Furfural production from hydrolysate of barley straw after dilute sulfuric acid pretreatment

Sung Bong Kim, Ja Hyun Lee, Xiaoguang Yang, Jiwon Lee, and Seung Wook Kim[†]

Department of Chemical and Biological Engineering, Korea University, Anam-dong, Sungbuk-gu, Seoul 136-701, Korea

Abstract−Lignocellulosic biomass contains various fermentable sugars and versatile compounds, and should be isolated selectively. In this study, a two step process for furfural production is suggested. Dilute acid pretreatment, which solubilizes hemicellulose, was performed on barley straw at 110-190 °C temperature with 0.1-2% sulfuric acid for 2-20 min and a liquid portion of the hydrolysate was utilized. Using this hydrolysate, furfural production was conducted. Approximately 140-200 °C temperature induced the hydrolysis and pyrolysis of the hydrolysate. The initial reaction rate was found to be 2.84×10^{-5} mol/L·sec at 180 °C when reacted for 5 min, 48.5% of theoretical furfural production was obtained, and it was faster than the generally used one step furfural production methods. In addition, a high temperature gradient for pre-heating showed improvement of temperature control.

Keywords: Furfural, Dilute Acid Pretreatment, Hydrolysate, Pyrolysis, Barley Straw

INTRODUCTION

Furfural is an inhibitor for cell growth and metabolism of microorganisms in bioprocesses [1,2]. But furfural can be an important precursor of industrial chemistry and can be converted into various versatile chemical compounds [3,4]. Ethyl levulinate, C10-15 alkanes, alcohols, and various diols can be derived from it. The US Department of Energy identified furfural as one of the top 30 platform chemicals [5]. Furfural is produced from agricultural waste biomass. Pentosans, contained in the cell walls of woody plants, grass, and agricultural biomass, can be used for the production of furfural and lignocellulosic biomass [6]. With the recent attention paid to global warming and environmental issues, utilization of lignocellulosic biomass is anticipated as an alternate to petroleum products, in spite of the hard degradable structure of the biomass [7]. This hurdle can be overcome with the introduction of a pretreatment process and partial hydrolysis using dilute acid.

Dilute acid pretreatment (DAP) hydrolyzes the rigid structure of the plant cell wall, which consists of bunches of polymeric glucose backbone chains containing β (1→4) glucosidic bonds between each glucose monomer, relatively weak hydrogen bonds between each polymer bunch, and amorphous portions of hemicellulose and lignin to support the structure [8,9]. In the course of the process, xylan is removed by acid hydrolysis. High temperature and appropriate acid concentrations pretreat biomass well to remove a large portion of hemicellulose, but leave almost all the glucan [10, 11]. Thus, pretreatment using dilute sulfuric acid was previously studied statistically and optimized [12]. After DAP, residual waste

hydrolysate media could be used as a feedstock for chemical derivates because the media contains xylose, furans, organic acids, and phenolics which are from a heteropolymer xylan having branches consisting of ferulic acid, acetic acid and so on or lignin, a complex irregular structure of phenolics [1,7,13].

Furfural is formed from pentosan by pyrolysis, which is a dehydration reaction after hydrolysis. Hydrolysis of the chain polymer of sugars is the main reaction of lignocellulosic biomass and furfural is formed in after the hydrolysis. Cai et al. [5] explained the mechanism of reaction of furfural formation, which is suggested by Nimlos and co-workers [5,14].

An H_2O molecule breaks the glucosidic bond and forms pentoses, such as xylose and arabinose. Then, the hydrolyzed pentose releases H_2O molecules by dehydration to form furfural. After the first dehydration of xylose, dehydrofuranose is formed as an intermediate. And additional dehydration of two moles of H_2O follows. The reaction requires a strong Brønsted acid as a catalyst to lower the activation energy of the reaction. Furfural production was performed as a one-step production. The reaction was generally performed at 120-180 °C for 5-10 min, which are relatively low temperatures and a long reaction time. It can also be done at relatively high temperatures and a short reaction time (over 210 °C and in 5 min) [15,16].

