Carbohydrate Polymers 80 (2010) 1168–1171

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

The study of factors influencing the depolymerisation of cellulose using a solid catalyst in ionic liquids

Hisanori Watanabe *

Kanagawa Environmental Research Center, 1-3-39 Shinomiya, Hiratsuka, Kanagawa 254-0014, Japan

ARTICLE INFO

Article history:
Received 1 December 2009
Received in revised form 15 January 2010
Accepted 20 January 2010
Available online 25 January 2010

Keywords:
Ionic liquid
Cellulose
Solid catalyst
Glucose
Ethanol

ABSTRACT

Cellulose is the most abundant biomass in the world and constitutes a large fraction of plant biomass. The tight hydrogen-bonding network and van der Waals interactions greatly stabilise cellulose, making it notoriously resistant to hydrolysis. Hence, more efficient pre-treatment procedures are required for the conversion of cellulose to monosaccharides. In this study, the depolymerisation of cellulose and wood in ILs using a solid catalyst is performed successfully. Depolymerisation produces three types of substances: total reducing sugar (TRS), glucose and ethanol.

With Avicel, yields of TRS, glucose and ethanol are 76.3% (w/w), 17.2% (w/w) and 4.2% (w/w), respectively. With wood, yields of TRS, glucose and ethanol are 25.6% (w/w), 11.5% (w/w) and 7.7% (w/w), respectively.

The time courses of product yields indicates that the depolymerisation of cellulose in [C_4mim]Cl, using Dowex, is similar to the depolymerisation with concentrated H_2SO_4.

1. Introduction

In the past decade, there has been extensive economic development in developing countries, e.g. BRICs. These developments cause to extinguish numerous fossil fuels and exhaust large amount of greenhouse gas, e.g. carbon dioxide and would elevate surface temperature of earth. The use of renewable energy, especially biomass, instead of fossil fuels would help to address this crisis. Today, many bioethanol plants in which sugarcane and bagasse can be fermented are being constructed.

Cellulose is the most abundant biomass in the world (Ragauskas et al., 2006) and constitutes a large fraction of plant biomass, e.g. wood, wheat bran, straw and cotton. It is a highly crystalline polymer of D-anhydroglucopyranose units joined together in long chains by β-1,4-glycosidic bonds. The tight hydrogen-bonding network and van der Waals interactions greatly stabilise cellulose (Nishiyama, Sugiyama, Chanzy, & Lnagan, 2003), making it notoriously resistant to hydrolysis.

However, yeast produces bioethanol by using only glucose, nor cellulose. Therefore, cellulose must be pre-treated, e.g. degraded using acids or enzymes, to produce bioethanol.

Cellulose gives rise to monomeric glucose after complete hydrolysis with various processes that are catalyzed by mineral acid or enzymes (Zhang & Lynd, 2004). Hence, more efficient pre-treatment procedures are required for the conversion of cellulose to monosaccharides.

Ionic liquids (ILs) that have a cation and anion pair and are liquids under 373 K have been investigated for their use as solvents in organic reactions in recent years (Rogers & Seddon, 2002). Swatloski, Spear, Holbrey, and Rogers (2002) reported that cellulose dissolved in 1-butyl-3-methylimidazolium chloride ([C_4mim]Cl) forms a homogeneous solution. This dissolution might make the cellulose microfibrils accessible to catalysts. Rinaldi, Palkovits, and Schuth (2008) reported that solid catalysts, e.g. Amberlyst 15 DRY, are powerful tools for the hydrolysis of cellulose in IL to produce monosaccharides, disaccharides, reducing sugars, furfural and 5-hydroxymethylfurfural. However, the manner in which other products and factors influence the reaction, e.g. reaction temperature and type of IL, was not shown.

Herein, we demonstrate ethanol production through the hydrolysis of cellulose using a solid catalyst in different ILs and reveal the factors that influence the reaction.

2. Materials and methods

2.1. Material

The cellulose sample Avicel was purchased from Sigma (St. Louis, USA) and was dried under vacuum at 373 K for 24 h before use.

