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Production of furfural and cellulose from barley straw using acidified zinc chloride

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Abstract−An effective fractionation process was sought to produce furfural and cellulose-rich solid from barley straw. Acidified zinc chloride ($ZnCl_2$) was used as a catalyst in order to achieve hemicellulose recovery in the form of liquid hydrolysate. This fractionation process recovered 55.6% of XM (xylan and mannan) in the untreated barley straw under best reaction conditions (10% acidified $ZnCl_2$, 150 °C, 30 min, and 1/15 of S/L ratio). Hemicellulose hydrolysate was converted into furfural using hydrothermal reaction without additional catalyst. The furfural conversion yield at various reaction temperatures (150, 180, and 210 °C) was in the range of 59.9-64.5%. The two parameters that affected performance in fractionation processing were reaction temperature and time. Reaction severity (Log R_0) was used to evaluate the effects of two processing parameters on hemicellulose recovery. In the $ZnCl_2$ treatment, the data indicated that the proper range of severity was 2.95-3.07 because the XM recovery yield decreased as the reaction condition became more severe beyond that point.

Key words: Barley Straw, Fractionation, Severity Factor, $ZnCl_2$, Hemicellulose

INTRODUCTION

The conversion of lignocellulosic biomass to biofuels and chemicals can be achieved by various chemical or biological methods. Lignocellulosic biomass is comprised primarily of cellulose, hemicellulose, lignin, and others. Cellulose and hemicellulose portions in lignocellulosic biomass are carbohydrates, which can be converted into fuels and chemicals by fermentation. To produce fuels and chemicals from lignocellulosic biomass, cellulose and hemicellulose in this feedstock should be hydrolyzed to produce various monomeric sugars (fermentable sugars) either by acid or enzymes. The acid hydrolysis of lignocellulosic biomass can degrade cellulose and hemicellulose into monomeric sugars without pretreatment. However, the acid used in processing biomass must be recovered for environmental and economical reasons. It has been challenging to develop a low-cost acid recovery process to meet these needs [1,2]. Therefore, biological conversion is currently being accepted as a reasonable way to produce biofuels and chemicals.

In general, the pretreatment of lignocellulosic biomass is a necessary step prior to enzymatic saccharification and sugar fermentation (cellulose and hemicellulose). Various pretreatment methods and strategies using different catalysts and process schemes have been suggested for the utilization of lignocellulosic biomass. Pretreatment strategies can be divided into two types: one that increases the accessibility of cellulose and hemicellulose to enzyme without significant fractionation or constituent destruction, and another that separates or depolymerizes certain component(s) significantly and, as a result, increases the total conversion yield of each component. In general, the former concept is called "pretreatment" and the latter is called "fractionation." Many pretreatment methods cannot be clearly defined by these two terms and a large number of pretreatment methods have more or less both pretreatment and fractionation effects.

The biorefinery concept has been generally accepted as an alternative to the conventional petroleum industry, which can produce fuels, power, and chemicals from biomass in the same way that today's petroleum refineries produce various fuels and multiple products from petroleum [3-6]. In line with the biorefinery concept, the fractionation of biomass, followed by the conversion of each intermediate product stream, fits well into a biorefinery concept so that multiple products can be produced from biomass constituents including sugars (cellulose and hemicellulose; carbohydrates), lignin (hydrocarbons), protein, and so on. In other words, the fractionation of lignocellulosic biomass into its three main constituents, namely cellulose, hemicellulose, and lignin, before downstream processing, is one of the most effective ways to enhance the total utilization of lignocellulosic biomass because early separation of components which are not related to the conversion reaction directly can improve total processing efficiencies and yields.

The development of an effective fractionation method could be beneficial not only in producing biofuels such as ethanol but also in generating other valuable bio-based chemicals from carbohydrates and lignin. An effective fractionation method of lignocellulosic biomass is called for to enhance the economics in biomass refining; for example, lignin can be a valuable by-product that has relevant extensiveness as a co-product in the future biorefinery industries [7]. To date, various methods using various chemicals have been suggested for the fractionation and pretreatment of lignocellulosic materials [8-10]. Although a few of them may be effective, they have encountered a problem with low xylan purity and recovery

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yield in liquid hydrolysate due to low selectivity for xylan solubilization and consequently contamination by soluble lignin. In this study, a fractionation method using $ZnCl_2$ is investigated to separate hemicellulose (mainly xylan) and to produce furfural from xylan subsequently. $ZnCl_2$ is chosen because it has many desirable characteristics as a fractionation reagent. It is an effective swelling chemical reagent for cellulose and $ZnCl_2$ is a salt that has high selectivity for hemicellulose solubilization [11]. At an elevated temperature, zinc ions can react with cellulose to form zinc-cellulose complex, which is more susceptible to enzymatic hydrolysis [12]. Acidified $ZnCl_2$ can be an effective catalyst to maximize furfural production because it creates a low-pH hemicellulose hydrolysate after reaction [13]. Zinc chloride can expose the crystalline cellulose core by separating the hemicellulose from the biomass [13,14]. After $ZnCl_2$ treatment, most cellulose and lignin are retained in the solids, and the cellulose could then be converted into ethanol by fermentation. On the other hand, solubilized hemicellulose in the liquid hydrolysate at low pH could then be directly converted to furfural at a high temperature (150-190 °C). Furfural is a high-value building block for the production of fibers, pharmaceuticals, plastic resins, food additives, fuel additives, and so on.

