DISSOLUTION OF PENTOSAN IN CORN STALK BY HOT WATER AND PURIFICATION USING ION EXCHANGE RESIN

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Corn stalk is a lignocellulosic material containing up to 22.52% pentosan and has great potential industrial applications. Hot-water extraction was used to extract hemicellulose from corn stalk in this study. The results showed that xylose and arabinose are the main sugars existing in the hot-water extract (HWE). The ratio of xylose to arabinose depended on extraction temperatures and ranged from 7.90 at 140°C to 10.40 at 170°C.The maximum yield of pentose was65.4% (134.72 g xylose per kg corn stalk)at 160°C for 180 min extraction. The sugars in HWE were purified by selective elimination of lignin-derived compounds by using ion exchange resin and the results showed that up to85.21% was removed. The study indicated that the combination of hot-water extraction with resin treatment is an effective and economic means for hemicellulose production from corn stalk.

Keywords: corn stalk, hemicellulose, pentosan, hot-water extraction

INTRODUCTION

The most abundant renewable resource on the earth, biomass, continues to receive a great deal of attention as a potential valuable commercial feedstock for fuels, chemicals and materials by means of biorefinery. Corn stalk, a leading biomass, has desirable attributes as a feedstock due to its high yield, low cost and renewability. Accurate data on annual corn stalk production in China is not readily available, although it is estimated to be about 200 to 250 million dry tons of corn stalk per year. It is widely acknowledged that most is incinerated, except a small percentage, which is retained on the field following harvest to maintain soil organic carbon levels. Nowadays, researchers are focusing on the use of corn stalk as a viable feedstock and fermentation medium, and on developing effective bioconversion processes.[1-3]

Similar to most agricultural residues, corn stalk is mainly composed of cellulose, hemicellulose and lignin, where the cellulose fibers are surrounded by hemicelluloses and lignin matrix.[4] The separation and application of cellulose from corn stalk have been investigated widely,[5-8] while the study on hemicellulose from corn stalk has mainly focused on the hydrolysis process and the production of biofuel.[9-11] There are only a few reports on the purification of the sugar in the hydrolysate of corn stalk, especially on how to eliminate lignin from the hydrolysate in order to optimize the separation of oligosaccharides, xylitol, ethanol, etc.

There are many extraction methods as known from previous research,[12-15] including steam explosion, microwave irradiation, acid or alkali treatment, and organic solvent based extraction.

Hot-water extraction is regarded as an alternative approach for recovering hemicellulose from biomass, because it consumes a very little amount of chemicals and demonstrates high environmental friendliness. Furthermore, most of the water-soluble hemicellulose can be extracted by hot water, where the natural molecular structure of the polysaccharides, including the polymerization degree (DP), and glycosidic linkages are always retained to a large extent, which facilitates its potential use in numerous industries. However, the presence of other dissolved compounds in the extraction solution (ES), except for sugars, e.g., lignin degradation products, hampers the utilization of the dissolved hemicelluloses for bioconversion.[16-18]

Therefore, the removal of lignin from the ES is of great importance. In previous researches, activated charcoals and ion exchange resin were used to remove the phenolic compounds (lignin) and acetic acid from the pre-hydrolysis liquor (PHL) of lignocellulose, and achieved a remarkable effect.[19-21]

It has been shown that pentose is the main hemicellulose in corn stalk.[22-23]The present study was done to determine more accurately the composition of corn stalk and the content of pentose as a function of hot-water extraction, in which variables, such as temperature and holding time, were optimized to achieve the highest yield of pentose. Ion exchange resin was used to remove lignin from the hot-water extraction solution (ES) for the purification and subsequent accumulation of hemicellulose from corn stalk.

EXPERIMENTAL

Materials

Air-dried corn stalk was obtained from a local farm (Jinan, China). All leaves were removed prior to hot-water extraction.

