A COMPARATIVE STUDY OF THE HYDROLYSIS OF HEMICELLULOSES OBTAINED FROM TANZANIAN SUGARCANE BAGASSE UNDER DIFFERENT CONDITIONS

Protibha Nath Banerjee

Abstract— The xylose is the major sugar component present in the hemicelluloses of lignocellulosic biomass and the economic interest lies in the conversion of xylose to xylitol as it finds its application as sweetener for diabetic patients. The economic interest in xylitol production can be enhanced if the needed xylose solutions can be obtained from the hydrolysis of low-cost lignocellulosic wastes. Therefore, the primary objective of this study was to see the effect of different acids of different concentration and reaction time on the hydrolysis of hemicelluloses obtained from Tanzanian sugarcane bagasse. The hemicelluloses obtained by pressurised hot water and alkaline peroxide extraction from sugarcane bagasse were hydrolysed using sulphuric acid and phosphoric acid of different concentration and different reaction time. The hydrolysates after filtration were analysed by HPLC using Aminex HPX87P column and RID detector. The results showed that the maximum yield of xylose can be obtained using 1N sulphuric acid for 90 min at 100˚C.
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Index Terms— Sugarcane bagasse, acid hydrolysis, hemicelluloses, HPLC, .

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1 Introduction

The agro-industrial residues are one of the potential source of different monomeric sugars which has not been explored to its full potential. However, in the recent years these residues are gaining potential interest as raw materials for industrial application. Reusing and recycling of these residues will not only resolve the environmental issues associated with their build-up but will also help in adding value, creating employment and boosting socio-economic security of the rural people. Sugarcane bagasse is a kind of agricultural residue produced in large quantities by sugar industry in Tanzania. The major components of sugarcane bagasse are cellulose, hemicellulose and lignin with minor amount of ash and other lipophilic materials. Xylose (75-80%) is the major monomeric sugar of the hemicelluloses of bagasse followed by arabinose and minor quantities of other monomeric sugars. Xylose find its applications in many industrial sectors. Among others, the conversion of xylose to xylitol is of interest as it is used as sweetener for diabetic patients. Xylitol has important advantages over glucose or saccharose, such as anticarcinogenicity, low caloric value and negative heat of dissolution (Kim, Ryu, & Seo, 1999; Parajoo, Dom11nguez, & Dom11nguez,1996; Silva, Felipe, &Mancilha, 1998). The economics of the xylitol production process can be enhanced if the xylose is obtained from low cost agro-industrial waste like sugarcane bagasse hemicelluloses. Mineral acids are known to act as good catalyst for the hydrolysis of hemicelluloses and release of sugar monomers. In the present study sulphuric acid and phosphoric acid of different concentration and different reaction time at 100˚C was carried out and the hydrolysates were analysed by HPLC using Aminex HPX87P column and RID. The effect of different acid, acid concentration and reaction time were studied and the effectiveness of the hydrolysis was evaluated in terms of xylose yield.

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2 MATERIAL AND METHODS

2.1 Sugar composition of hemicelluloses

Each hemicellulosic fraction (1 mg) was transferred to a pear-shaped flask and dried in a vacuum oven at 40°C for 1 hour. Two mL of 2M HCl in anhydrous methanol was added to each flask and the samples were then kept at 105°C for 3 hours. A calibration solution containing equal amount (0.1mg/mL) of each sugar monomers and uronic acids (except 4-O-MeGlcA) was also subjected to methanolysis under similar condition. All samples were cooled to room temperature and neutralized by addition of 200 µL of pyridine. 1 mL of 0.1mg/mL sorbitol solution was added as internal standard to all the samples. The methanol was evaporated in stream of nitrogen, dried under vacuum at 40°C, silylated and analysed by GC according to Sundberg method (Sundberg etal, 1996 and Banerjee, 2007 & 2014).
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2.2 Content of bound lignin

Lignin associated with the hemicelluloses was determined by the AcBr method according to Iiyama and Wallis, (1988). The structural composition of lignin was determined by pyrolysis GC–MS with tetramethylammonium hydroxide (TMAH) addition (Banerjee, 2014).