We performed fractionation experiments to separate hemicellulose using acidified zinc chloride. The reaction conditions for hemicellulose separation, such as zinc chloride concentrations, reaction temperature, reaction time, and solid/liquid ratio, were investigated. Furfural production tests from solubilized hemicellulose without additional chemical were also conducted and reported.

MATERIALS AND METHODS

1. Barley Straw

The barley straw was provided by the Bioenergy Crop Research Center, National Institute of Crop Science (NICS), and Rural Department Administration (RDA) located in Muan, Jeollanamdo, Korea. The barley straw was ground using a laboratory blend mill (Blender 7012s, Waring Commercial, CT, USA) and then sieved to a nominal size of 14-45 mesh. The ground barley straw was dried at 45± 5 °C for 24 h. The average moisture content of ground barley straw was determined to be 5.2%. The initial composition of the barley straw, as determined by the National Renewable Energy Laboratory (NREL, Golden, CO) -Laboratory Analytical Procedure (LAP [15,16]), is shown in Table 1.

Table 1. Initial composition of barley straw

Components	Dry solids (%, w/w)
Glucan	38.0
Xylan	16.5
Mannan	3.3
Arabinan	2.1
Acid insoluble lignin	18.3
Acid soluble lignin	2.0
Extractives (by water)	17.7
Extractives (by ethanol)	2.2
Ash	1.0
Crude protein	2.8
Subtotal	103.9

Note: The data in the table show the mean value (n=3, SD<0.4, SD: standard deviation)

All numbers in the table are based on the oven-dry biomass

2. Batch Reaction and Experimental Design

The batch reactor (bomb reactor) for the $ZnCl_2$ treatment was constructed from 316 stainless steel tubes (1.0 cm internal diameter [ID]×20.0 cm length [L]; 15.7 cm^3 internal volume). The tubes were sealed with 316 stainless steel caps (Swagelok Cat. #SS-810-C). High temperature molded transition junction style thermocouple probes (Omega.com®, Cat. #HJMTSS-125-6) were installed inside the reactor to monitor the reaction temperature.

For the $ZnCl_2$ treatment, two different $ZnCl_2$ concentrations were tested-solutions of 5.0% $ZnCl_2$ with 0.06% hydrochloric acid (HCl) and 10.0% $ZnCl_2$ with 0.12% HCl. Six-tenth gram (based on oven dried weight) of barley straw was packed into the bomb reactor. The bomb reactor was heated by using two separate baths: the first bath for rapid preheating was set at 240 °C using molten salt, which was higher than the target temperature, and the second bath was set at target temperature. To elevate the reactor temperature, the reactor was submerged into the first bath. When the reactor temperature reached the desired reaction temperature (150-190 °C), the reactor was transferred to the second bath (silicone oil). This system can elevate the reactor temperature to the target temperature in about 1.5 min. Placement of reactor into the second heating bath is considered as reaction time zero and preheating time is not included in the reaction time. After the completion of the reaction, the reactor was immediately transferred to an iced water bath, quenching the reaction for 10 min. Solid and liquid were removed and recovered from the reactor, which were subjected to a filtration. Treated solid residues were collected and washed with DI-water and dried at 45 °C for 24 h. All liquids and solids were analyzed for carbohydrates and lignin content according to NREL-LAP [16,17].

3. Furfural Production

Hemicellulose (XM) hydrolysate was prepared in the $ZnCl_2$ treatment, which was used for the furfural production test. The treatment conditions were as follows: 10.0% acidified $ZnCl_2$, 1/15 of solid/liquid ratio, 150 °C of reaction temperature, and 40 min reaction time. The furfural production experiments were performed using a stainless steel batch reactor. The furfural production experiments were at three different reaction temperatures (150, 180, and 210 °C) for 5 min-180 min. In each experiment, 10.0 ml of hemicellulose hydrolysate (2.6 g/*l* glucan, 8.1 g/*l* XM, 1.3 g/*l* arabinan) was loaded in the aforementioned batch type reactor. A temperature-programmable GC oven controlled the reaction temperature. The reactor was placed in a GC oven for preheating to the desired reaction temperature and kept at a constant reaction temperature. The preheating step took 10 min and was not counted toward the reaction time. After the reaction, the reactor was immediately transferred into ice water and allowed to cool for 5 min to stop the reaction. The reacted liquid products were analyzed to quantify the sugars and furfural in the product following the NREL-LAP [17].

