2012 International Conference on Future Environment and Energy
IPCBEE vol.28(2012) © (2012)IACSIT Press, Singapoore

Furfural production from miscanthus by one step pyrolysis

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Abstract. Miscanthus was pyrolyzed with 1~2% of dilute sulfuric acid to produce furfural a versatile compound. At first, hydrolysis for investigation of miscanthus composition and furfural production was performed using sulfuric acid, and important factors are investigated using statistical method. Fractional factorial design was employed for statistical analysis. The factors are determined to be temperature, reaction time and sulfuric acid concentration. Investigation ranges are 160~200°C of temperature, 0.5~ 50 min of reaction time and 0.5~4% of sulfuric acid concentration. The optimal conditions are found to be 180°C, 20 min of reaction time and 2% of sulfuric acid concentration. When the conditions were employed, about 55% of furfural production was reached. Also furfural recovery was performed

Keywords: Hyrolysis, Pyrolysis, Furfural, Dilute sulfuric acid, Statistical analysis

1. Introduction

Furfural is a versatile derivative, and it can be utilized for a building block of furfuryl alcohol production and a component of fuels or liquid alkanes. But in bio process, furfural is a critical compound because it inhibits cell growth and metabolism. Furfural could be converted from xylose and usually produced from biomass in which hemicellulose is abundant. Miscanthus is consisted of about 28% of hemicellulose and it could be degraded into monomer xylose and subsequently pyrolyzed to furfural.

In this study miscanthus was converted to furfural by hydrolysis and pyrolysis. Notable factors are analyzed using fractional factorial design. FFD analyzes the efficiency of each concerned factor and determined factors are optimized at various conditions. After all, recovery of furfural was performed using solubility in solvent.

2. Materials and Methods

Miscanthus from Honam area in Korea was kindly provided by Chang-hae ethanol corp., and stored in condition of 20°C and 70% humidity. Celluclast from *Trichoderma reesei* and Novozyme1881 *Aspergillus niger* were used for enzymatic hydrolysis of the biomass.

Dilute sulfuric acid pretreatment of rice straw was performed in an oil bath using a well-sealed tube reactor with 1.2 cm diameter and 18 cm length. Oil bath contained pre-heating, reaction and cooling baths. Temperature of the pre-heating bath was maintained at 210℃ for fast heat transfer, whereas that of the cooling bath was kept at room temperature. Dilute sulfuric acid pretreatment was performed as following conditions; 142℃ of temperature, 1.21% of sulfuric acid concentration and 11.6 min of reaction time without heating and cooling time.

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Fractional factorial designs (FFD) of 2^{n-1} were carried out. This design uses two levels of each factor from furfural production to determine an optimal condition of critical factors to a linear approximation. In the first one, to identify and eliminate parameters, FFD was performed in order to study the effects of temperature, acid concentration and reaction time. Table 1 show the coded values of ANOVA and Table 2 shows the design of experiment contained results.

Analysis of the solid biomass was performed to estimate its absolute composition, according to National Renewable Energy Laboratory (NREL, USA) standard procedures [12]. For dilute acid hydrolysis, the biomass mixture with a diluted acid solution of sulfuric acid (72%, w/w) was heated to 121°C in an autoclave. After heating and cooling, the mixture was neutralized with calcium carbonate. The supernatant of the biomass composition was then analyzed by High-performance liquid chromatography (HPLC) with an Aminex® HPX-87 H ion exclusion column (BIO RAD). HPLC conditions were a column temperature of 50°C, a refractive index detector and 0.005 N H_2SO_4 mobile phase at a flow rate of 0.8 mL/min. The amount glucose after saccharification and ethanol production yield were also measured by HPLC.

