Fig. 4. Yields of (a) 2-HAF, (b) 5-HMF, and (c) furfural obtained by treatment of *C. japonica* with 90% [Py]Cl and 10% water (w/w) solution at 120 °C with various sample loadings

The maximum yields of 2-HAF at all sample loadings were obtained at 30 min or 1 h. At a sample loading of 6 wt.%, the maximum yield of 2-HAF was 4.88 wt.% and was achieved in 30 min, which was higher than the yields achieved at all other sample loadings. The maximum yield of 5-HMF was 3.26 wt.% at a sample loading of 0.1 wt.%, and the maximum yield of furfural was 1.58 wt.%, at a sample loading of 6 wt.%. The total maximum yields of 2-HAF, 5-HMF, and furfural at sample loadings of 0.1 wt.%, 2 wt.%, and 6 wt.% were 8.91 wt.%, 8.43 wt.%, and 9.24 wt.%, respectively. Although the total maximum yields of furan compounds were almost the same, the amounts of furan compounds obtained at the sample loading of 6 wt.% were much greater than those obtained at sample loadings of 0.1 wt.% and 2 wt.%. The optimum sample loading for furan production from *C. japonica* was therefore 6 wt.%. These results suggested that the optimum conditions for obtaining furan compounds, giving the highest yields, were treatment of *C. japonica* with 90% [Py]Cl and 10% water (w/w) solution at a sample loading of 6 wt.% for 30 min at 120 °C.

Normal- and Large-Scale Treatments of *C. japonica*

The scale-up of the *C. japonica* treatment under reflux using the optimum conditions was investigated. Figure 5 shows the yields of furan compounds from *C. japonica* obtained by normal- and large-scale treatments with 90% [Py]Cl and 10% water (w/w) solution.