300-700 kton of furfural is currently produced worldwide annually, and the market demand is increasing. Furfural and its derivates could compete with petroleum-based products as a renewable alternative in the future. The production cost of furfural must be reduced by 1000 $/t by improving the yield in order to be competitive with petroleum products [5]. The utilization of residual hydrolysate waste after DAP should contribute to the reduction of production cost. Fig. 1 shows the schematic of furfural production using hydrolysate. In this study, barley straw was pretreated with dilute sulfuric acid, and the effects of such conditions were investigated. After the pretreatment of the barley straw, furfural was produced

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[†]To whom correspondence should be addressed.
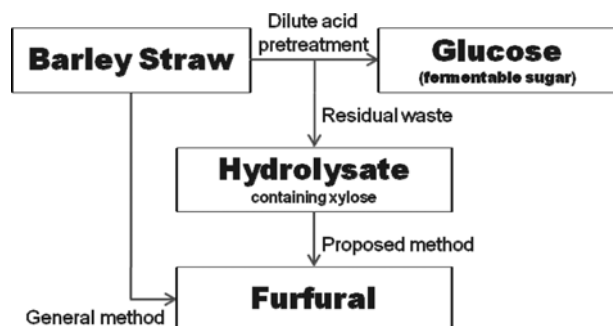E-mail: kimsw@korea.ac.kr

Fig. 1. Schematic diagram of furfural production from barley straw.

from the isolated waste hydrolysate liquid. The study also compares the two steps process for furfural with the one-step process.

MATERIALS AND METHODS

1. Materials

Barley straw was provided by the Biochemical Engineering Laboratory of Kyonggi University. The straw was stored at 20° and about 70% relative humidity (RH) in the dark. The barley straw was milled and homogenized for biomass size of 50-60 mesh (250-300 µm). Sulfuric acid (95% H_2SO_4) was purchased from Dae Jung Chemical, Korea.

2. Dilute Acid Pretreatment and Pyrolysis

Reactions such as DAP and pyrolysis were performed in an oil bath using a well-sealed tube reactor with 1.2 cm diameter and 18 cm length and contained pre-heating, reaction, and cooling baths. The pre-heating bath was maintained at 180-240 $^\circ$C for fast heat transfer, whereas the cooling bath was kept at room temperature. Sulfuric acid (H_2SO_4) was employed as a catalyst to hydrolyze xylose from the straw. The solid-to-liquid ratio was 1 : 35. DAP was investigated at 110-190 $^\circ$C with, 0.1-2% sulfuric acid and 2-20 min reaction time. We determined 150 $^\circ$C temperature, 1.16% sulfuric acid for 17 min by statistical method as ideal [12], and the liquid portion (hydrolysate) was separated by filtration. Pyrolysis of the hydrolysate was performed by using the same tube reactor at 160-200 $^\circ$C for 30 min. A fundamental experiment was performed to determine the ratio of solid (biomass) to liquid, and 1 : 35 of solid to liquid was employed in this study.

3. Analytical Methods

The solid biomass was analyzed to estimate its absolute composition, according to National Renewable Energy Laboratory (NREL, USA) standard procedures [17]. For dilute acid hydrolysis, the biomass mixture was combined with a dilute acid solution of sulfuric acid (72%, w/w) at 121 $^\circ$C in an autoclave. After heating and cooling, the mixture was neutralized with calcium carbonate.

The yield, based on the dry weight of furfural, was calculated using the following equation [5]:

$$\% \text{ furfural yield} = \frac{\text{Weight of furfural formed}}{\text{Dry weight of xylan utilized}} \times 100$$

High-performance liquid chromatography (HPLC) was employed to analyze the supernatant composition (xylose and furfural) with an Aminex® HPX-87H ion exclusion column (BIO RAD). HPLC

was performed at a column temperature of 55 $^\circ$C with a refractive index (RI) detector in 0.005 N H_2SO_4 mobile phase at a flow rate of 0.6-0.8 mL/min for 20-60 min.