4. Analytical Methods

The solid and liquid samples, such as the treated and untreated barley straw, and the liquid hydrolysate were analyzed for carbohydrates (sugars) and lignin contents following the NREL LAP [14]. Each was analyzed in duplicate. The carbohydrate compounds were

Table 2. Reaction severities vs. conditions and reactions

Reaction conditions			Log R_0 [-]	Reaction conditions			Log R_0 [-]
Temperature [°C]	$ZnCl_2$ conc. [%]	Reaction time [min]		Temperature [°C]	$ZnCl_2$ conc. [%]	Reaction time [min]	
150	5	10	2.47	150	10	10	2.47
		20	2.77			20	2.77
		30	2.95			30	2.95
		40	3.07			40	3.07
160	5	10	2.77	160	10	10	2.77
		20	3.07			20	3.07
		30	3.24			30	3.24
		40	3.37			40	3.37
170	5	5	2.76	170	10	5	2.76
		10	3.06			10	3.06
		20	3.36			20	3.36
180	5	3	2.83	180	10	3	2.83
		5	3.05			5	3.05
		10	3.36			10	3.36
190	5	3	3.13	190	10	3	3.13
		5	3.35			5	3.35
		10	3.65			10	3.65

determined by HPLC (high performance liquid chromatography; Bio-Rad Aminex HPX-87H & 87P column) and Cation H micro-guard cartridge (30 mm×4.6 mm) equipped with a refractive index detector (Waters 2414, Waters Co., Milford, MA, USA). The carbohydrate content in the liquid samples was determined by secondary acid hydrolysis (4% H_2SO_4, 121 °C, 1 h). The Bio-Rad Aminex HPX-87H column allows the analysis for sugars, organic acids, and other degradation products; however, this column does not distinguish between xylose, mannose, and galactose, which are generally reported as the aggregate XMG (since there is no galactose, it is reported as XM in this study).

5. Reaction Severity Factor

The two parameters that determine reaction severity are reaction temperature and reaction time. The conditions used include five different reaction temperatures (150, 160, 170, 180, and 190 °C) and five different reaction times (5, 10, 20, 30, and 40 min). The concept of reaction severity, which combines residence time and temperature, is often used in biomass research. The severity factor is defined by Overend and Chormet (1987) [18]:

$$\text{Log } R_0 = \text{Log}\left[t \times \text{Exp}\frac{(T-100)}{14.75}\right] \tag{1}$$

where t is time (min), T is the temperature (°C), and 14.75 is an empirical parameter related with activation energy and temperature. The severity conditions for these parameters vary from R_0=296.1 to R_0=13398.4. The broad categories of low, medium, and high severities are determined using the log of the severity function (Log R_0). These broad categories are defined as having the following Log R_0: low (2.47-2.95), medium (3.06-3.46), and high (3.53-4.13). Log R_0 is used to predict the trend of sugar and decomposition product yield through the regression of experimental data.

In this study, two different $ZnCl_2$ concentrations (5% and 10%) keeping 0.06 of $HCl/ZnCl_2$ ratio (i.e., 0.06 and 0.12% hydrochloric acid (HCl), respectively) were tested and these $ZnCl_2$ solutions have hydrochloric acid concentrations, which can result in a pH change. To include the effect of acidification, the combined severity factor has been suggested to be used [19]:

$$\text{Log CSF} = \text{Log } R_0 - \text{pH} \tag{2}$$

CSF is the combined severity factor. However, increasing $ZnCl_2$ concentrations from 5% to 10% in this study does not increase the HCl concentration substantially. In other words, the pH difference between two solutions is marginal. Therefore, a severity factor without pH term is used (Eq. (1)). Table 2 summarizes reaction conditions tested in this study and their reaction severities.

6. Purity and Selectivity

To quantitatively evaluate the fractionation effects of various reaction conditions on XM, the purity and selectivity of XM components are adopted and modified as follows [20,21]:

$$\text{XM purity } (P_X) = \frac{\text{XM [g] in liquid}}{(\text{Glucan} + \text{XM} + \text{Lignin [g] in liquid hydrolyzate})} \times 100 \tag{3}$$

$$\text{XM selectivity } (S_X) = \frac{m_{XM}}{m_{Lignin}} \tag{4}$$

Where, m_{XM} and m_{Lignin} are the mass loss rate of XM and lignin from the solid.