Wood from sugi (*Cryptomeria japonica*), which is one of the most common softwood in Japan, was selected as feedstock. Sugi

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* Tel.: +81 (0) 463 24 3311; fax: +81 (0) 463 24 3300.
E-mail address: watanabe@k-erc.pref.kanagawa.jp.

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doi:10.1016/j.carbpol.2010.01.039

wood was ground with a Wiley mill. The component analysis and characteristics of sugi wood (*Cryptomeria japonica*) were shown in Table 1.

As a solid catalyst, Dowex 50WX8 was purchased from Wako Pure chemical industries, Co. Ltd. (Tokyo, Japan). Ionic liquids were purchased from Kanto chemical Co. Ltd. (Tokyo, Japan) and used without further purification.

2.2. Reaction procedure

Cellulose (0.1 g) in [C_4mim]Cl was heated with stirring at 373 K, ambient pressure until clear solution was formed. To this cellulose solution was quickly added Dowex 50WX8 (0.1 g; water content is 53% (w/w)) and a reactor was capped tightly. The reactor was heated at 373, 383, 393, 403 or 413 K. At different reaction time intervals, samples were withdrawn, quenched with air and poured 9 ml of deionised water. The aqueous solutions were centrifuged at 10,000 rpm for 5 min, subjected to total reducing sugar (TRS), glucose and ethanol analysis.

2.3. Analysis method

The amount of TRS was measured using the DNS method (Li & Zhao, 2007). The glucose concentration was determined using a high-performance liquid chromatograph (Shimadzu LC-9A, Kyoto, Japan) with an shim-pack SCR-101C column, column oven (Shimadzu CTO-6A, Kyoto, Japan) and refractive index detector (Shimadzu RID-10A, Kyoto, Japan).

The ethanol concentration was determined using a gas chromatograph with FID detector (Shimazu GC-15A, Kyoto, Japan) and DB-WAX column.

2.4. Calculation of TRS, glucose and ethanol yields

TRS, glucose and ethanol yields were calculated by the Eqs. (1)–(3), respectively.

$$\text{TRS yield } (\%) = \text{Amount of TRS production (g)}/0.1\ \text{(g)} * 100 \tag{1}$$

$$\text{Glucose yield } (\%) = \text{Amount of glucose production (g)}/0.1\ \text{(g)} * 100 \tag{2}$$

$$\text{Ethanol yield } (\%) = \text{Amount of ethanol production (g)}/0.1\ \text{(g)} * 100. \tag{3}$$

3. Results and discussion

Table 2 summarised glucose and ethanol yields from Avicel and wood (*Cryptomeria japonica*) in different ILs. Maximum glucose and ethanol productions were obtained using [C_4mim]Cl. The highest dissolution rate of cellulose was obtained using [C_4mim]Cl. Glucose and ethanol productions might be related to the dissolution rate of cellulose in each IL. A lesser amount of glucose was obtained from wood than from Avicel.

Table 1
Component composition and chemical analysis of sugi wood used in this study.

Cellulose (wt.%)	Hemicelluloses (wt.%)	Lignin (wt.%)	Ash (wt.%)
(a) Component composition			
43	27	25	0.5

C (wt.%)	H (wt.%)	O (wt.%)	N (wt.%)	S (wt.%)	Cl (wt.%)
(b) Elementary analysis					
51.13	6.44	42.13	0.30	<0.01	<0.01