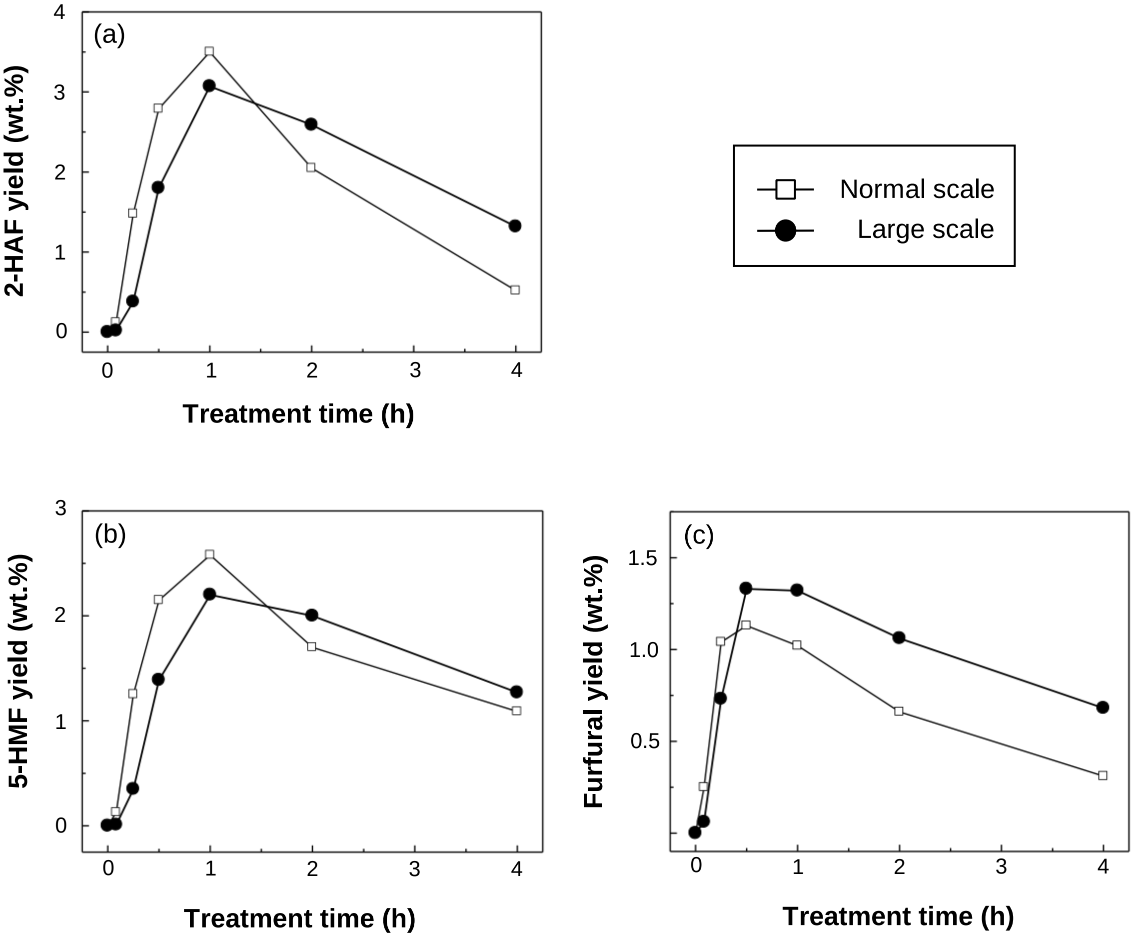

Fig. 5. Yields of (a) 2-HAF, (b) 5-HMF, and (c) furfural obtained by normal- and large-scale treatment of *C. japonica* with 90% [Py]Cl and 10% water (w/w) solution under reflux

The maximum yields of 2-HAF and 5-HMF were achieved at 1 h in both cases, and the maximum yield of furfural was obtained at 30 min in both cases. The yields of 2-HAF obtained at the normal and large scales were 3.50 wt.% and 3.07 wt.%, respectively, and those of 5-HMF were 2.58 wt.% and 2.20 wt.%, respectively. These data indicated that there were no significant differences between the normal- and large-scale yields of 2-HAF and 5-HMF. However, the maximum yield of furfural at the large scale increased slightly in treatment for 30 min. These results showed that the scale-up of the *C. japonica* treatment under the optimum conditions were successful. This process can be used on an industrial scale for the efficient production of furan compounds from lignocellulosics.

Treatment of *C. japonica* with [Py]Cl without Water Addition

C. japonica was treated with [Py]Cl without water addition to investigate the high-temperature production of furan compounds. Figure 6 shows the yields of furan compounds from *C. japonica* obtained by treatment with [Py]Cl at 140 °C, 160 °C, and 180 °C without water addition.