RESULTS AND DISCUSSION

1. Fractionation of Barley Straw Using $ZnCl_2$

1-1. Effect of Reaction Time and Temperature on Sugar Recovery

Fig. 1 presents the effects of reaction time and temperature on XM recovery. Five different temperatures (150, 160, 170, 180, and 190 °C) with two different $ZnCl_2$ concentrations (5% and 10%) are

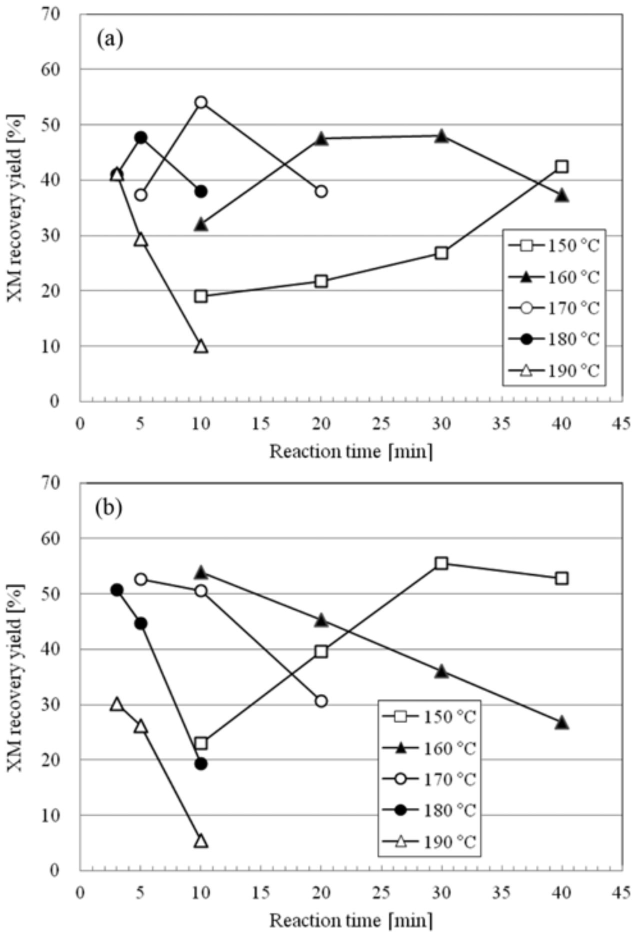

Fig. 1. Effect of reaction time and reaction conditions on XM (xylan+mannan) recovery yield in $ZnCl_2$ treatment with different reaction conditions: (a) 5 wt% $ZnCl_2$, S : L=1 : 15; (b) 10 wt% $ZnCl_2$, S : L=1 : 15.

compared with extended reaction time (3-40 min). The XM recovery yields with 5% and 10% acidified $ZnCl_2$ are shown in Fig. 1(a) and (b), respectively.

In case of 5% $ZnCl_2$ treatment at 150 °C (Fig. 1(a)), XM recovery yields increase gradually as reaction time increases from 5 min to 40 min, while XM recovery yields with $ZnCl_2$ treatment at 190 °C decrease rapidly to 10.2% within 10 min of reaction time. As reaction time and acidified $ZnCl_2$ concentration increase, the hemicellulose (XM) released into liquid may undergo degradation reactions at high temperatures. The same phenomenon is also observed in the ensuing experiments with 10% $ZnCl_2$. From 160-180 °C, the same trends occur: XM recovery yields increase to a certain temperature and then decrease as reaction time increases. The $ZnCl_2$ treatments at 150, 160, and 170 °C reach the maximum yields within 20, 10, and 5 min, respectively. Among them, the highest yield (54.1%) is observed with a reaction at 170 °C for 10 min.

In the case of 10% $ZnCl_2$ treatment at 150 °C (Fig. 1(b)), it is slightly different from the 5% $ZnCl_2$ treatment. The XM recovery yields increase gradually as reaction time increases from 5 min to 30 min, reach the maximum (55.6%), and then decrease. Overall, with 10% $ZnCl_2$ treatments at higher temperatures (160-190 °C), XM recovery is decreased as the reaction time increases. Among them, the lowest XM recovery yield (5.4%) is obtained with a 190 °C reaction temperature.