2.3 Hydrolysis of hemicellulosic fraction from sugarcane bagasse

10 mg of H_1 and H_2 (steam treatment extracted hemicelluloses) and H_3 and H_4 (alkali extracted hemicelluloses) were hydrolysed using 0.5 N and 1 N sulphuric acid and phosphoric acid for 60 min and 90 min respectively. The samples were diluted with water (1:10 v/v), centrifuged to separate the water-insoluble matter and analysed by HPLC using Aminex HPX87P column and RID detector.

3 RESULTS AND DISCUSSION

3.1 Sugar composition of hemicelluloses

The major sugar units from methanolysis of steam extracted hemicelluloses was xylose (43.1and48.0%), followed by arabinose (25.1and24.3%) and glucose (16.8 and 15.2%) (Table1). The arabinose to xylose ratio was much lower in alkali extracted hemicelluloses than the steam treated hemicelluloses, indicating that the alkaline extraction resulted in more linear structures, while extraction with steam resulted in the release of hemicelluloses with more branching. These data indicate that steam treatment probably released more branched galactoarabinoxylans and β-glucans. In case of alkali treated samples (Table1), xylose was the predominant sugar (80.8 and 81.2%) followed by arabinose (6.4–6.7%), uronic acids, particularly glucuronic acid (0.4and0.7%) and 4-O-MeGlcA (0.6and0.7%), suggesting that the alkali-soluble hemicelluloses from sugarcane bagasse mainly consists of glucuronoarabinoxylans or L-arabino-(4-Omethyl-glucurono)-D-xylans. A low Ara/Xyl ratio would indicate a high degree of polymerization with little branching. The ratio of Ara/Xyl of the hemicelluloses obtained from alkaline treatment was lower (0.08) compared to the hemicelluloses obtained from steam treatment, indicating that the hemicelluloses obtained by alkali treatment were less branched than those from steam treatment.

3.2 Content of bound lignin

The hemicelluloses from steam treatment had higher lignin content (11.3–9.4%) than the corresponding alkali-soluble hemicelluloses (5.4 and 5.0%) suggesting that the a-benzyl ether linkage between lignin and hemicelluloses were significantly cleaved during alkaline peroxide treatment (Table 2). The associated lignin in the Hemicellulosic fractions were dominated by syringyl units, except in H2 indicating that syringyl units cleaved off significantly during steam treatment at higher temperature.

3.3 Hydrolysis of hemicellulosic fractions from sugarcane bagasse

The hemicelluloses from steam treatment (H1& H2) and alkaline peroxide extracted (H3&H4) were hydrolysed using 0.5 N and 1 N sulphuric acid and phosphoric acid for 60 min and 90 min respectively. Sulphuric acid was found to be more effective for the hydrolysis of xylans to xylose than phosphoric acid. The maximum yield was obtained when the hemicelluloses were hydrolysed using 1N sulphuric acid for 60 min at 100 ˚ C. The hemicelluloses on hydrolysed with 1N sulphuric acid for 60 min at 100 ˚ C resulted in the release of 0.38, 0.44, 0.73 and 0.71 mg/mL from H1, H2, H3 & H4 respectively which accounts for 90% xylose of the original xylose present in the hemicelluloses. The hemicelluloses on hydrolysis with 1N sulphuric acid for 90 min at 100 ˚ C resulted in the release of 0.36, 0.41, 0.68 and 0.69 mg/mL from H1, H2, H3&H4 respectively which accounts for 85% xylose of the original xylose present in the hemicelluloses. This results indicates that higher reaction time resulted into the release of less xylose which may be due to the degradation of xylose monomers released in the hydrolysate. The hemicelluloses on treatment of 0.5N sulphuric acid has not resulted into significant release of xylose from the xylans. On the other hand, phosphoric acid hydrolysis has resulted into a maximum release of 0.2, 0.23, 0.41 and 0.43 mg/mL xylose from H1, H2, H3&H4 respectively which accounts for 46.5%, 51.3%, 50.6% and 53% of the original xylose present in the hemicelluloses. Therefore, these data reveal that sulphuric acid is more effective in the hydrolysis of xylans to xylose as compared to phosphoric acid. However, hydrolysis with sulphuric acid for longer reaction time results into degradation of xylose monomers in the hydrolysate which is not very prominent in case of phosphoric acid. The optimum condition for the hydrolysis was found to be 1N sulphuric acid for 60 min at 100˚C.