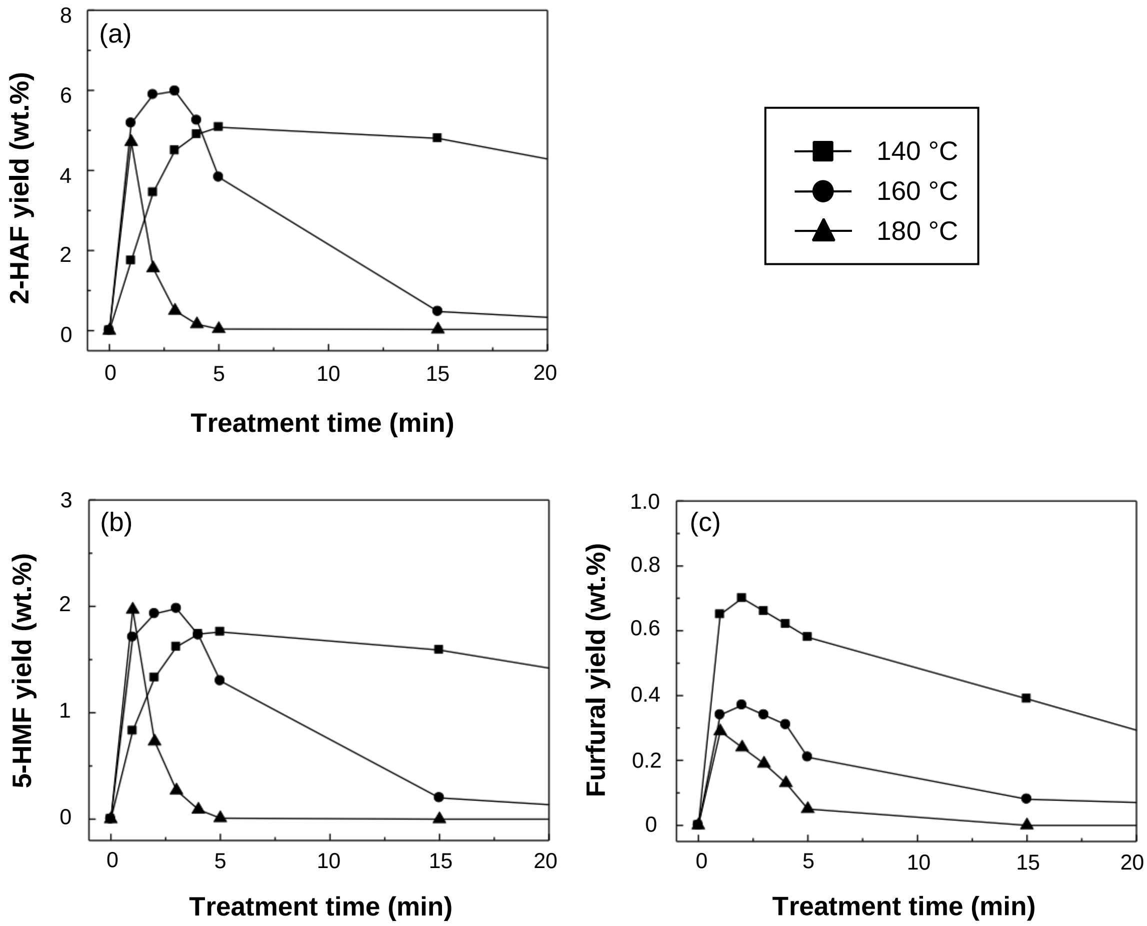

Fig. 6. Yields of (a) 2-HAF, (b) 5-HMF, and (c) furfural obtained by treatment of *C. japonica* with [Py]Cl without water addition

The yields of furan compounds reached a maximum within 10 min at all three temperatures. In the treatment at 180 °C, the maximum yields of 2-HAF, 5-HMF, and furfural were achieved at 1 min, and they were completely transformed into other compounds within 15 min. The yields of 2-HAF and 5-HMF in the treatments at 160 °C and 140 °C reached a maximum at 3 min and 5 min, respectively. 2-HAF and 5-HMF were then gradually converted to other compounds at both temperatures. The results showed that furan compounds were converted to other compounds in [Py]Cl at high temperatures.

Table 1 lists the maximum yields of furan compounds obtained from *C. japonica* by treatment with [Py]Cl-water under the optimum conditions (entry 1) and with [Py]Cl without water addition at various temperatures (entry 2 to entry 4). The maximum yields of 5-HMF and furfural in entry 1 were 2.78 wt.% and 1.58 wt.% respectively, which were the highest yields achieved under any of conditions. The maximum yields of 2-HAF were 5.08 wt.% and 5.98 wt.% obtained by treatment at 140 °C and 160 °C respectively without water addition (entry 2 and entry 3), which were higher than those in entry 1. In terms of the maximum total yield of furan compounds, entry 1 was the highest. Therefore, the most effective treatment conditions for the efficient production of furan compounds were the optimum conditions determined by the above experiments.

Table 1. Maximum Yields of 2-HAF, 5-HMF, Furfural, and Total Yields of Furan Compounds obtained by Treatment of *C. japonica* with [Py]Cl, with or without Water Addition, under Various Conditions

Entry	Water Addition (wt. %) [a]	Temperature (°C)	Time (min)	Yield (wt.%)			
				5-HMF	2-HAF	Furfural	Total [b]
1	10	120	30	2.78	4.88	1.58	9.24
2	0	140	5	1.76	5.08	0.70	7.54
3	0	160	3	1.98	5.98	0.37	8.33
4	0	180	1	1.97	4.71	0.29	6.97

* (a) In [Py]Cl, (b) Total yield of 5-HMF, 2-HAF and furfural.