The two ILs that included the lactate anion yielded less glucose and ethanol than ILs with chloride and bromide. Inter- and intra-D-anhydroglucopyranose hydrogen bonds are formed in crystalline cellulose and these bonds resist dissolution in common solvents, e.g. water, alcohol and benzene. An electron-donating anion, such as chloride, is considered to distort the hydrogen bonds in crystalline cellulose, which is connected to the OH function of D-anhydroglucopyranose. This causes molecular level structural changes in the form of cellulose i.e. from crystalline to amorphous. In contrast, lactate seemed to have a weaker affect on the hydrogen bonds in crystalline cellulose than chloride and bromide. From the above observations it can be suggested that ILs that have a lactate anion resulted in lesser glucose and ethanol production than ILs with a chloride or bromide ion. Glucose yields from Avicel and wood at 373, 383, 393, 403 and 413 K are represented in Fig. 1. Glucose production increased with an increase in reaction temperatures from 373 K to 393 K and decreased with an increase in reaction temperatures from 393 K to 413 K. The highest glucose yield, 17.2% (w/w), was obtained at 393 K from Avicel and 11.5% (w/w) from wood. Wood consists of cellulose, hemicellulose and lignin. Cellulose microfibrils in wood are filled with hemicellulose and lignin. Glucose yields from wood were lower than those from Avicel, which might be because the cellulose component of wood is less accessible to solid catalysts than in Avicel.

The solid catalyst, Dowex 50WX8, is a cation exchanger that contains sulfonic groups. Usually, strong interaction of the sulfonic groups with the imidazolium cation of IL is observed in bulk water. Partial existence of a three-dimensional structure in bulk IL, a hydrogen-bonding network involving the anion and the ring as well as the *n*-alkyl hydrogen atoms, creates a strong hydrophobic interaction between the two *n*-alkyl groups of the imidazolium cations and a unique corrugated sheet structure of the imidazolium rings (Saha, Hayashi, Kobayashi, & Hamaguchi, 2003; Hayashi, Ozawa, & Hamaguchi, 2003). This structure might restrict the mobility of the imidazolium cation of IL. As a result, the ether linkages of carbohydrate polymer dissolved in the ILs could be easily attacked by the sulfonic groups. From the preceding explanation, it appears that the interactions of the sulfonic groups with the imidazolium cation of IL in bulk IL are weaker than those seen in bulk water.

The time courses of TRS produced from Avicel and wood are represented in Fig. 2. These reveal that the TRS yield from Avicel increased with time until 0.5 h and then decreased from 1 h. In contrast, the TRS yield from wood maintained almost the same value at all reaction times. The maximum TRS yields from Avicel and wood were 76% (w/w) and 26% (w/w), respectively. Rinaldi et al. (2008) reported that the TRS from microcrystalline cellulose and wood (spruce) were approximately 27% (w/w) and 23% (w/w) in 5 h, respectively, and Li and Zhao (2007) reported that the TRS from Avicel and spruce were 73% (w/w) and 71% (w/w), respectively. The TRS yield from Avicel reported in this study is higher than the values reported by Rinaldi et al. (2008) and Li and Zhao (2007).

To better understand the solid acid catalyzed hydrolysis of cellulose and wood in [C_4mim]Cl, regression analyses of the experimental data were performed by the non-linear least squares curve fitting method with the Origin 7.0 software. The analyses indicated that the kinetics of Avicel most likely follows a consecutive first-order reaction sequence, where the k_1 for TRS formation and the k_2 for TRS degradation were 0.0875 min^{-1} and 0.007 min^{-1}, respectively. Therefore, according to this study, TRS degradation was slower than TRS formation. Moreover, the k_1 value was higher than the values reported by Li and Zhao (2007).

Table 2
Glucose and ethanol yield from Avicel and wood (*Cryptomeria japonica*) in different ILs. *Reaction conditions* : Avicel (0.1 g, corresponding to approximately 0.62 mmol of anhydroglucose, $C_6H_{10}O_5$) or wood (0.1 g) dissolved in 2 g of IL, Dowex 50WX8 (0.1 g), reaction time is 3 h, reaction temperature is 393 K.