4 CONCLUSION

The hemicellulose obtained from sugarcane bagasse by sequential extraction with steam treatment and alkaline peroxide treatment were hydrolysed using 0.5 N and 1 N sulphuric acid and phosphoric acid for 60 min and 90 min respectively. The hydrolysis with sulphuric acid was found to be more effective for the depolymerisation of xylans to xylose monomer as compared to phosphoric acid hydrolysis. However, hydrolysis with sulphuric acid for longer reaction time results into release of lower xylose monomers which may be due to degradation of xylose monomers released in the hydrolysate. The optimum condition for the hydrolysis was found to be 1N sulphuric acid for 60 min at 100˚C.

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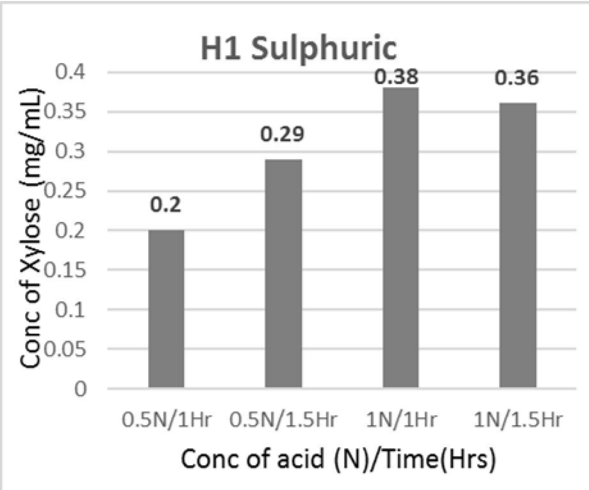