Treatment of Ball-Milled *C. japonica*

It was reported that about 70% of cellulose was not decomposed by treatment of *C. japonica* with a [Py]Cl-water mixture for 4 h at 120 °C (Yoshioka *et al.* 2016). Cellulose has a strong structure because of its high crystallinity. Therefore, the production of furan compounds from ball-milled *C. japonica* was investigated (Ogawa and Miyafuji 2015), which contained low-crystallinity cellulose (Agarwal *et al.* 2013). Figure 7 shows the yields of furan compounds obtained by treatment of ball-milled *C. japonica* with 90% [Py]Cl and 10% water (w/w) solution for 4 h at 120 °C. The maximum yields of 2-HAF and 5-HMF from ball-milled *C. japonica* were obtained at 1 h. The maximum yields of 2-HAF and 5-HMF from ball-milled *C. japonica*, *i.e.*, 6.33 wt.% and 6.92 wt.%, respectively, were higher than those obtained from *C. japonica* without ball-milling pretreatment (Table 1). Ball-milling increases the degradability of lignocellulosics because it decreases the cellulose crystallinity, molecular weight, and particle size (Chang and Holtzapple 2000; Hendriks and Zeeman 2009; Agarwal *et al.* 2013). Pretreatment of *C. japonica* by ball-milling therefore increased the yields of 2-HAF and 5-HMF. In contrast, the yield of furfural, which is mainly formed from pentoses in hemicelluloses, decreased. The reason for this decrease is not well understood. These results showed that the pretreatment of lignocellulosics by ball-milling was an excellent method for increasing the yields of C6 furan compounds.

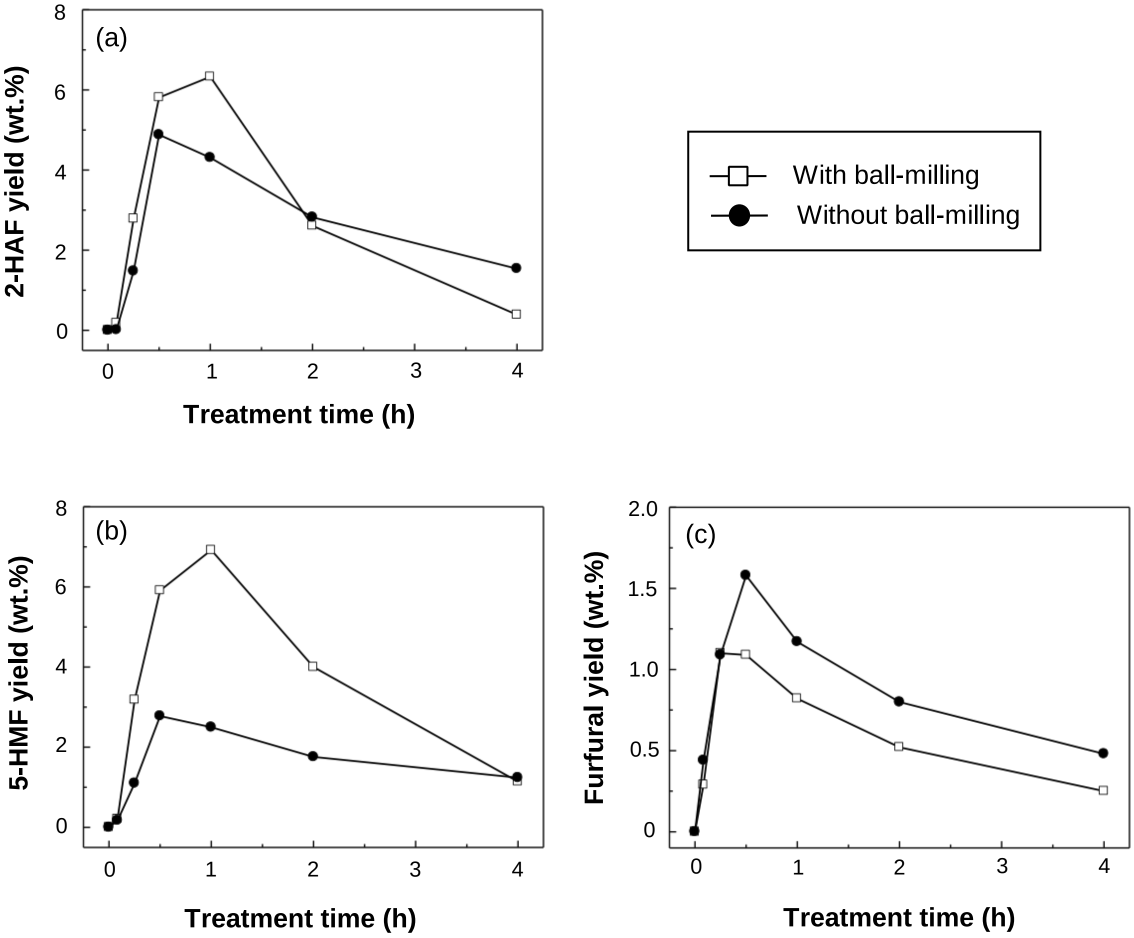

Fig. 7. Yields of (a) 2-HAF, (b) 5-HMF, and (c) furfural obtained by treatment of ball-milled *C. japonica* with 90% [Py]Cl and 10% water (w/w) solution for 4 h at 120 °C