Table 1. Coded values of each factors

	-1	**0**	**+1**
Temperature (X_1)	160°C	180°C	200°C
Particle size (X_2)	120-60 (1)	60-40 (2)	Under 40 (3)
Reaction time (X_3)	5 min	10 min	15 min
Solid/Liquid ratio (X_4)	1:4 (1)	1:7 (2)	1:10 (3)
Sulfuric acid concentration (X_5)	0.5%	1%	1.5%

Table 2. Fractional factorial design (FFD)

-	-	-	-	+
+	-	-	-	-
-	+	-	-	-
+	+	-	-	+
-	-	+	-	-
+	-	+	-	+
-	+	+	-	+
+	+	+	-	-
-	-	-	+	-
+	-	-	+	+
-	+	-	+	+
+	+	-	+	-
-	-	+	+	+
+	-	+	+	-
-	+	+	+	-
+	+	+	+	+
0	0	0	0	0
0	0	0	0	0
0	0	0	0	0
0	0	0	0	0

3. Results and Discussion

3.1. Fractional factorial design

Concerned factors for furfural production are temperature, acid concentration, solid/liquid ratio, particle size and reaction time. Fractional factorial design could indicate which factor is critical for result. Analysis of variance (ANOVA) has several indications which mean a profile of statistics of each factor. F-value means the efficiency of the factor and high F-value is bound to high efficiency of factor. It means that the change of factor induces the change of results, and little change of factor condition affects much change of results relatively if the factor has higher F-value. Critical factors were determined to be temperature, reaction time and sulfuric acid concentration (Data not shown). The other hand, liquid/solid ratio and particle size was relatively not critical for furfural production.

3.2. Effects of various temperatures and acid concentrations

Furfural production process was optimized at various temperatures, sulfuric acid concentrations and reaction time. Optimal temperature was determined to be 200°C. The condition of over 200°C was investigated and there is no enhancement. Sulfuric acid concentration was determined to be 1.5%, and reaction time was determined approximately 20 min. The mechanism of furfural production is that biomass is degraded into xylose by the effect of hydrolysis under acid media, and the xylose is pyrolyzed at high temperature. Xylose production is actually the process of biomass pretreatment, and furfural production is usually higher temperature and shorter reaction time than pretreatment reaction using dilute acid. Then, one step production of furfural from miscanthus could be needed to be investigated at over 200°C for short time (in 5min). And statistical analysis such as Composite central design (CCD) and Box behnken design (BBD) have to be followed to investigate the nature of tendencies and orientations of the profiles at each condition. Then, the results of this optimization could be utilized for fundamental data when the statistical analysis is performed.

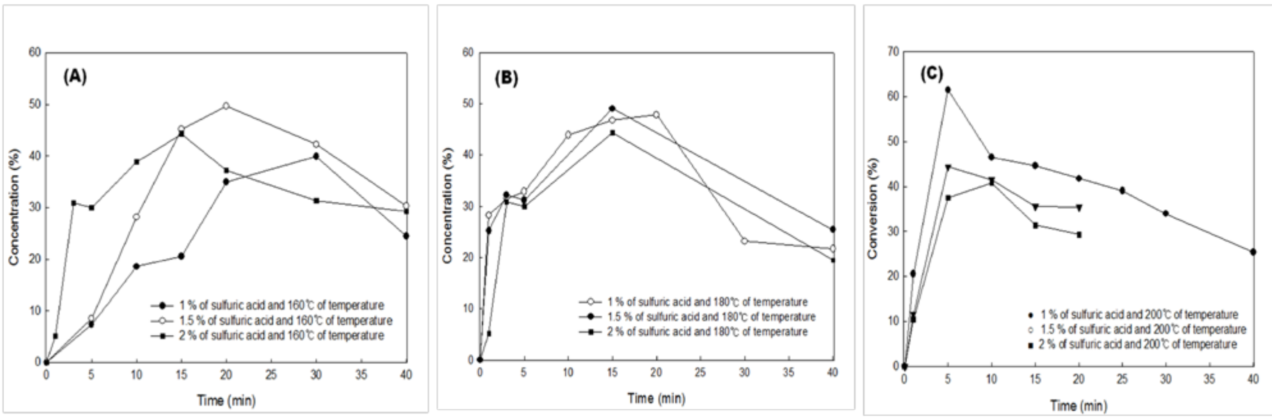

Fig. 1 Effects of temperatures (160°C, 180°C and 200°C), acid concentrations (1%, 1.5% and 2%) and reaction time on furfural production (A): Effects of sulfuric acid concentration at 160°C of temperature, (B): Effects of at Effects of sulfuric acid concentration at 180°C of temperature, (C): Effects of sulfuric acid concentration at 200°C of temperature