Type of IL	Glucose yield (%)		Ethanol yield (%)	
	Avicel	Wood	Avicel	Wood
1-Ethyl-3-methylimidazolium chloride	9.4	2.7	1.9	<0.5
1-Butyl-3-methylimidazolium chloride	17.2	11.5	4.2	7.7
1-Hexyl-3-methylimidazolium chloride	0.9	1.1	0.6	<0.5
1-Ethyl-3-methylimidazolium bromide	0.5	5.2	<0.5	0.6
1-Ethyl-2,3-dimethylimidazolium bromide	0.9	<0.5	<0.5	<0.5
1-Butyl-2,3-dimethylimidazolium bromide	<0.5	<0.5	<0.5	<0.5
1-Hexyl-3-methylimidazolium bromide	<0.5	3.2	1.0	6.3
1-Hexyl-2,3-diethylimidazolium bromide	0.5	2.9	0.6	0.6
1-Ethyl-3-methylimidazolium L-lactate	<0.5	1.0	<0.5	<0.5
1-Butyl-3-methylimidazolium L-lactate	<0.5	<0.5	<0.5	<0.5
N,*N*-Diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium bis(trifluoromethanesulufonyl)imide	<0.5	<0.5	<0.5	<0.5

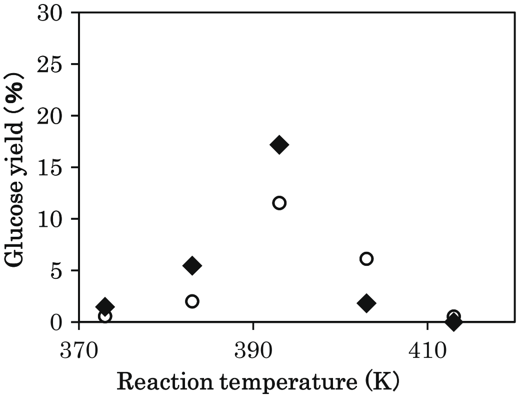

Fig. 1. Glucose yields from ♦ Avicel and ○ wood (*Cryptomeria japonica*) determined by HPLC at 373, 383, 393, 403 and 413 K. *Reaction conditions*: Avicel (0.1 g) or wood (0.1 g) dissolved in 2 g [C_4mim]Cl, Dowex 50WX8 (0.1 g), reaction time is 3 h.

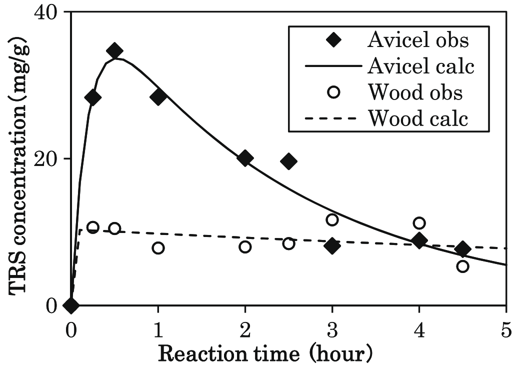

Fig. 2. Time cource of TRS from ♦ Avicel and ○ wood (*Cryptomeria japonica*) determined by DNS assay. *Reaction conditions*: Avicel (0.1 g) or wood (0.1 g) dissolved in 2 g [C_4mim]Cl, Dowex 50WX8 (0.1 g), reaction temperature is 393 K. Regression analysis of the experimental data by non-liner least squares curve fitting with the software Origin 7.0. Time-course of TRS concentration from Avicel (solid line) and wood (dash line) calculated by an equation: TRS concentration = $A*(k_1/(k_1-k_2))*(\exp(-k_2*t)-\exp(-k_1*t))$, where, A: 41.98 (Avicel), 8,239,000 (wood); k_1: 0.0875 (Avicel), 0.00095 (wood) k_2: 0.007 (Avicel), 757.8 (wood).

The cellulose hydrolysis method described in this study is a powerful tool for TRS formation.

The kinetics for wood did not follow a consecutive first-order reaction sequence; k_1 and k_2 were 0.00095 min^{-1} and 757.8 min^{-1}, respectively. Therefore, TRS degradation was faster than TRS formation. Moreover, k_1 for TRS formation from wood was slower than k_1 for TRS formation from Avicel, and k_2 for TRS degradation from wood was faster than k_2 for TRS degradation from Avicel, which might due to the macro and microscale structural differences between Avicel and wood.