CONCLUSIONS

1. Treatment with 90% pyridinium chloride ([Py]Cl) and 10% water (w/w) solution for 30 min at 120 °C achieved the optimum conditions in terms of the total yield of furan compounds from *C. japonica*. However, the maximum yield of 2-HAF was obtained by treatment with [Py]Cl for 3 min at 160 °C without water.
2. Treatment of *C. japonica* with 90% [Py]Cl and 10% water (w/w) solution under the optimum conditions was successfully scaled up 10-fold.
3. Pretreatment of lignocellulosics by ball-milling effectively increased the production of furan compounds.
4. These systems based on [Py]Cl with/without water addition are useful for efficient production of furan compounds from lignocellulosics. Because the furan compounds are rapidly converted to other compounds in solution, the development of methods for simultaneous production and extraction is needed to enable highly efficient production of furan compounds from lignocellulosics.

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REFERENCES CITED

Agarwal, U. P., Zhu, J. Y., and Ralph, S. A. (2013). "Enzymatic hydrolysis of loblolly pine: Effects of cellulose crystallinity and delignification," *Holzforschung* 67(4), 371-377. DOI: 10.1515/hf-2012-0116

Barry, A. L., Jones, R. N., and Thornsberry, C. (1983). "Cefuroxime, cefamandole, cefoxitin, and cephalothin in vitro susceptibility tests: Reassessment of the 'class representative' concept, confirmation of disk interpretive criteria, and proposed quality control guidelines," *Am. J. Clin. Pathol*. 80(2), 182-189. DOI: 10.1016/S0022-5347(17)50515-7

Brandt, A., Gräsvik, J., Hallett, J. P., and Welton, T. (2013). "Deconstruction of lignocellulosic biomass with ionic liquids," *Green Chem*. 15(3), 550-583. DOI: 10.1039/C2GC36364J

Caes, B. R., Teixeira, R. E., Knapp, K. G., and Raines, R. T. (2015). "Biomass to furanics: Renewable routes to chemicals and fuels," *ACS Sustain. Chem. Eng*. 3(11), 2591-2605. DOI: 10.1021/acssuschemeng.5b00473

Chang, V. S., and Holtzapple, M. T. (2000). "Fundamental factors affecting biomass enzymatic reactivity," *Appl. Biochem. Biotech*. 84(1), 5-37. DOI: 10.1385/ABAB:84-86:1-9:5

Dashtban, M., Gilbert, A., and Fatehi, P. (2014). "Recent advancements in the production of hydroxymethylfurfural," *RSC Adv*. 4(4), 2037-2050. DOI: 10.1039/C3RA45396K

Demir, A. S., Sesenoglu, Ö., Aksoy-Cam, H., Kaya, H., and Aydogan, K. (2003). "Enantioselective synthesis of both enantiomers of 2-amino-2-(2-furyl)ethan-1-ol as a flexible building block for the preparation of serine and azasugars," *Tetrahedron: Asymmetry* 14(10), 1335-1340. DOI: 10.1016/S0957-4166(03)00158-7

Hendriks, A. T. W. M., and Zeeman, G. (2009). "Pretreatments to enhance the digestibility of lignocellulosic biomass," *Bioresource Technol*. 100(1), 10-18. DOI: 10.1016/j.biortech.2008.05.027

Ito, R., Miyafuji, H., Miyazaki, Y., and Kawai, T. (2016). "Production of 5-hydroxymethylfurfural from wood by ionic liquid treatment," *J. Wood Sci*. 62(4), 349-355. DOI: 10.1007/s10086-016-1554-7