Fig.1: Xylose conc from the hydrolysis of H1 with Sulphuric acid

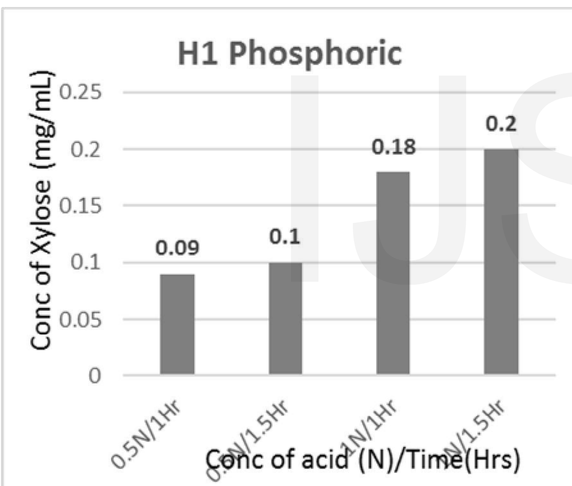

Fig.2: Xylose conc from the hydrolysis of H1 with phosphoric acid

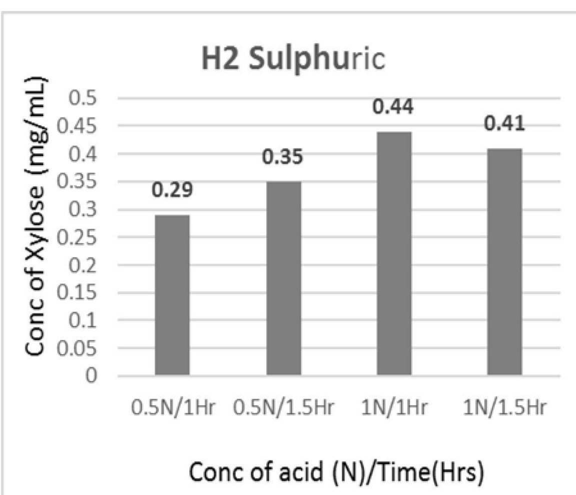

Fig.3: Xylose conc from the hydrolysis of H2 with Sulphuric acid

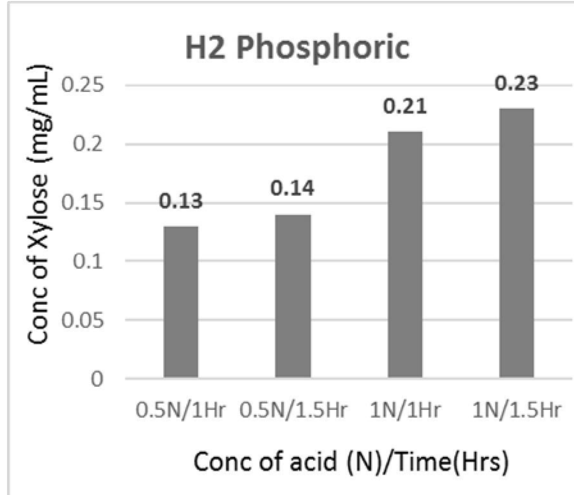

Fig.4: Xylose conc from the hydrolysis of H2 with phosphoric acid

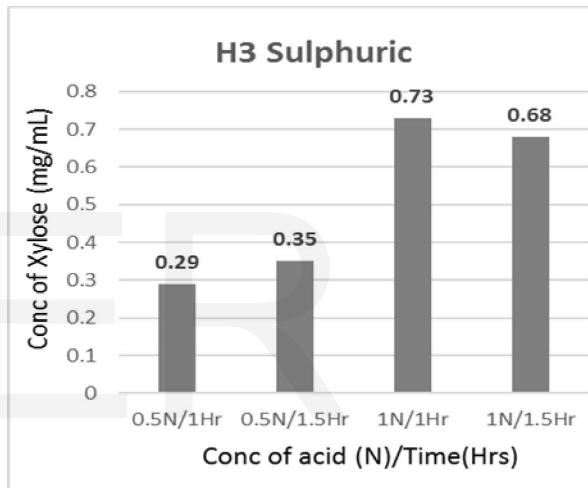

Fig.5: Xylose conc from the hydrolysis of H3 with Sulphuric acid

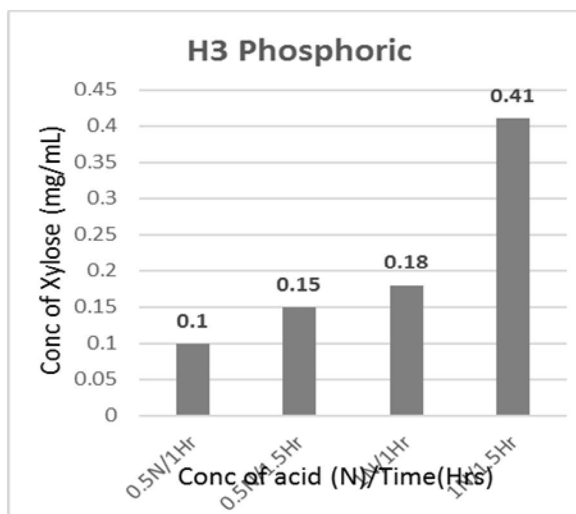

Fig.6: Xylose conc from the hydrolysis of H3 with phosphoric acid

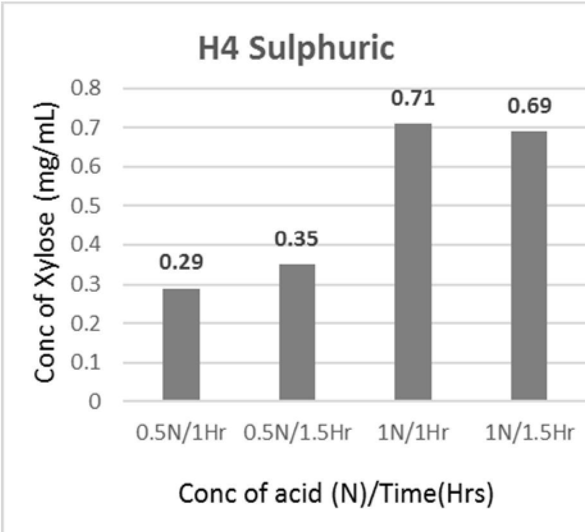

Fig.7: Xylose conc from the hydrolysis of H4 with Sulphuric acid

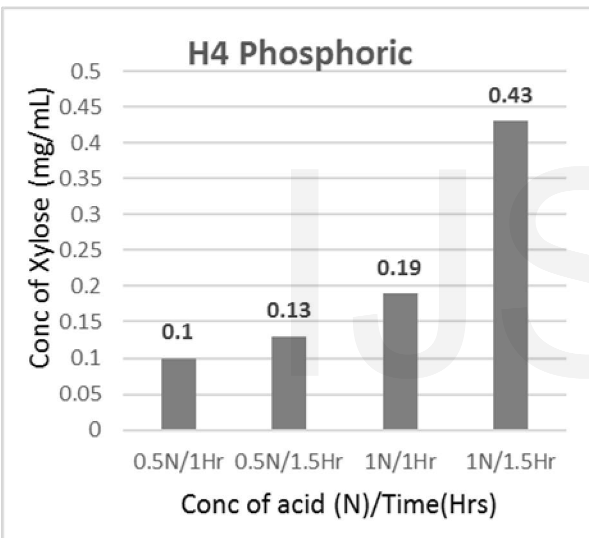

Fig.8: Xylose conc from the hydrolysis of H4 with phosphoric acid

Table 2: Lignin Content and P-Hydroxyphenyl (H), Guaiacyl- (G) and Syringyl- (S) Units determined in the Hemicellulosic Fractions from Sugarcane Bagasse by Pyrolysis GC-MS.

Hemicelluloses	Lignin content	H/G/S
H1	11.3	0.8/1.0/1.2
H2	9.4	1.0/1.0/0.6
H3	5.4	0.9/1.0/1.2
H4	5.0	0.8/1.0/1.0