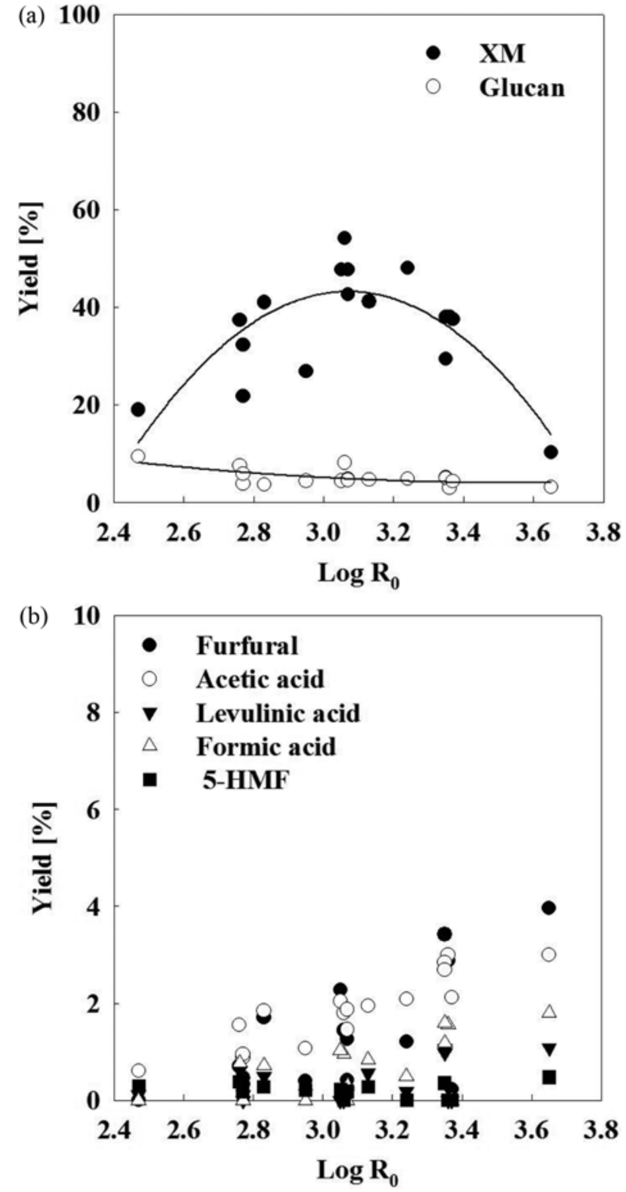

Fig. 2. Effect of reaction severity on (a) XM (xylan+mannan) and glucan yield (b) by-product yield in 5.0 wt% $ZnCl_2$ treatment.

1-2. Reaction Severity and Sugar Recovery in Liquid Hydrolysate

We investigated the influence of fractionation severity on yield of sugar and major degradation products. Comparisons of sugar yields and decomposed product yields obtained from different fractionation conditions were simplified with the use of the severity factor, Log R_0, which combines reaction time and temperature into one variable. Since the hemicellulose sugar fraction in the liquid hydrolysate is predominantly composed of xylan and mannan only, the XM yield is mainly presented in this study.

The effects of severity (Log R_0) on XM and glucan recovery yields in the liquid hydrolysates following fractionation using 5% $ZnCl_2$ solution are presented in Fig. 2(a). In this comparison, 16 different liquid samples containing different quantities of sugars are analyzed by the NREL-LAP method [15], and the yields for glucan and XM concentrations are plotted against Log R_0. As shown in Fig. 2(a), the XM recovery yields in hydrolysates increase as Log R_0 increases to 3.06, and then xm recovery yields decrease with higher severity. Solubilization of glucan is not significant with all tested conditions, which is in the range of 2.9-9.4%. The highest XM recovery yield (54.1%) is obtained at Log R_0=3.06 and glucan yield at this point is 8.2%. Fig. 2(b) presents the productions of various by-products formed during the hemicellulose solubilization in the 5% $ZnCl_2$ treatment. At certain severe reaction conditions with an acid catalyst, it is reported that some of the liberated sugars undergo dehydration to form furfural from the pentoses and 5-hydroxymethylfurfural (HMF) from the hexoses. Furfural and 5-HMF can be further converted into formic acid and levulinic acid, respectively. This result agrees well with the analysis results reported by Weiss et al. and Um and van Walsum [22,23]. In Fig. 2(b), concentrations of formic acid, acetic acid, and furfural increase as Log R_0 increases, while concentrations of 5-HMF remain at a low level. Among degradation products, furfural production is most rapid and high with increasing Log R_0 and acetic acid is the second. At Log R_0=3.06, furfural and acetic acid productions are 0.96 g/*l* and 1.20 g/*l*, respectively.

Fig. 3(a) presents the effects of severity (Log R_0) on XM and glucan recovery yields in the liquid hydrolysates following fractionation using 10% $ZnCl_2$ solution. Seventeen different conditions are tested and compared in terms of the glucan and XM recovery yields. We have observed a similar trend with Fig. 2, but the maximum xylan recovery (55.6%) is achieved with relatively low Log R_0, which is at Log R_0=2.95. At this point, glucan solubilization also occurs but it is substantially lower (5.7%) than that of xylan. Fig. 3(b) also presents the production of various by-products formed during the reaction in Fig. 3(a). As the reaction conditions become more severe beyond Log R_0=2.95, XM recovery yield decreases and it drops to 5.4% at