RESULTS AND DISCUSSION

1. One-step Furfural Production from Barley Straw

Barley straw was used to produce furfural at 160 $^\circ$C-200 $^\circ$C in a stainless tube reactor in a 1 : 35 ratio of solid to liquid. One-step
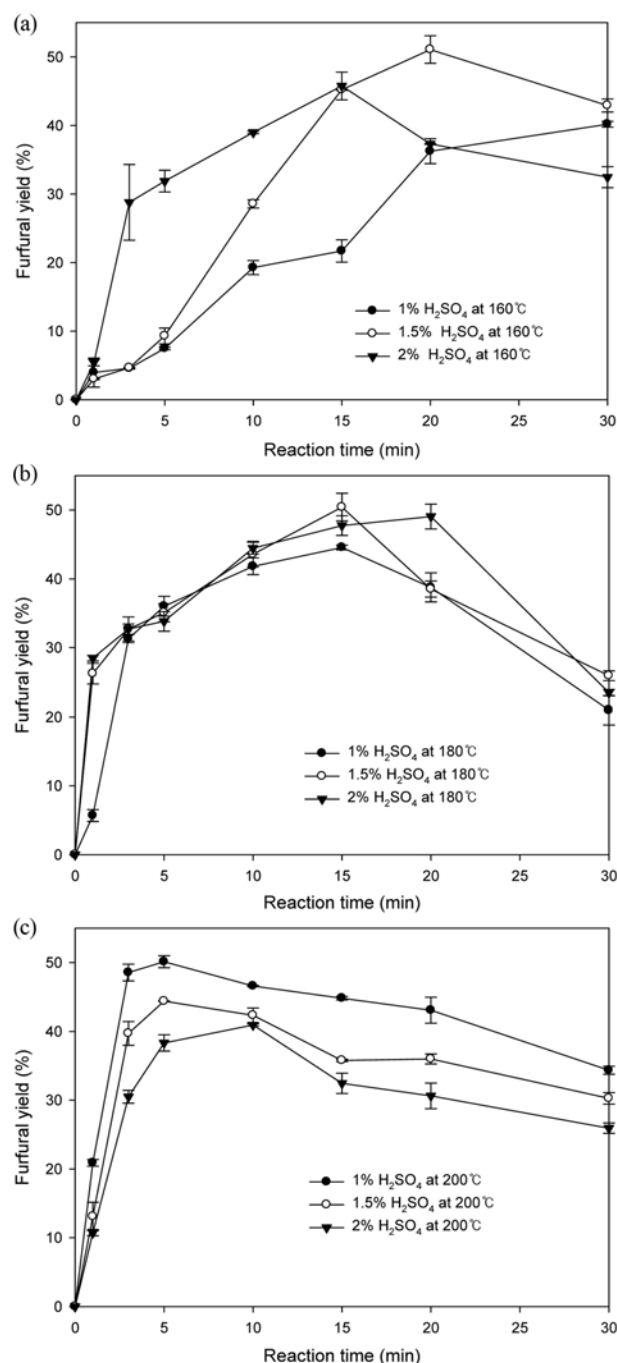

Fig. 2. One step production of furfural. Effects of reaction temperature and acid concentration on furfural yield. (a) 160 $^\circ$C, (b) 180 $^\circ$C, and (c) 200 $^\circ$C.

furfural production includes mainly two mechanisms. Hydrolysis of lignocellulosic biomass is the primary reaction. Hemicellulose, a heteropolymer, is degraded into xylose monomers and is solubilized in acid media. The second reaction converts solubilized xylose into furfural by dehydration and pyrolysis [18]. Fig. 2 shows the effects of different temperatures and acid concentrations on furfural production from barley straw. Furfural was produced at 160 °C with 1%, 1.5%, and 2% sulfuric acid. When 1%, 1.5%, and 2% sulfuric acid were added at 160 °C, initial reaction rates were found to be $3.03{\times}10^{-5}$ mol/L·sec, $3.11{\times}10^{-5}$ mol/L·sec, and $1.67{\times}10^{-4}$ mol/L·sec, respectively. The increase of production was rapid when 2% acid was used while the productivity slope of less than 2% samples was not as steep. The times to reach maximum yield were different for different concentrations. As acid concentration increased, the time for maximum yield was shorter. When 2% sulfuric acid was used, maximum yield was 44.3% at 15 min, whereas 1.5% yielded 51.07% at 20 min and 1% yielded 40.17% at 30 min.