Hot-water extraction of corn stalk

Corn stalks were cut and the average particle size was less than 10 mm. Hot-water extraction was conducted in a computer-controlled digester. The oven dry weight of corn stalk in each extraction was 100 g. The water to corn stalk ratio (L/W) was kept at 10 (v/w). The highest temperature of extraction ranged from 140 °C to 170 °C with an extraction time of 300 min. During extraction, 10ml extraction liquors were taken every 30 min for analysis.

Resin treatment of ES

The ion exchange resin sample (Amberlite IRA-900) was used for adsorption; it is a macroporous weak base anion exchange resin with quaternary amine functional groups. The ES of corn stalk was cooled down to room temperature prior to the resin treatment. The resin was added into the flask containing ES with a weight ratio of 1:10, and the mixture was shaken at 150 rpm at room temperature for 60 min, followed by centrifugation at the speed of 3000 rpm. The supernatant was referred to as “resin-treated ES”.For the regeneration of the exchanger, the resin was collected and washed with 1 M NaOH and 1 M HCl to remove organic and inorganic pollutants, and then washed several times to neutral with deionised water.

Analysis

The moisture content of ground corn stalk was determined by drying approximately 2 g of each sample in a forced-air oven at 105 °C for 4 h.

The extractives and chemical composition of corn stalk were determined by following NREL laboratory analytical procedures.[24-25] Structural carbohydrates in biomass were reported as percentages of glucan and xylan. Glucan is basically cellulose, xylan and arabinan are the major hemicellulose constituents. Lignin, the major noncarbohydrate component, is the sum of acid-insoluble and acid-soluble lignin, acid-insoluble lignin was measured gravimetrically and corrected for ash in biomass.

The content of ash was determined by the Chinese standard methods for non-wood raw materials. The test specimen was transferred to a crucible, carbonized gently over a Bunsenburner, ignited in a muffle furnace at 575 ±25 °C, and then the residue was weighed as ash.

Monosaccharides were determined using an ion chromatograph equipped with a CarboPac PA20 column (Dionex-5000, Thermo Fisher Corporation) and an electrochemical detector (ED50). A detailed procedure according to a previously used method was used.[26] De-ionized water was used as eluant at a flow rate of 0.5 mL/min. 0.2 mmol/L NaOH was used as regeneration agent with 0.5 mL/min flow rate and 0.5mmol/L NaOH was used as supporting electrolyte with 0.5 mL/min flow rate. The samples were filtered (bore size is 0.22 μm) and diluted prior to analysis. An additional acid hydrolysis was conducted with 4% sulfuric acid at 121°C in an oil bath for 120 min to hydrolyze the polysaccharides. The content of monosaccharides in the post acid hydrolysate therefore represented the total saccharides in the ES. Their contents were calculated based on the difference of the monomeric sugar content before and after acid hydrolysis.

The ES was diluted by a sulfuric acid solution of the same pH value as the samples, and then, the lignin content in the ES was identified by UV/Vis absorbance (Agilent 8453, USA) at the wavelength of 205 nm, based on TAPPI Standard UM250.[27]

The chroma of ES was determined by the CPPA method.[28] A five hundred color units (C.U.) platinum cobalt standard solution was used for the chroma. The pH of the samples was adjusted to 7.6 before testing. The absorbance was measured with an Aglient-8453 series UV-Vis spectrophotometer at 465 nm. The chroma of ES was calculated as follows (1):

$$\text{Chroma (C.U.)} = (500 \times A_2)/A_1 \quad (1)$$

where A_1 is the absorbance of 500 C.U. platinum cobalt standard solution at 465 nm, and A_2 is the absorbance of the sample at 465 nm.