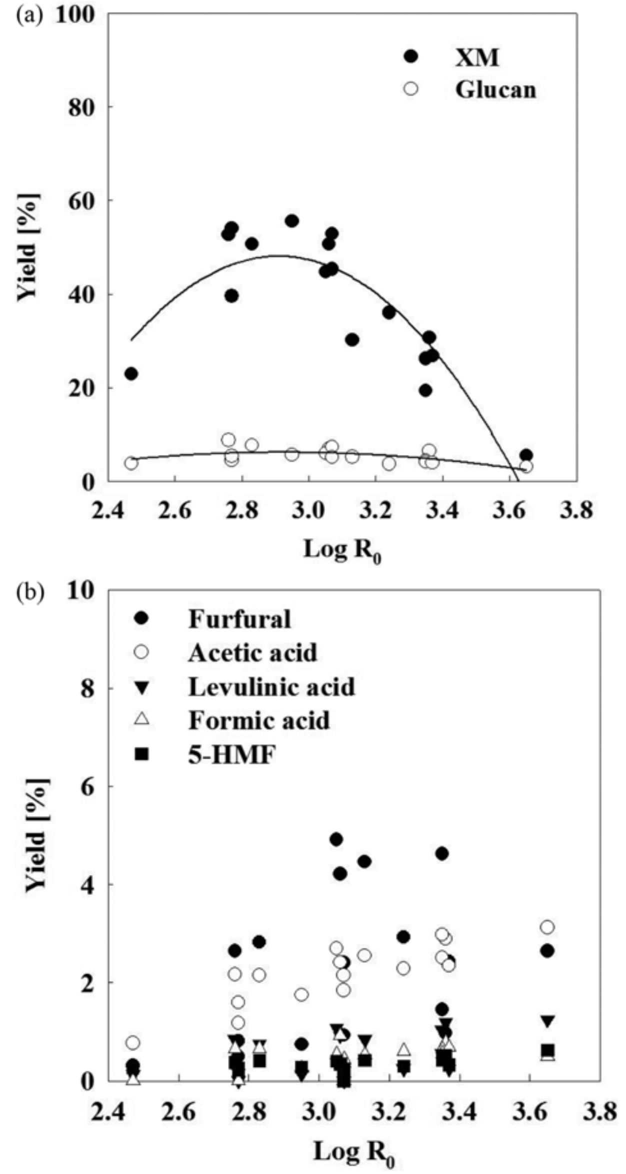

Fig. 3. Effect of reaction severity on (a) XM (xylan+mannan) and glucan yield (b) by-product yield in 10.0 wt% $ZnCl_2$ treatment.

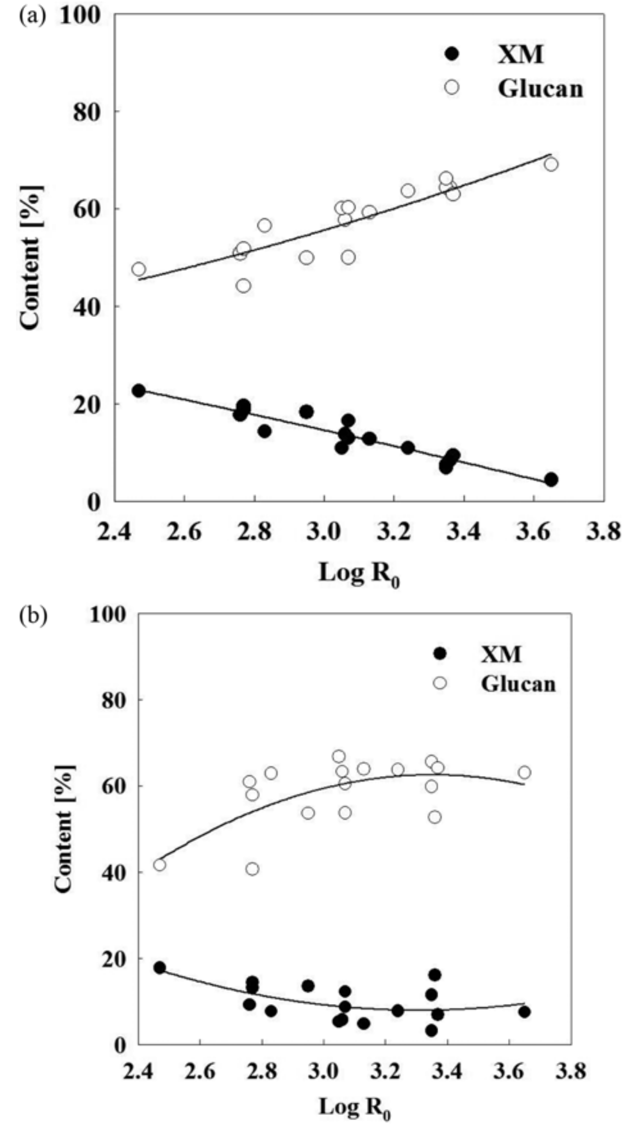

Fig. 4. Effect of reaction severity on composition in the $ZnCl_2$ treated solids: (a) 5.0 wt% $ZnCl_2$ treatment (b) 10.0 wt% $ZnCl_2$ treatment.

Log R_0=3.65. Compared to Fig. 2(b), more furfural and acetic acid formation is observed in the reaction using 10% $ZnCl_2$. The highest furfural production (4.9% based on untreated biomass weight) is observed when the Log R_0 value is 3.37 and then it decreases to 2.7%. At this point, 3.12% acetic acid yield is obtained.

1-3. Reaction Severity and Sugar Remaining in Residual Solid

Glucan and XM contents in the residual solids are also analyzed and presented in Fig. 4. Figs. 4(a) and 4(b) show glucan and XM content in the residual solids after 5% and 10% acidified $ZnCl_2$ treatments, respectively.