Moreau, C., Durand, R., Razigade, S., Duhamet, J., Faugeras, P., Rivalier, P., Ros, P., and Avignon, G. (1996). "Dehydration of fructose to 5-hydroxymethylfurfural over H-mordenitesc," *Appl. Catal. A-Gen*. 145(1-2), 211-224. DOI: 10.1016/0926-860X(96)00136-6

Ogawa, S., and Miyafuji, H. (2015). "Reaction behavior of milled wood lignin in an ionic liquid, 1-ethyl-3-methylimidazolium chloride," *J. Wood Sci*. 61(3), 285-291. DOI: 10.1007/s10086-015-1461-3

Ragauskas, A. J., Williams, C. K., Davison, B. H., Britovsek, G., Cairney, J., Eckert, C. A., Frederick Jr. W. J., Hallett, J. P., Leak, D. J., Liotta, C. L., *et al.* (2006). "The path forward for biofuels and biomaterials," *Science* 311(5760), 484-489. DOI: 10.1126/science.1114736

Ragauskas, A. J., Beckham, G. T., Biddy, M. J., Chandra, R., Chen, F., Davis, M. F., Davison, B. H., Dixon, R. A., Gilna, P., Keller, M., *et al.* (2014). "Lignin valorization: Improving lignin processing in the biorefinery," *Science* 344(6185), 1246843. DOI: 10.1126/science.1246843

Swatloski, R. P., Spear, S. K., Holbrey, J. D., and Rogers, R. D. (2002). "Dissolution of cellose with ionic liquids," *J. Am. Chem. Soc*. 124(18), 4974-4975. DOI: 10.1021/ja025790m

Tadesse, H., and Luque, R. (2011). "Advances on biomass pretreatment using ionic liquids: An overview," *Energ. Environ. Sci*. 4(10), 3913-3929. DOI: 10.1039/C0EE00667J

Trost, B. M., and Yeh, V. S. (2002). "Stereocontrolled synthesis of (+)-boronolide," *Org. Lett*. 4(20), 3513-3516. DOI: 10.1021/ol026665i

Van Putten, R. J., Van Der Waal, J. C., De Jong, E. D., Rasrendra, C. B., Heeres H. J., and De Vries, J. G. (2013). "Hydroxymethylfurfural, a versatile platform chemical made from renewable resources," *Chem. Rev*. 113(3), 1499-1597. DOI: 10.1021/cr300182k

Yang, L., Li, G., Yang, F., Zhang, S. M., Fan, H. X., and Lv, X. N. (2011). "Direct conversion of cellulose to 1-(furan-2-yl)-2-hydroxyethanone in zinc chloride solution under microwave irradiation," *Carbohyd. Res*. 346(14), 2304-2307. DOI: 10.1016/j.carres.2011.07.005

Yokoyama, K., and Miyafuji, H. (2016). "Production of furan compounds from rice straw with ionic liquid treatment," *J. Jpn. Inst. Energy* 95(10), 902-908. DOI: 10.3775/jie.95.902

Yoshioka, K., Yamada, T., Ohno, H., and Miyafuji, H. (2015). "Production of 2-hydroxyacetylfuran from lignocellulosics treated with ionic liquid−water mixtures," *RSC Adv*. 5(88), 72405-72409. DOI: 10.1039/C5RA14205A

Yoshioka, K., Kawazoe, Y., Kanbayashi, T., Yamada, T., Ohno, H., and Miyafuji, H. (2016) "Reaction behavior of *Cryptomeria japonica* treated with pyridinium chloride−water mixture," *RSC Adv*. 6(112), 110964-110969. DOI: 10.1039/C6RA18970A

Zakrzewska, M. E., Bogel-Łukasik, E., and Bogel-Łukasik, R. (2010). "Ionic liquid-mediated formation of 5-hydroxymethylfurfural−A promising biomass-derived building block," *Chem. Rev*. 111(2), 397-417. DOI: 10.1021/cr100171a

Zuo, X., Venkitasubramanian, P., Busch, D. H., and Subramaniam, B. (2016). "Optimization of Co/Mn/Br-catalyzed oxidation of 5-hydroxymethylfurfural to enhance 2,5-furandicarboxylic acid yield and minimize substrate burning," *ACS Sustain. Chem. Eng*. 4(7), 3659-3668. DOI: 10.1021/acssuschemeng.6b00174

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