The time courses of glucose yields from Avicel and wood are represented in Fig. 3. The results reveal that the glucose yield from Avicel increases with an increase in the reaction time until 2.5 h and then decreases with time from 3 h. The glucose yield from wood increases with an increase in reaction time until 3 h, but which decreases with an increased in reaction time from 4 h. The maximum glucose yield was 27.7% (w/w) from Avicel and 11.5% (w/w) from wood.

The depolymerisation of cellulose with concentrated H_2SO_4 followed a random hydrolysis mechanism, in which both endoglycosidic and exoglycosidic scission occurred, but the endoglycosidic product, oligoglucose, was the major product during the initial hydrolysis stage.

In this study, shorter reaction times favoured TRS yield, and the glucose yield increased with an increase in the reaction time, which suggests that the mechanism of cellulose depolymerisation in [C_4mim]Cl, using Dowex, is similar to the depolymerisation mechanism with concentrated H_2SO_4.

The liquids, which were depolymerized in ILs by using Avicel at each reaction time (0.25, 0.5, 1, 2, 2.5, 3, 4 and 4.5 h), presented brown colors. However, the liquids produced by the depolymerisation of wood with shorter reaction times (0.25, 0.5 and 1 h) were light yellow in color; longer reaction times (2, 2.5, 3, 4 and 4.5 h) gave brown colors. These color differences suggest that the reaction with wood was more difficult than that with Avicel.

Wood is composed of cellulose, hemicellulose and lignin. Hemicellulose and lignin are filled between the cellulose microfibrils. The glucose yield from wood was less than that from Avicel, which

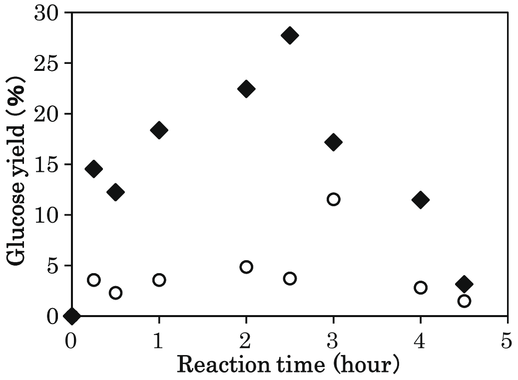

Fig. 3. Time courses of glucose yield from ♦ Avicel and ○ wood (*Cryptomeria japonica*) determined by HPLC. *Reaction conditions*: Avicel (0.1 g) or wood (0.1 g) dissolved in 2 g [C_4mim]Cl, Dowex 50WX8 (0.1 g), reaction temperature is 393 K.

might be because the cellulose in wood is less accessible to solid catalysts than that in Avicel.

Rinaldi et al. (2008) reported that approximately 3% (w/w) mono- and disaccharides were produced from α-cellulose. Li and Zhao (2007) reported that 39% (w/w) glucose was produced from Avicel and 36% (w/w) from spruce. The glucose production in this study is higher than the mono- and disaccharides reported by Rinaldi et al. (2008) and smaller than the values reported by Li and Zhao (2007). Therefore, the depolymerisation of cellulose and wood in ILs using a solid catalyst, as performed in this study, would be more suitable for TRS formation rather than glucose formation.

4. Conclusion

Depolymerisation of cellulose in ILs using Dowex produces three types of substances: total reducing sugar (TRS), glucose and ethanol.

With Avicel, yields of TRS, glucose and ethanol were 76.3% (w/w), 17.2% (w/w) and 4.2% (w/w), respectively. With wood, yields of TRS, glucose and ethanol were 25.6% (w/w), 11.5% (w/w) and 7.7% (w/w), respectively.

Shorter reaction times favoured TRS yield and glucose yield increased with an increase in the reaction times, which indicates that the depolymerisation of cellulose in [C_4mim]Cl, using Dowex, is similar to the depolymerisation with concentrated H_2SO_4.

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