RESULTS AND DISCUSSION

Comparison of extraction performance among cold water, hot water and benzene-ethanol

The results for the compositional analysis are summarized in Table1. The percentage of lignin is 21.66%, which is close to the 22.52% of pentosan. Hot-water extraction is slightly superior to cool-water and benzene-ethanol extractions, which can achieve 20.35% of dry material from corn stalk. Ion chromatography analysis showed that the carbohydrates of corn stalk were 68.13% glucan, 24.34% xylan, 5.71% arabinan, 1.61% galactan and 0.20% mannan. Glucan, xylan and arabinan were therefore the main carbohydrates in corn stalk. The mass losses of biomass were measured after hot-water extraction under the different conditions. The yields of pretreated corn stalk were of 79.24%, 76.18%, 73.20% and 71.71%, corresponding to 140 °C, 150 °C, 160 °C and 170 °C, respectively.

pH of hot-water ES under different temperature and holding time

The acetyl groups in the hemicellulose of corn stalk can be transformed into acetic acid during hot-water extraction, and result in a decrease of pH. The initial pH of the mixture of corn stalk and water was 6.17 before heating. However, it decreased with temperature. When the temperature reached holding temperature, the pH values were 5.54, 5.47, 5.32 and 5.19, corresponding to 140 °C, 150 °C, 160 °C and 170 °C. Under the different holding temperatures, the variations of pH with holding time are shown in Fig.1. The ash contents of pretreated biomass under different conditions were measured in order to further explore what affected the pH value of the extraction liquor during prehydrolysis. Under the different holding temperatures, the ash contents were of 2.42% (140 °C), 2.23% (150 °C), 2.38% (160 °C) and 2.34% (170 °C), respectively. It is can be seen that the differences of ash content among the pretreated corn stalks are insignificant, which indicates that more acetic acid was generated at higher holding temperatures and longer holding time, and then resulted in a lower pH.

Effect of temperature and holding time on the yield of pentose

The main carbohydrate in hot-water ES is pentose, as already mentioned earlier in this report. The extraction patterns of pentose under different temperatures and different holding times are shown in Fig.2. The yields of pentose initially increased and then decreased at the four holding temperatures, due mainly to more and more pentose converted into furfural with the extension of holding time. The high yield of pentose could not be obtained under the lower temperatures (140 °C, 150 °C). The highest yields were of only 35.88% and 43.71% (based on the total amount of pentose in corn stalk) at 140 °C and 150 °C, respectively. The maximum yield of 65.40%was obtained at 160 °C with a holding time of 180min, and with a mass loss of 26.80% for dry initial substrate. It was found to be the most effective extraction condition for pentose, and used in the following experiments.

Table 1
Chemical composition of corn stalk (based on dry matter, %)

Water	Ash	Extraction			Pentosan	Cellulose	Lignin
		Cool-water	Hot-water	Benzene-ethanol			
12.31	3.12	12.32	20.35	7.78	22.52	42.18	21.66

