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Conversion of agro-industrial corn and coconut by products into higher value-added products

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ABSTRACT

Agro-industrial by-products such as corn cobs, corn fiber, coconut debris and coconut fiber can be converted into high quality products such as glucose, xylose and xylitol, involving two important conversion processes: acid hydrolysis using sulfuric acid (H_2SO_4) and yeast fermentation. Prior to acid hydrolysis, delignifying the samples with alkali is necessary as it can reduce lignin interferences. Results clearly showed that the lignin removal from corn cobs, corn fiber, coconut debris and coconut fiber were 30.12±0.37, 37.71±0.71, 40.52±0.85 and 27.92±0.47%, respectively. However, the delignification process might also reduce the glucose and xylose contents from acid hydrolysates. In this study, the samples were hydrolyzed using 1, 3, 5 and 7% (v/v) H_2SO_4 with a ratio of 1:15 (g sample: mL acid) at 100ºC for 1 hour. It was found that maximum sugar contents from corn cobs and corn fiber can be obtained from the 3% H_2SO_4 treatment, while those from the coconut debris and coconut fiber were at 5% H_2SO_4. As determined by HPLC technique with the hydrolysates obtained by these conditions, it demonstrated that the glucose and xylose yields from corn cobs, corn fiber, coconut debris and coconut fiber were 9.72±0.86 and 9.91±0.51%, 3.46±0.14 and 10.70±0.12%, 0.22±0.12 and 2.53±0.33%, and 5.65±0.15 and 5.28±0.5% (w/w), respectively. During acid hydrolysis, however, inhibitory substances such as furfural, hydroxymethylfurfural and phenolics were simultaneously formed, accordingly, detoxification may then be required. The findings of a study of detoxification were that treatments with activated charcoal can reduce furfural and phenolic compounds but some sugars would be partially lost. An ion exchange chromatographic method would be more appropriate since it can minimize a number of these compounds into levels which can do no harm to fermenting yeasts (i.e. *Saccharomyces*, *Candida* spp.) as well as eliminating sugar loss.

Keywords: acid hydrolysis, xylose, glucose, by-products

INTRODUCTION

Lignocellulosic materials from crop by-products such as corn and coconut are inexpensive sources and widely found in Thailand. Corn is an important agricultural crop which is generally grown for industry, and by-products are generated annually at a high rate. Coconut is another crop that is grown in the coastal areas of many tropical countries and its wide variety of products are being applied in food and non-food products. Their compositions are mainly cellulose, hemicelluloses and lignin. (Palmqvist and Hahn-Hägerdal, 2000) Both celluloses and hemicelluloses contained in these by-products can be converted into glucose and xylose which are potential substrates for conversion to higher valued-added products such as ethanol and xylitol. Acid hydrolysis is rather simple and rapid (Mussatto and Roberto, 2003) which can generate a mixture of sugars that can then be biotechnologically converted by yeast. However, there are other substances such as furfural, hydroxymethylfurfural, acetic acid and phenolic compounds produced through hydrolysis. These compounds need to be removed because their toxicity might cause microbial cell morphological change or even death. (Domịnguez *et al*., 1997) Several detoxification treatments involve neutralization, overliming, activated charcoal adsorption and ion exchange resin have been effectively used. Adjustment of pH is normally performed and when combined it with the above methods, it can enable the hydrolysate to be used for fermentation. Conditions such as acid concentration and operation temperature are also important since they are responsible for degradation of sugars and maintained an appropriate level of toxic compounds for microbial activity.

The objectives of this research are to study the conversion of agro-industrial by-products with diluted sulfuric acid at 100˚C together with determining the efficiency of detoxification treatments and to quantify the glucose and xylose contents in the hydrolysates from corn and coconut by-products.

METHODOLOGY

1. Raw Materials

Corn cobs and corn fiber were freshly supplied from Chiangmai Frozen Foods Public Co., Ltd., Chiang Mai, and coconut debris and coconut fiber were in dried formed and obtained from Thai Coconut Fibre Industries Co., Ltd., Bangkok. All samples were size-reduced, dried and stored with initial moisture contents of not more than 2% for the corn and between 0.9-4.0% for coconut ones.

2. Preparation of Hydrolysates

By-products samples were individually mixed with 100 mL of 10% ammonium hydroxide (NH_4OH) solution at 5% solid content in a 250 mL Erlenmeyer flask and incubated in a shaker 160 rpm for 24 hr. The mixture was then filtered to separate the solid from the ammonia solution. The treated solid sample was washed and dried at 70˚C until the ammonia evaporated.

