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ARABINOXYLANS FROM TANZANIAN SUGARCANE BAGASSE UNDER DIFFERENT CONDITIONS

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ABSTRACT

In the recent year's agro-industrial and forest residues are gaining potential interest as raw materials for industrial application. Reusing and recycling of these lignocellulosic 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 (Banerjee etal, 2014)and 80% of them are burnt by sugar and distillery plant to generate electricity[2] which is a misutilization of nature's precious material due to lack of proper biorefinery technologies. In the present study, non-cellulosic heteropolysaccharides was sequentially isolated from Tanzanian sugarcane bagasse using hot water (160°C and 170°C) followed by alkali treatment at different temperatures. The present study showed a promising sequential extraction for isolating arabinoxylans hemicelluloses with different degree of branching and molar mass from Tanzanian sugarcane bagasse. Low-molar-mass hemicelluloses (8000 and 10,000 g/mol), with more branching, were more easily extracted by hot water treatment, while high-molar-mass (18,000 and 24,000 g/mol) and more linear hemicelluloses were dissolved in the subsequent alkaline peroxide treatment. The hot water extracted sugarcane bagasse for 15 min resulted in the release of 23% and 25% of polymeric hemicelluloses of the total hemicelluloses in the raw material while alkaline post treatment of the residue from water extracted resulted in the release of 53% and 51% polymeric hemicelluloses of the total hemicelluloses in the raw material. Consequently, products with a high aggregated value could be developed using this xylan-rich fraction as an ingredient for industrial products.

Keywords: Sugarcane bagasse, Arabinoxylans, Degree of branching, Molar mass, SEC-MALLS

I.INTRODUCTION

Sugarcane bagasse is a kind of agricultural residue produced in large quantities by sugar industry. About 54 million dry tons of bagasse is produced annually throughout the world (Rodrigues et al., 2003 and Rowell & Keany, 1991) and about 80% of this is used in sugar and distillery plants as a source of energy (Pandey, Soccol, Nigam & Soccol, 2000) which is a misutilization of nature's precious material due to lack of proper biorefinery technologies. Bagasse generally contains 40-45% cellulose and 25-35% hemicellulose, an amorphous polymer

usually composed of xylose, arabinose, galactose, glucose, mannose and smaller amount of 4-O-methyl glucuronic acid. The remainder is mostly lignin plus lesser amount of minerals, waxes and other compounds (Jacobsen & Wymen 2002). Thus, in view of large availability of sugarcane bagasse and its importance as a raw material from industrial waste, there is a great potential of producing value added chemicals from its lignocellulosic constituents, such as hemicelluloses, in a biorefinery concept. Xu et al. (2006) isolated the hemicelluloses from sugarcane bagasse after alkaline treatment followed by organic solvent extraction. Peng et al. (2010) reported the characterization of sugarcane bagasse hemicelluloses obtained by hot water extraction at one temperature only (i.e. 55°C), followed by alkaline extraction. Banerjee *etal* (2014) reported the characterisation of non-cellulosic heteropolysaccharides from sugarcane bagasse obtained by pressurized hot water at different temperatures followed by alkaline peroxide extraction. In the present study, the hemicelluloses were first isolated by hot at two temperatures followed by alkaline peroxide extraction and the hemicelluloses obtained were characterized by chemical and spectroscopic methods.

II.EXPERIMENTAL

2.1Materials

Sugarcane bagasse was washed with water, air dried and then dried at 65°C for 24 h. The oven dried bagasse was ground in a Wiley mill to particles passing a 20-mesh screen and extracted with ethanol and toluene (2:1 v/v) in accordance with Tappi Method T204 om-88. The sugarcane bagasse was found to contain cellulose (49%), hemicelluloses (23%), lignin (21%), extractives (3%), and ash (3%).

2.2 Methods

Isolation of hemicelluloses by hot water treatment

Extractive free sugarcane bagasse (10 g) was subjected to hot water at 160°C and 170°C for 15 min. The extracts were cooled, filtered and concentrated to one-third of its volume at 40°C under reduced pressure. The solubilized hemicelluloses were isolated by precipitation of the concentrated filtrates with 3 vol of 95% EtOH, washed first with acetone and then with MTBE. The precipitated hemicelluloses were dried under vacuum at 40°C for 12 hours and are designated as **H_1 and H_2**.

Isolation of alkaline peroxide soluble Hemicellulosic fragments

Each of the foregoing hot water treated residues were post treated with 3% alkaline peroxide and magnesium sulphate (0.25%) with the pH adjusted to 11.6 with NaOH at 40°C for 12 hours. All the extracts were filtered off and washed with water. The combined supernatant fluids were neutralized to pH 6.0 with dropwise addition of 6M HCl over an ice bath. All the extracts were concentrated to one-third of its volume at 40°C under reduced pressure and precipitated with 3 vol of 95% EtOH. The precipitates were washed first with acetone and then with MTBE. The precipitated hemicelluloses were dried under vacuum at 40°C for 12 hours. These hemicelluloses are designated as **H_3 and H_4**.

2.3 HPSEC analysis

Molecular weight of the hemicellulosic fractions was determined using high-performance size-exclusion chromatography (HPSEC) and refractive index detection (Reed, 1995). Four gel permeation ultra-hydrogel columns in series, with exclusion sizes of 7x106, 4x105, 8x104 and 5x103 Da, were used. The eluent was 0.1M aq. NaNO2 at 0.6 mL/min. The samples, previously filtered through a membrane (0.22µm), were injected at a concentration of 2 mg/mL. The *dn/dc* value was taken as 1.5 and the results were processed with software provided by the manufacturer (Wyatt Technology Corporation).