At 180 °C, samples showed similar tendencies in productivity and maximum yield. Three duplicated samples were examined, and initial reaction rates of the three were found to be $2.08{\times}10^{-4}$ mol/L·sec, $2.16{\times}10^{-4}$ mol/L·sec, and $2.11{\times}10^{-4}$ mol/L·sec, respectively. Maximum yield of 1%, 1.5%, and 2% was 44.5% at 15 min, 50.4% at 15 min and 49.06% at 20 min, respectively. At 200 °C, production rates were relatively rapid compared to other temperatures. Maximum yields for the three concentration of acid were 50.1%, 44.3%, and 40.9%, respectively.

2. Pretreatment of Barley Straw for Two-step Furfural Production

The two-step process of furfural production consisted of biomass pretreatment using dilute acid followed by pyrolysis of the isolated residual waste hydrolysate liquid from the previous step. The one-step furfural production utilizes only the xylose portion, which is approximately 25-30% of the whole biomass weight [6]. Lignocellulosic biomass contains not only xylose, but also other fermentable sugars, and they should be isolated to reduce the solid waste of production and to enhance the economics of lignocellulosic biomass utilization process.

First, barley straw was pretreated at 110-190 °C using 0.1-2% sulfuric acid for 2-20 min. Fig. 3 shows the effects of the temperature (a), sulfuric acid concentration (b), and reaction time (c) on xylose yield. As the results show, appropriate conditions for xylose extraction from barley straw were about 150 °C temperature, 1% sulfuric acid, and about 15 min reaction time. The lower temperature induced insufficient xylose yield, and high temperature caused over-degradation of the barley straw. Also, temperature is directly concerned with the energy cost, then optimization must be followed. Samples over 1% acid concentration showed similar results to each other. As reaction time increased, xylose yield increased, and after 15 min, the yield decreased. At high temperature, long reaction time caused over-degradation of barley straw. Over-degradation is the loss of the desired product. At high temperature and longer times, the glucosidic bonds of the xylose are broken and undesired products are formed.

Subsequently, barley straw was pretreated at optimal conditions of 150 °C, 1.16% sulfuric acid, and 17 min reaction time [12]. When the pretreatment was performed at these conditions, the hydrolysate content was about 5.97 g/L xylose, 1.22 g/L glucose, and trace amounts of arabinose, galactose, and other minor products. Xylose
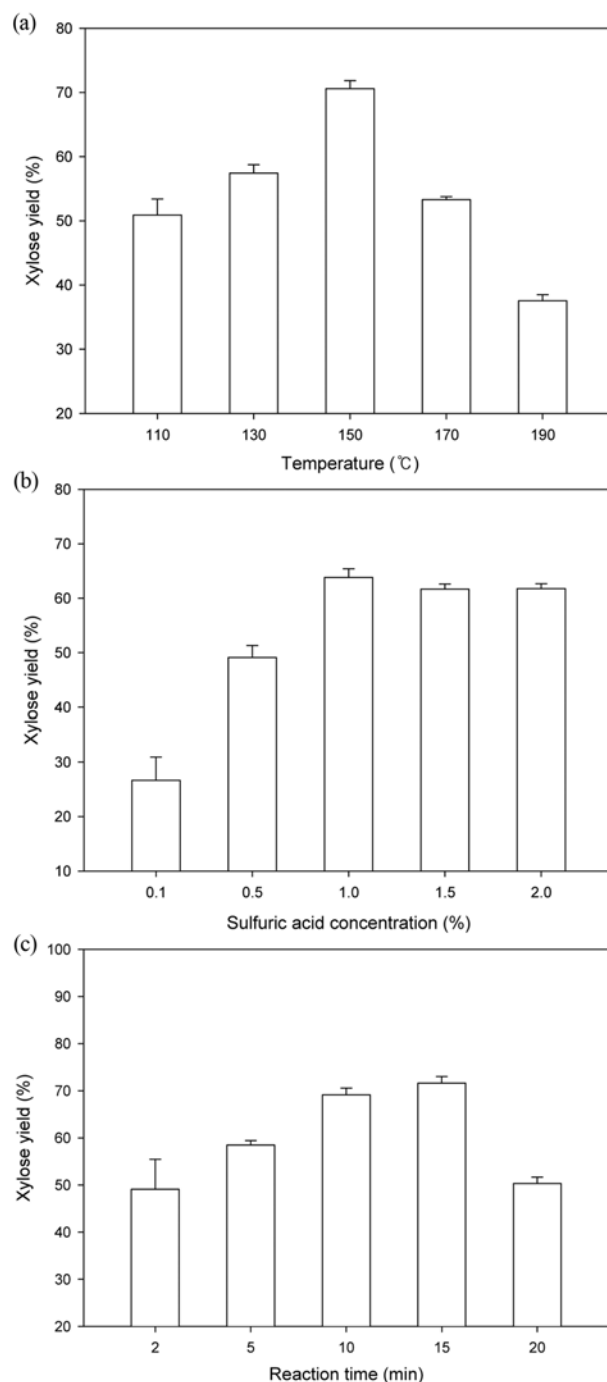