As reaction severity increases from 2.47 to 3.65, all tested samples contain more glucan and less XM content (Fig. 4(a) and (b)). In case of 5% $ZnCl_2$ treatments, Fig. 4(a) indicates that increasing severe reaction conditions gradually increases glucan content from 44.1% to 69.1% and decreases XM content from 22.6% to 3.2% in the remaining solids. This is due to the solubilization of hemicellulose during the treatment. In the treatment of barley straw using 10% $ZnCl_2$, a similar trend is observed in the reaction severity range of 2.47 to 3.07; however, this trend changes in the 3.07-3.65 range (Fig. 4(b)). The highest glucan content (66.8%) observed at the Log R_0 value is 3.05, and glucan content at higher reaction severities is almost the same. A similar trend is observed for XM content in the residual solids. It is speculated that hemicellulose (XM) solubilization generally occurs first and then severe reaction conditions such as high reaction temperature and longer reaction time affect glucan in the solid. This result indicates that treatment using 10% $ZnCl_2$ can reduce the reaction time and lower the reaction temperature, but in order to calculate the economics in $ZnCl_2$, recovery or recycling cost should be considered.

1-4. Mass Balance, Purity (P_X), and Selectivity (S_X)

Table 3 summarizes the compositions in the pretreated solids and liquids with their EMB (extraction mass balance) for the selected samples. To compare the effects of $ZnCl_2$ treatment with the simple treatment with no zinc chloride addition, barley straw was treated using hot-water at the same conditions. The EMB values are calculated in order to confirm the composition analysis results. For all treated samples with acidified $ZnCl_2$ solution and without $ZnCl_2$, the EMB values for both glucan and XM are in the range of 95.3-100.1% and 91.1-105.4%, respectively, which is close to 100%. This indicates that sugar analyses are performed properly and the results are reliable.

To utilize biomass-derived sugar effectively, separation of each component with high purity is essential. For maximum recovery of XM with minimal contamination by soluble lignin, the XM recovery/removal and lignin retention are two major factors in the study. To evaluate these two factors more quantitatively, we introduced the selectivity (S_X) and purity (P_X) for XM. As defined in the Eq. (4), S_X is the ratio of the XM removal reaction over lignin removal reaction. P_X and S_X data are summarized in Table 3. For $ZnCl_2$ treatment, P_X decreased (75.1→70.5) as the Log R_0 increased, while S_X decreased (6.4→5.4) first, and then increased; $ZnCl_2$ treatment with Log R_0=3.06 resulted in the highest value (6.7). Log R_0=2.77 was the best reaction condition in terms of the P_X. On the other hand, hot-water treatment without zinc chloride was not effective to solubilize XM effectively, which resulted in P_X and S_X values in the range of 24.0-26.7 and 0.2-0.3, respectively. This result indicated that $ZnCl_2$ treatment is highly selectivity for XM removal, which resulted in high recovery yield with high purity compared to those of hot-water treatment.

2. Furfural Production from Hydrolysate

Hemicellulose hydrolysate is prepared using acidified 10.0% $ZnCl_2$. This hydrolysate contains 2.6 g/*l* glucan, 8.1 g/*l* XM, and 1.3 g/*l* arabinan, which is subjected to the furfural production test. In this process, acidified $ZnCl_2$ is used as the solvent and the hydrolysates

Table 3. Mass balance, P_X, and S_X in $ZnCl_2$ treatment and hot-water treatment

No	Conditions[a]	Treatment[b]	Sample	Solid remaining [%]	Solid [%]		Liquid [%]		XM[c] purity (P_X)	XM selectivity (S_X)	EMB[d] [%]	
					Glucan	XM[c]	Glucan	XM			Glucan	XM
-	-		Untreated	100	38	19.8	-	-	-	-	-	-
1	Log R_0=2.95	$ZnCl_2$	Pretreated	64.7	53.6	13.5	2.1	11.0	72.2	5.3	96.8	99.8
			Pretreated[e]		34.7	8.8						
		Without $ZnCl_2$	Pretreated	72.1	48.5	25.6	1.0	2.4	26.7	0.2	94.5	105.4
			Pretreated[e]		34.9	18.5						
2	Log R_0=2.77	$ZnCl_2$	Pretreated	61.5	57.9	14.4	2.1	10.7	75.1	6.4	95.3	99.2
			Pretreated[e]		35.6	8.9						
		Without $ZnCl_2$	Pretreated	72.9	46.1	24.9	1.0	2.2	25.6	0.3	91.1	102.9
			Pretreated[e]		33.6	18.2						
3	Log R_0=3.06	$ZnCl_2$	Pretreated	61.0	57.6	13.7	3.1	10.7	70.5	6.7	100.1	96.3
			Pretreated[e]		35.2	8.36						
		Without $ZnCl_2$	Pretreated	75.2	46.0	24.8	1.0	2.3	24.0	0.2	93.7	105.4
			Pretreated[e]		34.6	18.6						

