Acetic Acid Catalyzed Steam Explosion for Improving the Sugar Recovery of Wheat Straw

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Acetic acid-catalyzed steam explosion pretreatment was applied to wheat straw at temperatures of 190 and 210 °C for 2, 6, and 10 min of residence time. The effects of pretreatment conditions on the total gravimetric recovery, hemicellulose sugars, glucose content, and yield of the enzymatic hydrolysis of cellulose were studied. The results indicated that the total gravimetric recovery decreases while the solubility of hemicellulose and the yield of cellulose enzymatic hydrolysis increase as the pretreatment severity increases. Pretreatment at 190 °C with a 2-min residence time resulted in the highest total gravimetric recovery, 58.9%. The optimum defiberation, glucose content, and enzymatic hydrolysis yields of 70.4 and 79.6%, respectively, occurred following pretreatment at 210 °C with a 10-min residence time. The optimal pretreatment condition was determined to be 190 °C for 10 min. Under the optimum conditions, the recovery yield of all sugars reached 42.7%. This pretreatment resulted in the highest recovery yield of all sugars.

Keywords: Acetic acid; Steam explosion; Pretreatment; Wheat straw; Enzymatic hydrolysis

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INTRODUCTION

With the continued depletion of the world's fossil fuel-based energy reserves, there has been an increasing worldwide interest in alternative sources of energy. Bioethanol, a fuel that can be produced from renewable resources such as lignocellulosic biomass, has drawn considerable attention in recent years. Throughout the world, huge amounts of unused wheat straw residues are generated every year (Tabka *et al.* 2006), and only a small percentage is used for applications such as feedstock for the pulp and paper industry (Carrillo *et al.* 2005; Pan and Sano 2005). Wheat straw is quite fibrous in nature, so its suitability for the production of ethanol has been assessed in a number of studies (Fang *et al.* 2002; Mosier *et al.* 2005; Pan and Sano 2005; Nigam 2001; Ranganathan *et al.* 1985). Ethanol production from wheat straw involves pretreatment, saccharification, and fermentation. Pretreatment of wheat straw is essential for efficient enzymatic hydrolysis (Nigam 2001; Pan and Sano 2005; Ranganathan *et al.* 1985). The object of pretreatment is to decompose the network of lignin, disrupt the crystalline structure of cellulose, and make cellulose more accessible to the enzymes that convert carbohydrate polymers into fermentable sugars (Martinez *et al.* 1990). Pretreatment methods for lignocellulosic materials have been extensively studied. Of the numerous procedures, steam explosion has received particular attention since it makes lignocellulosics more readily digestible by enzymes (Ballesteros *et al.* 2002; Martinez *et al.* 1990).

Previously, acid-catalyzed steam explosion has been used extensively to improve the enzymatic hydrolysis of cellulose from both hardwood and softwood, as well as to increase the recovery of soluble hemicellulose sugars (Cullis *et al.* 2004; Martinez *et al.* 1990; Nunes and Pourquie 1996). It is expected that acid-catalyzed steam explosion would have the same effects on wheat straw or any other fibrous material. And there are some publications dealing with acid catalysed steam explosion of wheat straw, for example Ballesteros *et al*. (2006) and Fang *et al*. (2011). The objective of this research was to determine the effects of acetic acid-catalyzed steam explosion pretreatment on the solubilization of hemicellulose, enzymatic convertibility of cellulose, and recovery of both polysaccharides in wheat straw.

EXPERIMENTAL

Raw Material and Steam Explosion Pretreatment

Raw wheat straw was purchased from a local harvest in Shuangkou, Tianjin City, China. The wheat straw was air-dried at room temperature and crushed in a hammer mill, then screened through a 5-mm mesh to remove oversize particles and through a 2-mm mesh to remove undersize particles. The moisture content was determined to be 23% by weight.

The wheat straw samples were soaked in 5% (w/w) acetic acid for approximately 12 h at room temperature. The excess acetic acid solution was separated by filtration.

Pretreatment of acetic acid-treated raw material was carried out in a steam explosion pretreatment unit of a 7-L reaction vessel (BL-08, Beijing Forestry University, China) designed to reach a maximum operating pressure of 3.5 MPa. First, 200 g of acetic acid-treated raw material was manually added to the reactor and heated with saturated steam. The steaming time was measured starting from the moment that the reactor reached the target temperature. At the end of the allotted steaming time, the quick-opening ball valve was opened to discharge the contents of the reactor rapidly into a collection device. After cooling to approximately 40 °C, the pretreated material was separated into a solid fraction and a water-soluble portion *via* filtration. Both the water-soluble portion and the solid fraction were analyzed for their carbohydrate contents. The pretreatment temperatures tested were 190 °C and 210 °C, and the residence times tested were 2, 6, and 10 min.