3. Acid Hydrolysis

Dried solid samples with and without ammonia treatment were mixed with diluted sulfuric acid (H_2SO_4) (1-5% for corn and 1-7% H_2SO_4, v/v for coconut samples) in the ratio of g sample to mL acid at 1:15. The condition was performed in magnetic-stirred flask at 100˚C for 1 hr. After the reaction was completed, the solids were separated by filtration. The volumes of filtrates and washes were then brought together and analyzed for contents of glucose, xylose, furfural and phenolic compounds.

4. Detoxification

4.1 Overliming

Hydrolysates overliming was conducted with calcium hydroxide ($Ca(OH)_2$) to pH 10 and solid precipitates were separated by vacuum filtration. The solutions were then adjusted with 1% HCl to lower the pH to 6.0 and kept cool.

4.2 Activated Charcoal Adsorption

The solutions were mixed with activated charcoal pellets (granular 2.5 mm, Merck) at the ratio of 10:1, and stirred at 30˚C for 30 hr. The solutions were recovered by filtration.

4.3 Ion Exchange Resin Treatment

Amberlite IR 93; weak base anion exchange resin (Sigma) was washed respectively with 1 N NaOH, DI water, 1 N HCl, DI water, 1 N NaOH and water before packed into columns. Resin was washed until the effluent pH was 7 before the hydrolysate was applied. The effluents were collected in fraction and tested with *p*-bromoanilineacetate reagent to detect the xylose content (Deschatelets and Yu, 1986). The selected fractions were collected together.

5. Analytical Methods

The concentrations of glucose and xylose were determined by High Performance Liquid Chromatography (HPLC) (Agilent HP1100) with Refractive Index Detector (RID) and Econosphere NH_2 (250 mm×46 mm) operational column temperature at 30˚C using 75% acetonitrile as a mobile phase, flow rate 1 mL/min and 10 µL sample inject volume. *Furfural* is analyzed with Gas Chromatography (GC) (Agilent 6890) using HP-1 methyl siloxane capillary column (30.0 m×320 µm×0.25 µm) *Phenolic compound* was assayed by Folin-Ciocalteau method and measured by UV spectrophotometer (Genesys 20) at 760 nm. (Waterman and Mole, 1994)

RESULTS AND DISCUSSION

The acid hydrolysis was carried out at sulfuric acid concentrations ranging from 1 to 7% (v/v) H_2SO_4 with the same reaction time and operational conditions. The results exhibited that diluted acid can hydrolyze the sample under mild condition to obtain the glucose and xylose whereas delignifying the samples with alkali prior to acid hydrolysis can also reduce the lignin interferences from materials as the results of lignin reduction from corn cobs, corn fiber, coconut debris and coconut fiber were 30.12±0.37, 37.71±0.71, 40.52±0.85 and 27.92±0.47% (w/v), respectively. Even though this method is able to reduce lignin content from materials without much sugar loss (Table 1), it might reduce a few contents of glucose and xylose from the hydrolysates.

All samples were hydrolyzed using 1, 3 and 5% (v/v) H_2SO_4 with the ratio of 1:15 (g sample: mL acid) at 100˚C for 1 hr. It was found that corn by-products had the maximum sugar content obtained from the 3% H_2SO_4 treatment while the coconut samples were at 5% H_2SO_4. Further experiments were carried out for both coconut samples at 7% H_2SO_4 and it was shown that 5% was still the most appropriate condition (Table 2). It revealed that the glucose and xylose yields, as determined by HPLC, from corn cobs, corn fiber, coconut debris and coconut fiber were 9.72±0.86 and 9.91±0.51%, 3.46±0.14 and 10.70±0.12%, 0.22±0.12 and 2.53±0.33%, and 5.65±0.15 and 5.28±0.50% (w/w), respectively. It obviously appeared that different raw materials' characteristics would lead to different acid hydrolysis conditions.

During acid hydrolysis, however, inhibitory substances such as furfural and phenolic compounds were simultaneously formed; detoxification would then increase the hydrolysate fermentibility with yeast. Results from Table 3 exhibited the yield of remaining glucose, xylose, furfural and phenolic compounds generated from all treatments. It was also found that activated charcoal adsorption can reduce furfural and phenolic compounds but some sugars would partially be lost. As the results when compared to non-treated treatment, the glucose and xylose contents from corn cobs, corn fiber, coconut debris and coconut fiber were 13.08±0.22 and 9.46±0.22%, 8.55±0.11 and 11.63±0.70%, 7.60±2.14 and 13.32±1.42%, and 1.98±0.72 and 14.29±1.65% (w/w), respectively. Although, reduction efficiency of furfural was in a considerable level (less than 0.5 g/L), phenolic compounds from corn cobs and corn fiber were more than 0.1 g/L which could be harmful to the fermenting yeasts (i.e. *Saccharomyces*, *Candida* spp.). (Massatto and Roberto, 2004) This finding differed from the ion exchange treatment which less sugar loss was occurred when compared to non-treated treatment and the results clearly showed that the glucose and xylose contents attained from corn cobs, corn fiber, coconut debris and coconut fiber were 24.95±2.22 and 18.46±1.88%, 14.10±0.027 and 16.66±0.25%, 4.93±0.36 and 14.71±2.40% and 1.43±0.52 and 24.81±0.39% (w/w), respectively. Moreover, it can efficiently minimize a number of these compounds into a level which can do no harm to fermenting yeast.