3.3. Recovery of furfural

After production, investigation of furfural recovery by solvent was performed. Various solvents were listed, and Table 3 is the solvents list. The name of solvent is treated Solvent # because investigation The liquid from pyrolysis was consisted of furfural and sugars such as glucose and xylose which is hydrolyzed from miscanthus. Furfural has a nature of solubility, and if furfural concentration is over 83 g/L, furfural is precipitated and no more solubilization. But in hydrolysates liquid of this study, furfural concentration is lower than the solubility (83 g/L) and furfural and sugar is solubilized in water at the same time. Then, the solvent must solubilize furfural selectively but there is no solubility for sugars. Various solvents were investigated, and four solvents were noticed. Solvent 2 and Solvent 3 could not solubilize sugars, but furfural solubilization was not notable (37.14% and 30.84%, respectively). And Solvent 4 was not satisfied the condition. Solvent 1 was superior for recovery of furfural from the liquid and no solubilization of sugars.

Furfural was solubilized about 88.87% from liquid and 94.5% of xylose was remained at liquid. Fig. 2 shows the mixture of solvent1 and hydrolysates liquid and concentrated furfural by evaporation. Xylose utilization also could be concerned. Xylose could be converted to value added products by chemical and biological method. Furfural is known to be a critical inhibitor for fermentation. Then a study about the effect of furfural concentration for fermentation is needed if the xylose is used for carbon source of fermentation.

Table 3. Comparison of removal rate using various solvents. Xylose of 20 g/L and Furfural of 10 g/L was solubilized in the reference solution. The mixture of non-polar solution and reference solution was stirred for 20 min.

Solvents	Xylose(20 g/L)	Furfural (10 g/L)	Recovery
Solvent 1	18.901 g/L	1.112 g/L	88.87%
Solvent 2	19.391 g/L	6.285 g/L	37.14%
Solvent 3	19.594 g/L	6.915 g/L	30.84%
Solvent 4	11.166 g/L	4.386 g/L	56.13%

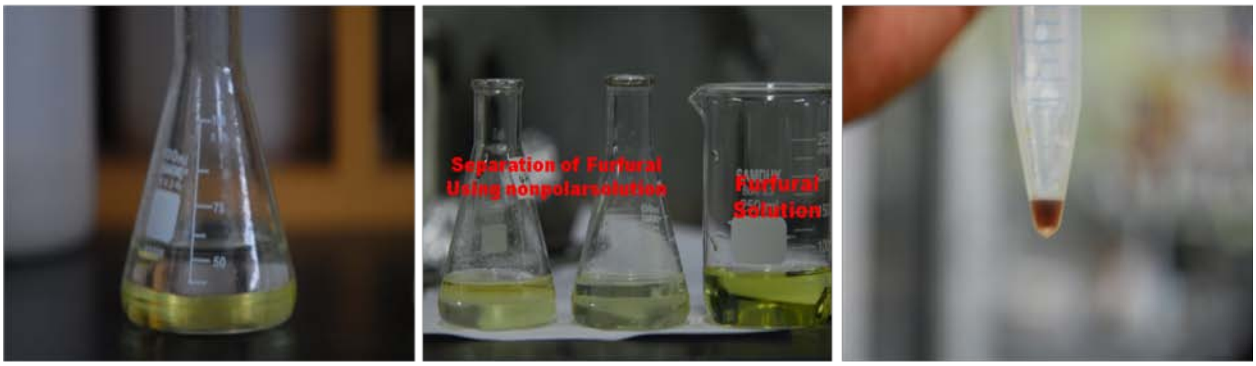

Fig. 2 Investigation of various solvents which is non-polar and solubilize the furfural. (A): Divided layer of water and solvent. In water layer, xylose and furfural is solubilized. (B) After stirring for 20 min. (C) Purified furfural by concentration of evaporation

4. Acknowledgements

This Study was supported by Technology Development Program (309016-5) for Agriculture and Forestry, Ministry for Food, Agriculture, Forestry and Fisheries, Republic of Korea and the Advanced Biomass R&D Center (ABC-2010-0029799) of Korea Grant funded by the Ministry of Education, Science and Technology.

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