Analytical Methods

The chemical composition (moisture, ash, lignin, and total carbohydrate content) of the original and pretreated samples and the carbohydrate content in the water-soluble portion were analyzed according to ASTM-D 1106-84, ASTM-D 1107-84, ASTM-D 1110-84, ASTM-E 1721-95, and ASTM-E 1756-95.

Enzymatic Hydrolysis

Celluclast 1.5 L and Novozyme 188 (Novozymes Co., Ltd., Tianjin, China) were used in the enzymatic hydrolysis. The enzyme loadings of Celluclast 1.5 L and Novozyme 188 were 30 FPU/g substrate and 23 IU/g substrate, respectively. The cellulase activity of Celluclast 1.5 L was measured using the filter paper assay method developed by Mandels *et al.* (1976). The β-glucosidase activity of Novozyme 188 was determined according to the procedure developed by Berghem and Pettersson (1974). All experiments were performed at 50 °C on a rotary shaker running at 80 rpm for a duration of 72 h. The substrate concentration was 2% (w/v). At given elapsed times, samples were withdrawn from the reaction media, centrifuged, filtered, and analyzed.

RESULTS AND DISCUSSION

Composition of Wheat Straw

The chemical composition of the wheat straw used in this study is presented in Table 1.

Table 1. Chemical Composition of Wheat Straw

Component	Content (%w/w, dry basis)
Glucose	40.6
Mannose	0.8
Galactose	2.4
Xylose	19.2
Arabinose	2.4
Lignin	17.8
Ash	7.4

Effect of Pretreatment Conditions on Yield and Composition of the Water-Insoluble Fiber

The yield of water-insoluble fiber is an important index for the effectiveness of steam explosion pretreatment. Table 2 shows the effects of pretreatment conditions on the yield of water-insoluble fiber. As can be seen, the yield decreased with increasing pretreatment severity. With increases in residence time from 2 to 6 and 10 min, at a fixed pretreatment temperature of 190 °C, the yield decreased from 58.9 to 54.4 and 51.8%, respectively. The same trend was present at a constant pretreatment temperature of 210 °C, in which the yield decreased from 53.2 to 50.3 and 45.5%, respectively, with increases in retention time from 2 to 6 and 10 min. These values show that pretreatment for prolonged times can effectively enhance the solubilization of wheat straw.

The pretreatment temperature had a much greater effect on weight loss than the retention time did. At a constant retention time, a higher temperature resulted in more weight loss. These results show that pretreatment at higher temperatures led to enhanced dissolution of wheat straw and therefore lower yield. Furthermore, the effect of temperature on weight loss at lower retention time was more pronounced than that of lower temperatures at longer retention times. The most intense pretreatment (10 min residence time at 210 °C) resulted in the lowest yield, 45.5%. This change was largely due to the greater dissolution of hemicellulose and lignin under the high-intensity pretreatment conditions, which resulted in greater fiber liberation and lower yield. In addition, the further depolymerization of cellulose under more severe pretreatment conditions also contributed to the fiber loss.

Table 2. Effects of Acetic Acid-catalyzed Steam Explosion Pretreatment on Water-insoluble Wheat Straw Fiber

Pretreatment condition		Yield (%)	Glucose content (%)	Xylose content (%)	Mannose content (%)	Arabinose content (%)	Galactose content (%)
Temperature (°C)	Time (min)						
190	2	58.9	54.7	12.3	0.5	0.4	1.1
190	6	54.4	60.3	10.2	0.4	0.3	0.8
190	10	51.8	69.4	7.3	-	-	0.5
210	2	53.2	63.6	8.2	0.4	-	0.7
210	6	50.3	67.2	6.9	-	-	-
210	10	45.5	70.4	4.6	-	-	-

Effect of Pretreatment Condition on Sugar Composition of the Filtrate

As indicated in Table 2, steam explosion pretreatment significantly solubilized hemicellulose fractions. The extent of solubilization of the hemicellulose components was enhanced as the severity of the pretreatment increased. Arabinose was the sugar most sensitive to steam explosion pretreatment. As the pretreatment severity increased, the extent of solubilization of arabinose increased. At a pretreatment temperature of 190 °C, the arabinose dissolved completely within 10 min of retention time. In contrast, when the pretreatment temperature was increased to 210 °C, the arabinose dissolved completely at all three retention times tested. These results indicate that the pretreatment temperature had a much greater effect on arabinose solubilization than the retention time did. The same trend was present in the behaviours of galactose and mannose. Solubilization of xylose increased significantly as retention time increased from 2 to 10 min. When retention time was held constant, solubilization of xylose increased significantly with increasing temperature. These results show that acid-catalyzed steam explosion led to effective solubilization and hydrolysis of the hemicellulosic components of wheat straw.