Table 1 Effects of delignification treatment on the loss of glucose and xylose

Sample	**Lignin Reduction (% w/v)**	**Glucose Loss (% w/w)**	**Xylose Loss (% w/w)**
Corn cobs	30.12±0.37	0.259±0.0052	0.655±0.0038
Corn fiber	37.71±0.71	0.176±0.010	0.306±0.0063
Coconut debris	40.52±0.85	0.249±0.0034	0.231±0.0042
Coconut fiber	27.92±0.47	0.219±0.0038	0.396±0.0079

Table 2 Effects of acid concentrations on the hydrolysis of by-products

Sample	H_2SO_4 (% v/v)	Glucose (% w/w)	Xylose (% w/w)	Furfural (g/L)	Phenolic Compound (g/L)
Corn cobs	1	5.28±0.12	7.96±1.09	0.011±0.00088	0.48±0.0042
	3	9.72±0.86	9.91±0.51	0.025±0.0012	0.42±0.023
	5	8.79±0.74	7.18±0.56	0.142±0.0076	0.38±0.0021
Corn fiber	1	4.20±1.43	2.61±0.15	0.025±0.00083	0.34±0.0050
	3	3.46±0.14	10.70±0.12	0.0092±0.00052	0.41±0.043
	5	4.84±1.51	7.48±0.08	0.024±0.0019	0.22±0.042
Coconut debris	1	0.146±0.075	1.66±0.015	ND	0.039±0.0088
	3	0.214±0.058	2.46±0.010	ND	0.041±0.0046
	5	0.220±0.12	2.53±0.33	ND	0.029±0.017
	7	0.905±0.32	2.06±0.71	ND	0.0094±0.0015
Coconut fiber	1	2.09±0.82	1.10±0.76	ND	0.075±0.027
	3	2.17±0.65	3.06±0.62	ND	0.12±0.054
	5	5.65±0.15	5.28±0.50	0.014±0.0057	0.063±0.062
	7	2.95±0.14	2.40±0.92	0.074±0.0037	0.023±0.0077

Table 3 Effects of detoxification treatments on the product contents

Sample	Glucose (% w/w)			
	Not treated	**AC**	**IE**	**AC + IE**
Corn cobs	14.87±0.215	13.08±0.22	24.95±2.22	12.29±0.24
Corn fiber	13.06±0.035	8.55±0.11	14.10±0.027	14.10±0.027
Coconut debris	12.77±0.30	7.60±2.14	4.93±0.36	4.93±0.36
Coconut fiber	8.53±0.38	1.98±0.72	1.43±0.52	1.43±0.51
	Xylose (% w/w)			
	Not treated	**AC**	**IE**	**AC + IE**
Corn cobs	18.29±0.44	9.46±0.22	18.46±1.88	15.29±0.20
Corn fiber	19.16±0.14	11.63±0.70	16.66±0.25	10.76±1.57
Coconut debris	20.99±0.29	13.32±1.42	14.71±2.40	8.94±3.42
Coconut fiber	21.63±0.17	14.29±1.65	24.81±0.39	5.98±0.71
	Furfural (g/L)			
	Not treated	**AC**	**IE**	**AC + IE**
Corn cobs	0.025±0.0012	0.0084±0.00096	ND	ND
Corn fiber	0.0092±0.00012	0.0018±0.00099	0.0031±0.000215	ND
Coconut debris	0.0074±0.0011	ND	0.0014±0.000193	ND
Coconut fiber	0.014±0.0057	0.010±0.00	0.0014±0.000013	ND
	Phenolic Compound (g/L)			
	Not treated	**AC**	**IE**	**AC + IE**
Corn cobs	0.42±0.023	0.19±0.49	0.0082±0.0025	0.0070±0.00019
Corn fiber	0.41±0.043	0.24±0.012	0.0068±0.00028	0.0052±0.00040
Coconut debris	0.0286±0.017	0.0057±0.00096	0.0040±0.0012	0.0051±0.000014
Coconut fiber	0.063±0.062	0.0052±0.0023	0.0041±0.00025	0.0024±0.00014

AC: Activated charcoal adsorption, IE: Ion exchange resin

CONCLUSION

Coconut by-products showed potential possibilities as alternative sources for value-added products, such as xylitol produced by yeast fermentation when compared to corn by-products. Omitting treatment, e.g. delignification and activated charcoal adsorption may reduce the production cost.

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