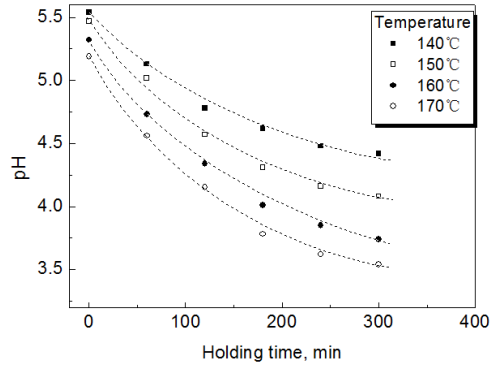

Figure 1: Variation of pH as a function of holding time

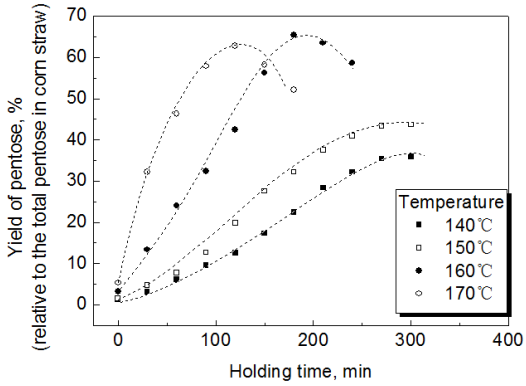

Figure 2: Effect of holding temperature and holding time on the yield of pentose

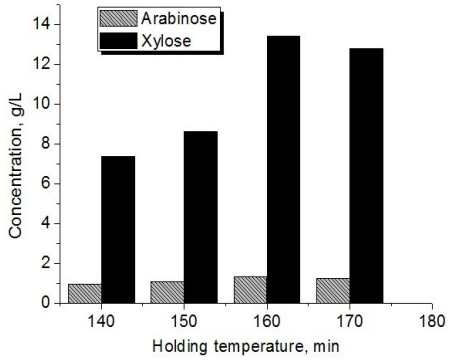

Figure 3: Concentrations of xylose and arabinose in different ESs

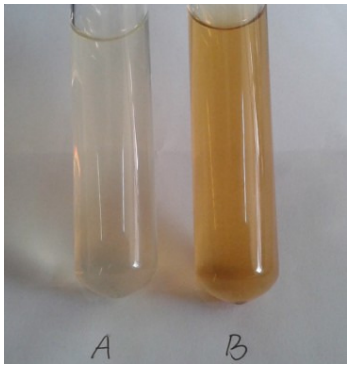

Figure 4: Extraction solutions before and after treatment by resin; A) Resin-treated ES; B) Original ES

Xylose and arabinose are the main pentoses in corn stalk. Concentrations were measured at different extracting temperatures, as shown in Fig.3. The ratios of xylose to arabinose at different temperatures (140 °C, 150 °C, 160 °C and 170 °C) were also determined. The ratio varied from 7.90 to 10.40. The highest yield of pentose was obtained at a holding time of 300min corresponding to 140°C (Fig.3), including 0.93 g/L (9.04 g/kg dry substrate) arabinose and 7.38 g/L (71.76 g/kg dry substrate) xylose in the extraction liquor. At 150 °C, the highest yield of pentose was also obtained at 300 min (holding time), in which 1.08 g/L (10.94 g/kg dry substrate) arabinose and 8.64 g/L (87.50 g/kg dry substrate) xylose were detected. When the temperature was increased to 160 °C, a pentose yield of 65.4% was obtained at 180 min. The content of arabinose increased slightly to 1.32 g/L (13.17 g/kg dry substrate), whereas the xylose concentration sharply increased to 13.44 g/L (134.72 g/kg dry substrate). At 170°C, the highest yield of pentose was obtained at 120 min, whereas the contents of arabinose and xylose in the ES began to decline to 1.23 g/L (12.26 g/kg dry substrate) and 12.78 g/L (127.36 g/kg dry substrate), respectively. The increase in pentose yield was mainly due to the release of xylose from corn stalk.

Sugar purification by ion exchange resin

The ES obtained at 160 °C was used for the resin treatment. Fig.4 shows the colors of both the original ES and resin-treated ES. The chroma of the resin-treated ES is lower than that ofthe original ES. Results showed that the chroma of ES decreased from 1630 C.U. to 138 C.U. after the treatment with resin.

It is well known that lignin is a major contributor to the chroma of a pulping effluent or extract solution of biomass.[29-30] The lower chroma of the resin-treated ES indicated a significant removal of lignin.

Fig.5 gives new evidence to certify that the removal of lignin resulted in the decrease of

chroma. UV-Visible spectroscopy of the original ES and treated ES are depicted in Fig.5 (all ES samples were diluted 12× prior to determining the absorption curves). An absorption peak was observed in the absorption curve of the original ES at 280 nm, which is ascribed to the absorption of lignin. Conversely, for the absorption curve of the resin-treated ES, there is no such large peak at the corresponding wavelength (280 nm); indeed, the peak value dropped to 0.25 from 3.19 in the original ES. The difference between the two curves at 280 nm illustrates that most of the lignin in the ES was removed after the treatment with resin.