Table 3 shows the effect of pretreatment conditions on the sugar composition (g/100 g of raw material) in the filtrate (the liquid fraction). At the same pretreatment temperature, a longer residence time resulted in more recovery of hemicellulose-derived sugars. Similarly, pretreatment at higher temperatures enhanced the recovery of hemicellulose-derived sugars. The highest recovery of hemicellulose-derived sugars, 69%, was obtained with a pretreatment temperature of 210 °C and a 10-min retention time. These observations imply that increasing both the pretreatment temperature and residence time could increase the recovery yield of hemicellulose-derived sugars.

Table 3. Effects of Pretreatment Severity on Sugar Composition of Filtrate (100 g Raw Material Basis)

Pretreatment condition		Glucose (g)	Hemicellulose-derived sugars (g)				Hemicellulose recovery (%)
Temperature (°C)	Time (min)		Xylose	Mannose	Arabinose	Galactose	
190	2	1.1	4.7	0.1	1.5	0.8	33.1
190	6	1.2	7.1	0.1	1.6	1.1	44.7
190	10	1.5	10.2	0.5	2.0	1.4	62.9
210	2	1.4	8.7	0.1	1.9	1.2	53.6
210	6	1.6	10.1	0.5	1.8	1.9	64.1
210	10	1.7	11.3	0.5	1.8	1.9	69.4

Effect of Pretreatment Condition on the Cellulose of Water-insoluble Fiber

The cellulose content of the water-insoluble fiber increased consistently with increasing pretreatment temperature and time, as shown in Table 2. The cellulose content ranged from 54.7 to 70.4%, depending on the pretreatment severity. These observations clearly indicate that the steam explosion pretreatment resulted in significant hydrolysis of hemicelluloses, yielding residues rich in cellulose.

Effect of Pretreatment Condition on the Enzymatic Hydrolysis Yield of the Water-insoluble Fiber

As indicated in Table 4, pretreatment severity had a great impact on hydrolysis yield. The hydrolysis yield increased at higher pretreatment temperatures and longer residence times. At 190 °C, increasing residence time from 2 to 6 and 10 min resulted in increases in hydrolysis yields from 62.6 to 68.4 and 75.5%, respectively. When the pretreatment temperature rose from 190 to 210 °C, a similar trend was observed. These data implied that both raising pretreatment temperature and increasing residence time could increase hydrolysis yield. However, the pretreatment temperature had a much greater effect on the hydrolysis yield than did the retention time. The maximum hydrolysis yield, 79.6%, was reached under a pretreatment temperature of 210 °C with a residence time of 10 min.

Table 4. Effects of Pretreatment Severity on Enzymatic Hydrolysis Yield of Water-insoluble Fiber

Pretreatment condition		Enzymatic hydrolysis yield (%)
Temperature (°C)	Time (min)	
190	2	62.6
190	6	68.4
190	10	75.5
210	2	67.8
210	6	74.8
210	10	79.6

Optimization of the Steam Explosion Pretreatment Parameters

Pretreatment effectiveness is usually evaluated in terms of the enzymatic cellulose hydrolysis yield and the recovery yield of both cellulose and hemicelluloses. A comparison of Tables 2, 3, and 4 shows that the maximum recovery yield of cellulose and hemicellulose and the maximum enzymatic cellulose hydrolysis yield occurred under different pretreatment conditions. Because effective recovery of all sugars is essential in improving the economy of the ethanol production process, a high recovery yield of all sugars is more important than a high yield of enzymatic cellulose hydrolysis. Therefore, the optimum pretreatment condition was at a temperature of 190 °C with a residence time of 10 min. Under the optimum conditions, the recovery yield of all sugars reached 42.7% (raw material basis).

CONCLUSIONS

1. Acetic acid catalyzed steam explosion is an efficient process for improving hemicellulose solubilization, enzymatic cellulose hydrolysis, and recovery of both cellulose and hemicellulose.
2. Using a pretreatment temperature of 210 °C with a 10 min residence time led to the highest dissolution of hemicellulose and the highest saccharification yield of the water-insoluble fiber.
3. The optimum pretreatment conditions were a temperature of 190 °C and a residence time of 10 min, which resulted in the highest recovery yield of all sugars.

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