Fig. 3. The effects of reaction temperature (a), sulfuric acid concentration (b), and reaction time (c) on xylose extraction from barley straw by dilute acid pretreatment.

was about 81.3% (w/w) of the hemicellulose portion of the barley straw. Also, phenolic compounds, furan compounds, and organic acids are present in the hydrolysate because of pretreatment. After pretreatment, biomass, a solid portion was saccharified by a hydrolysis enzyme to obtain fermentable sugar, and the hydrolysate of the pretreatment media was converted to furfural. The sugars (mainly glucose) were utilized to produce ethanol by fermentation as described in our previous work [12].
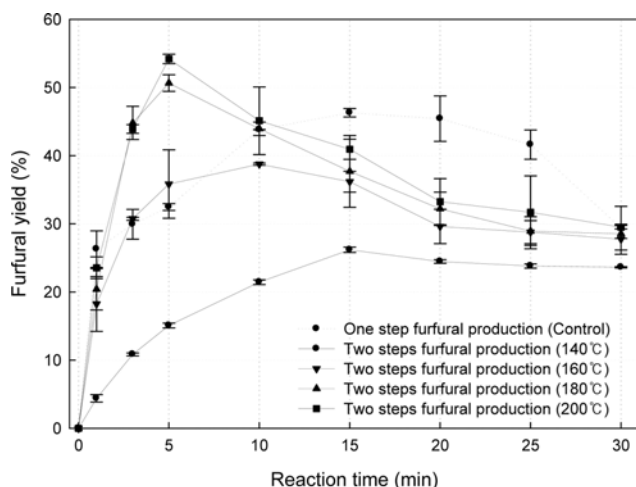
Fig. 4. Furfural production from hydrolysate of dilute acid pretreatment of barley straw.

Fig. 5. Effect of heat gradient on furfural production.

3. Pyrolysis of Hydrolysate for Two Steps Furfural Production

The hydrolysate of was pyrolyzed with sulfuric acid catalyst in hydrolysate at 140-200 °C. Fig. 4 shows the results of furfural production. When the reaction was performed at 140 °C, the production rate was slow. The temperature was insufficient for the dehydration reaction using aqueous acid catalyst (approx. 1.15% sulfuric acid). Comparison to the one-step process was also performed. Barley straw was directly hydrolyzed and pyrolyzed in a stainless tube reactor in 1 : 35 ratio of solid to liquid weights. The one-step process for furfural production is the existing method, at 180 °C, 1.5% sulfuric acid concentration, and 15 min reaction time, which were derived from the 'One-step furfural production from barley straw' section (Fig. 2).

As temperature of the reaction increased, the production rate was enhanced. When the temperature was over 180 °C, the initial reaction rates at 3 min were similar (2.84×10^{-4} mol/L·sec at 180 °C and 2.6×10^{-4} mol/L·sec at 200 °C). The maximum yields were 48.5% at 180 °C and 50.6% at 200 °C at 5 min, whereas the maximum of lower temperature was 22.5% at 140 °C at 15 min and 36.8% at 160 °C at 10 min. After the point of maximum yield, furfural yields for all samples decreased because of over-degradation. When the one-step production occurred, the initial reaction rate was 2.08×10^{-4} mol/L·sec, which is similar to two-step production, and the maximum yield was 47.7% at 20 min, which was lower than the two-step process. Comparison between one-step and two-step showed mostly similar tendency of productivity of maximum yield and initial reaction rate. But the maximum point of the two-step process was reached faster than the one-step process. In the one-step process, degradation of biomass and hydrolysis of hemicellulose may occur, and pyrolysis of degraded xylose could follow [18-21]. On the other hand, furfural production from hydrolysate only has one reaction of xylose pyrolysis into furfural.