A fixed amount of lignin is purported to coexist with carbohydrates in the ES of biomass, which certainly affects the purity of hemicelluloses.[31] Thus, the elimination of lignin from the ES facilitates the purification and the subsequent processing of hemicellulose. Treatments by activated carbon, ion exchange resin and nanofiltration have been previously proposed to remove lignin,[32] while resin treatment has been confirmed as one of the most effective means for its removal from the hydrolysis liquor. The ES of corn stalk was treated by ion exchange resin to eliminate the lignin. The characteristics of the original ES and the resin-treated ES, such as lignin, monosaccharide and polysaccharide concentrations, are presented in Table 2.

Resin treatment removed 85.21% of lignin, while 88.55% of sugars still remained. The recovery rate of monosaccharide was of 90.61%, higher than that of 88.13% of the polysaccharide. The pH of the ES increased to 5.9 from 4.2 of the original ES, which means a few acidic compounds were also removed. It is proposed that the resin treatment can remove most of the lignin from the ES of corn stalk, improve the feasibility of hemicelullose in the subsequent processing and ultimately, the purified sugars can be used as feedstock for furfural or xylitol production.

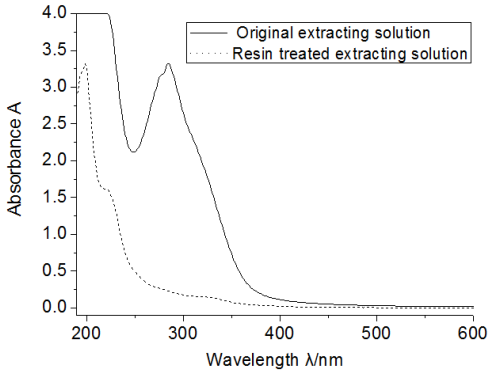

Figure 5: UV-Visible spectroscopy of ESs before and after treatment

Table 2
Chemical composition of various ES samples

Components	Original ES	Resin-treated ES
Lignin (g/L)	5.68	0.84
Monosaccharide (g/L)	2.77	2.51
Polysaccharide(g/L)	13.82	12.18

CONCLUSION

1) Corn stalk was cooked with hot water in a digester for hemicellulose extraction. The pH decreased gradually as a function of extraction time because of the production of acetic acid. The yields of hemicelluloses under different holding temperatures (140 °C, 150 °C, 160 °C, 170 °C) were determined, and it was confirmed that the pentoses, including xylose and arabinose, are the main sugars in the ES. In the four experiments, the yields of pentose showed the same variation trend of initially increasing and then gradually decreasing, due to the pentose in the ES converted into furfural with prolonged holding time. When the extraction was performed at a holding temperature of 160 °C for 180 min, the maximum

yield of pentose was 65.4%, in which 13.17 g/kg dry substrate arabinose and 134.72 g/kg dry substrate xylose were recovered, which can be regarded as an economic means for hemicellulose extraction from corn stalk.

2) The chroma of resin-treated ES dropped to 138 C.U. from 1630 C.U. in the original ES, and the absorption peak of UV-visible spectroscopy decreased from 3.19 to 0.25 at 280 nm, which indicated significant lignin removal by the resin treatment. The experimental results showed that the resin treatment could remove 85.21% of the lignin from the ES, whereas 88.55% sugars remained. This process is an alternative and effective mean for the improvement of hemicellulose recovery.