[a] Pretreatment conditions: 1: 150 °C, 10.0% (w/v) $ZnCl_2$, 30 min; 2: 160 °C, 10.0% (w/v) $ZnCl_2$, 10 min; 3: 170 °C, 5.0% (w/v) $ZnCl_2$, 10 min

[b] $ZnCl_2$: treatment using acidified zinc chloride solution; Without $ZnCl_2$: treatment using hot-water without zinc chloride

[d] Extraction mass balance (EMB)=($\Sigma C_{Li}+\Sigma C_{Si}$)/($\Sigma C_{Ri}$); where Ci is the mass of each sugar component as C_{Li} determined through HPLC chromatography. The subscripts L, S, and R refer to the extracted liquid, fractionated solids, and raw straw fractions, respectively

[e] Data are based on the oven-dry untreated biomass

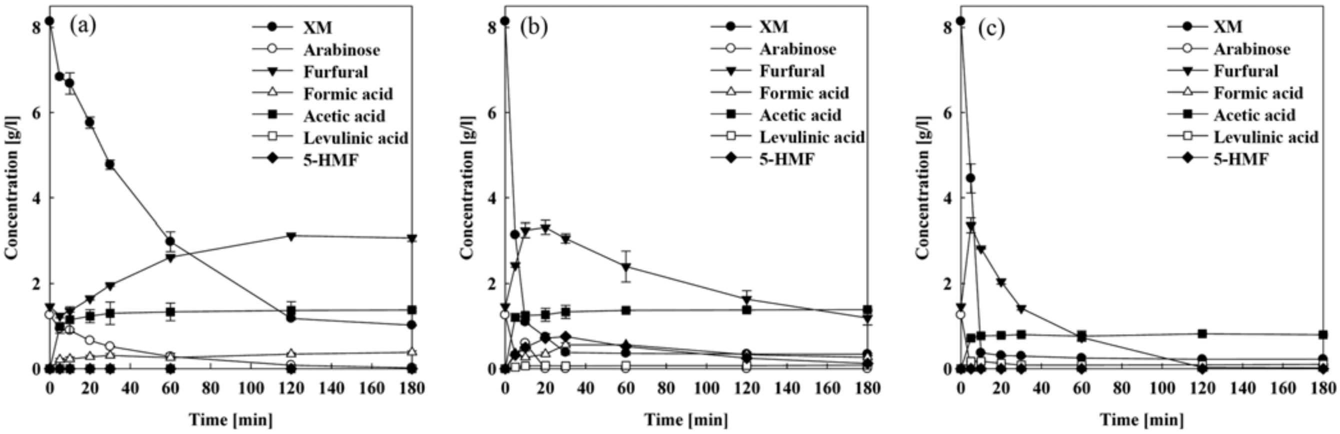

Fig. 5. Furfural production from hemicellulose hydrolysate at various reaction temperatures: (a) 150 °C (b) 180 °C and (c) 210 °C. Hemicellulose preparation conditions=150 °C, 10% $ZnCl_2$, and 30 min.

already contain 0.12% HCl; therefore, no additional catalyst is added.

Fig. 5 shows the furfural, XM, and arabinose concentration profiles in the liquid products at various reaction temperatures (150, 180, and 210 °C). Overall, the XM and arabinan concentrations decrease as the reaction time increases, while the reaction time to obtain the highest furfural concentration is different at each reaction temperature (150, 180, and 210 °C). The highest furfural conversion yield at each reaction temperature is in the range of 59.9-64.5%. With a 150 °C reaction, as the xylose and arabinose concentrations drop, the furfural concentration increases and reaches its highest concentration (59.9%) at approximately 120 min (Fig. 5(a)).

At 180 °C and 210 °C, the furfural conversion occurs within 10 min and 20 min, respectively, which is much faster than at 150 °C (Fig. 5(b) and (c)). However, the furfural production reaches a maximum, and then it gradually decreases. It is speculated that this phenomenon occurs because the pentose sugars are degraded to furfural, and further degradation could occur to form other degradation products such as levulinic acid, formaldehydes, furan, and formic acid [24,25]. The highest furfural conversion yields at the three different temperatures are 59.9%, 63.9%, and 64.5%, respectively.

CONCLUSION

The fractionation of barley straw using acidified $ZnCl_2$ solution is highly effective in recovering hemicellulose in biomass, resulting in a hemicellulose-rich hydrolysate and a cellulose-rich solid fraction. The celluloses in treated solids can be effectively converted into ethanol or other chemicals. The hemicellulose in the liquid hydrolysates is used as a source of furfural production with a maximum of 64.5% for the furfural yield. Furfural can be recovered by steam distillation, followed by water-furfural separation and purification. The proposed fractionation method using an acidified $ZnCl_2$ as a catalyst can serve as an effective recovery method for furfural from the $ZnCl_2$-furfural mixture. In addition to furfural recovery, recycling and purification methods for $ZnCl_2$ in the process should be developed in future studies. Improved utilization of biomass can be achieved through the proposed process because of the efficient recovery yield of each component and simple production of value-added chemical from hemicellulose hydrolysate.

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