Table 3: Concentration of xylose monomers released (mg/mL).

Sample	Acids	Conc of acids (N)	Time (hour)	Conc of xylose (mg/mL)
(H1)	H_2SO_4	0.5	1	0.2
			1.5	0.29
		1	1	0.38
			1.5	0.36
	H_3PO_4	0.5	1	0.09
			1.5	0.1
		1	1	0.18
			1.5	0.2
(H2)	H_2SO_4	0.5	1	0.29
			1.5	0.35
		1	1	0.44
			1.5	0.41
	H_3PO_4	0.5	1	0.13
			1.5	0.14
		1	1	0.21
			1.5	0.23
(H3)	H_2SO_4	0.5	1	0.29
			1.5	0.35
		1	1	0.73
			1.5	0.68
	H_3PO_4	0.5	1	0.1
			1.5	0.15
		1	1	0.18
			1.5	0.41
	H_2SO_4	0.5	1	0.21
			1.5	0.29
		1	1	0.71
			1.5	0.69

(H4)	H_3PO_4	0.5	1	0.08
			1.5	0.1
		1	1	0.14
			1.5	0.43

Table 1: Composition for the sugarcane bagasse hemicelluloses extracted sequentially by steam treatment (H1& H2) and alkaline peroxide (H3&H4).

	Hemicellulose sugar units composition [a]								4-O-Me GlcA	Ara/ Xyl Ratio
	Ara	Rha	Xyl	GlcA	GalA	Man	Gal	Glc		
H1	2.5	0.01	4.3	0.006	0.009	0.15	0.21	1.68	0.025	0.58
H2	2.43	0.009	4.8	0.005	0.008	0.06	0.2	1.52	0.02	0.51
H3	0.64	0.05	8.1	0.04	0.01	0.24	0.22	0.08	0.06	0.08
H4	0.67	0.01	8.12	0.07	0.07	0.21	0.24	0.07	0.07	0.08

[a] Expressed as mg of each sugars / 10 mg of Hemicelluloses

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