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REFERENCES

[1] S. Atsumi, A. F. Cann, M. R. Connor, C. R. Shen, K. M. Smith *et al*., *Metab. Eng*., **10**,305 (2008).
[2] S. Lee, M. O. Cho, C. H. Park, Y. Chung and J. H. Kim, *Energ. Fuel*., **22**, 3459 (2008).
[3] N. Qureshi, T. C. Ezeji, J. Ebener, B. S. Dien, M. A. Cotta *et al*., *Bioresour. Technol*., **99**, 5915 (2008).
[4] C. G. Yoo, C. Wang, C.Yu and T. H. Kim, *Appl. Biochem. Biotech*. **169**, 1648 (2013).
[5] S. Ryuand M. N. Karim, *Appl. Microbiol. Biotechnol*., **91**, 529 (2011).
[6] C. I. Ishizawa, T. Jeoh, W. S. Adney, M. E. Himmel, D. K. Johnson *et al*., *Cellulose*, **16**,677 (2009).
[7] A. Aden and T. Foust, *Cellulose*, **16**, 535 (2009).
[8] J. B. Stuart, L. K. Douglas and W. Adam, *BioEnerg. Res*., **7**, 509 (2014).
[9] K. A. Frank and S. W. Kevin, *J. Ind. Microbiol. Biotechnol*., **34**, 723 (2007).
[10] Q. Yong, X. Li, Y. Yuan, C. H. Lai, N. N. Zhang *et al*., *Appl. Biochem. Biotech*., **167**, 2330 (2012).
[11] X. B. Lu, Y. M. Zhang and Y. Liang, *Korean J. Chem. Eng*., **25**, 302 (2008).
[12] Y. Sun and J. Cheng, *Bioresour. Technol*., **83**, 1 (2002).
[13] S. G. Allen, D. Schulman, J. Lichwa and M. J. Antal, *Ind. Eng. Chem. Res*., **40**, 2934 (2002).
[14] L. W. Doner, H. K. Chau, M. L. Fishman and K. B. Hicks, *Cereal. Chem*., **75**, 408 (1998).
[15] R. B. Hespell, *J. Agr. Food. Chem*., **46**, 2615 (1998).
[16] B. Hahn-Hagerdal, K. Karhumaa, C. Fonseca, I. Spencer-Martins and M. F. Gorwa-Grauslund, *Microb.Biotechnol*., **74**, 937 (2007).
[17] A. Martinez, M. E. Rodriguez, M. L. Wells, S. W. York, J. F. Perston *et al*., *Biotechnol. Progr*., **17**, 287 (2001).
[18] H. T. Liu, H. R. Hu, M. S. Jahan, M. M. Baktash and Y. H. Ni, *J. Biobased Mater. Bio*., **8**, 1 (2014).
[19] M. Leschinsky, G. Zuckerstätter, H. K. Weber, H. Sixta and R. Patt, *Holzforschung*, **62**, 645 (2008).
[20] J. S. Gütsch and H. Sixta, *Holzforschung*, **65**, 511 (2011).
[21] J. S. Gütsch and H. Sixta, *Ind. Eng. Chem. Res*., **51**, 8624 (2012).
[22] [22] G. L. Hugh and J. D. Rousseau, *Biotechnol. Lett*., **14**, 421 (1992).
[23] R. Torget, P. Walter, M. HimmelandK. Grohmann, *Appl. Biochem. Biotech*., **28-29**, 75 (1991).
[24] A. Sluiter, R. Ruiz, C. Scarlata, J. Sluiter and D. Templeton, National Renewable Energy Laboratory (NREL), Golden, Colorado, 2005.
[25] A. Sluiter, B. Hames, R. Ruiz, C. Scarlata, J. Sluiter *et al*., National Renewable Energy Laboratory (NREL), Golden, Colorado, 2008.
[26] H. T. Liu, H. R. Hu, M. M. Baktash, M. S. Jahan, L. Ahsan *et al*., *Biomass. Bioenerg*., **66**, 320(2014).
[27] TAPPI, "UM 250. Acid-soluble lignin in wood and pulp", TAPPI useful method, 1991.
[28] Method CPPA, Technical section standard method H5P: color of pulp mill effluents, Montreal, Canada: Canadian Pulp and Paper Association, 1974.
[29] H. L. Chen, Y. C. Chen, H. Y. Zhan and S. Y. Fu, *Environ. Monit. Assess*., **175**, 321 (2011).
[30] X. Zhang, M. B. Tu and M. G. Paice, *BioEnerg. Res*., **4**, 246 (2011).
[31] J. J. Fenske, D. A. Griffin and M. H. Penner, *J. Ind. Microbiol. Biot*., **20**, 364 (1998).
[32] J. Shen, I. Kaur, M. M. Baktash, Z. He and Y. Ni, *Environ. Technol*., **35**, 2597 (2014).