4. Effect of Heat Transfer on Hydrolysate Pyrolysis for Furfural Production

In furfural production by pyrolysis from barley straw, high temperature causes the rapid formation of furfural from xylose, but degra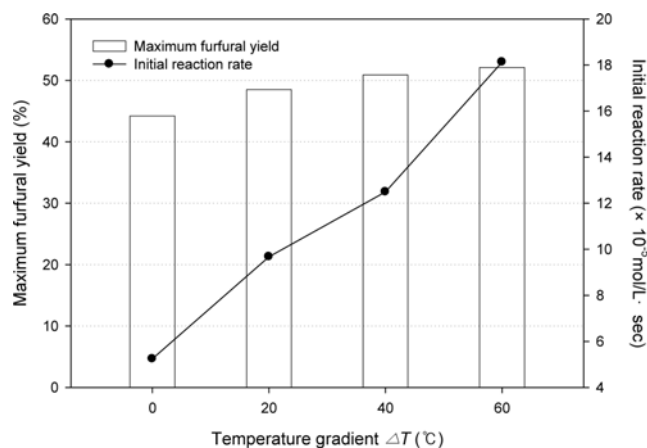dation rate was also fast. The precise control of conditions such as reaction time and temperature should be followed. The heat transfer of the stainless tube reactor with the oil bath is limited. It took approximately 5-8 min to reach 180 °C-200 °C with a pre-heating bath of 200 °C. Heating time is not within the reaction time, and as it is longer, the reaction time could be inaccurate. The increase of temperature follows the heat gradient, and as it gets at the desired temperature, the increase slows. During the heating, the reaction is also occurring and as the heating time gets longer, overdegradation and carbonization could increase and then the furfural yield would decrease [16]. The degradation and decrease of yield are shown after 5 min (Fig. 2). The heat transfer curve generally follows a logistic curve, and the convergence section of the desired temperature increases the heating time. A pre-heating bath decreases or eliminates the convergence section of heat transfer by introducing a higher temperature than the reaction temperature. Large ΔT (heat gradient) is responsible for rapid increase of temperature if other conditions for heat transfer rate do not change. Thus, various heat gradients were investigated. The main oil bath for the reaction was set at 180 °C and pre-heating bath temperatures were 180 °C, 200 °C, 220 °C, and 240 °C for comparison. From these pre-heating temperatures, the ΔT was 0 °C, 20 °C, 40 °C, and 60 °C. Pre-heating was performed until the temperature reached 175 °C when the tube reactor was moved into the 180 °C reaction bath. Fig. 4 shows the effects of ΔT on the initial reaction rate and the maximum yield of furfural. No pre-heating (ΔT=0) sample was a control and the initial reaction rate of the control was found to be 5.23×10^{-5} mol/L·sec. Its maximum yield was 36.7%. As ΔT increased, the initial reaction rate and maximum yield also increased. When ΔT was 60 °C, initial reaction rate was found to be 1.81×10^{-4} mol/ L·sec, and the maximum yield was approximately 56.1%. It was higher than a ΔT of 20 °C. Heating time was decreased with high ΔT in pre-heating step. Enhancement of the heat gradient and temperature control could increase the productivity. Also stainless, the material of tube reactor, should be enhanced to be of high thermal conductivity.

CONCLUSION

Furfural was produced from hydrolysate after DAP of barley

straw. Utilization of waste hydrolysate is recommended because of economic feasibility of the biorefinery process. When the reaction temperature was 180 °C with 200 °C pre-heating, the initial reaction rate was 2.84×10^{-5} mol/L·sec and there was 48.5%. A large temperature gradient induced short pre-heating time and a rapid increase of temperature enhanced both initial reaction rate and maximum yield.

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