2.4 Monosaccharide analysis

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 amout (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, 2014).

2.5 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 (Pranovich et al., 2005).

III. RESULTS AND DISCUSSION

3.1 Yield of Hemicelluloses

The hot water treatment of sugarcane bagasse at temperatures 160 and 170°C for 15 min resulted in the release of 23.0%, and 25.0% of polymeric hemicelluloses of the total hemicelluloses in the raw material (Table 1). The lignin associated with the hot water treatment hemicelluloses was 12.0%, 10.5% which accounts for 3.4%, and 3.2% of the original lignin, respectively. The alkaline peroxide post-treatment of the residues resulted in the release of 51.4% and 53.86% polymeric hemicelluloses of the total hemicelluloses in the raw material (Table 1). The lignin associated with the hemicelluloses extracted with alkaline peroxide was 6.0%, and 4.9%, which accounts for 3.7%, and 2.8% of the original lignin, respectively. This result indicated that alkaline peroxide treatment significantly cleaved, probably, the a-ether and ester bonds between lignin and hemicelluloses.

3.2 Non-cellulosic Carbohydrate Composition

The major sugar units from methanolysis of hot water extracted hemicelluloses was xylose (45.2and45.7%), followed by arabinose (27.2and23.7%) and glucose (8.2 and 9.8%) (Table1). The arabinose to xylose ratio was

much lower at 170°C than at 160°C (0.6–0.52), indicating that the high-temperature extraction resulted in more linear structures. These data indicate that hot water treatment probably released more branched galactoarabinoxylans and β-glucans. In case of alkali treated samples (Table1), xylose was the predominant sugar (79.1and82.3%) followed by arabinose (3.1–4.1%), uronic acids, particularly glucuronic acid (1.1and2.1%) and 4-O-MeGlcA (2.1and1.7%), 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 (0.04) compared to the hemicelluloses obtained from hot water treatment, indicating that the hemicelluloses obtained by alkali treatment were less branched than those from hot water treatment.

Table 1: Yield and composition of the sugarcane bagasse hemicelluloses extracted sequentially by hot water treatment and alkaline peroxide (H1 - H4).

Yield[a]		**Total**[b] **sugar content**	**Hemicelluloses sugar units composition**[c]									**Ara/Xyl Ratio**
			Ara	Rha	Xyl	GlcA	GlaA	Man	Gal	Glu	4-O-Me-GlcA	
H_1	60	87.9	27.2	0.6	45.2	0.6	1.5	2.1	2.4	8.2	0.1	0.6
H_2	65	89.4	23.7	1.1	45.7	1.5	1.1	2.6	3.5	9.8	0.4	0.52
H_2	130	93.8	3.1	0.1	79.1	1.1	0.1	2.9	2.4	2.9	2.1	0.04
H_4	123	94.9	4.1	0.1	82.3	2.1	0.3	1.0	0.2	3.1	1.7	0.05

[a]Expressed as mg/g of sugarcane bagasse

[b]Expressed as weight percent of total precipitated yield

[c]Expressed as weight percent of total precipitated yield

3.3 Molar mass determination

The hemicelluloses from the hot water treated extracts showed a relatively low degree of polymerization with molar-masses of 8000 and 10,000 g/mol (Table 2). On the other hand, high-molar-mass (18,000 and 24,000 g/mol) hemicelluloses were released during alkaline extraction. Additionally, the alkali-soluble hemicelluloses have broader molar-mass distribution with polydispersity indices from 3.7 and 4.1, while hemicelluloses from the hot water treated extracts showed narrow molar-mass distribution with polydispersity indices of 1.2 and 1.4.

Table 2: Weight average (Mw) and number average (Mn) molar mass and polydispersity (Mw/Mn) of hemicellulosic fractions released during extraction of sugarcane bagasse with hot water treatment and alkaline peroxide.

	H_1	**H_2**	**H_3**	**H_4**
M_W	8000	10000	18000	24000
M_n	6600	7000	4500	6500
M_W/Mn	1.2	1.4	4.1	3.7

3.4 Lignin Analysis

The hemicelluloses from hot water treatment had higher lignin content (12–10.5%) than the corresponding alkali-soluble hemicelluloses (6.0 and 4.9%) suggesting that the a-benzyl ether linkage between lignin and hemicelluloses were significantly cleaved during alkaline peroxide treatment (Table 3). The associated lignin in the Hemicellulosic fractions were dominated by syringyl units, except in **H_2** indicating that syringyl units cleaved off significantly during hot water treatment at higher temperatures (170°C).

Table 3: Lignin Content and *P*-Hydroxyphenyl (H), Guaiacyl- (G) and Syringyl- (S) Units determined in the hemicellulosic fractions from sugarcane bagasse by pyrolysis GC-MS

	Lignin content[a]	H/G/S[#]
H_1	12	0.8/1.0/1.2
H_2	10.5	1.0/1.0/1.6
H_2	6	0.4/1.0/1.2
H_4	4.9	1.2/1.0/1.1

[a]Expressed as weight percent of total precipitated yield.

[#] H = p-hydroxy phenyl, G = guaiacyl, S = syringyl.

IV. CONCLUSION

The present study showed that Low-molar-mass hemicelluloses, with more branching, were more easily extracted by hot water treatment, while high-molar-mass and more linear hemicelluloses were dissolved in the subsequent alkaline peroxide treatment. Moreover, noticeable differences in the chemical composition and molar-mass characteristics were observed among the hemicelluloses obtained from hot water and alkaline peroxide treatment. This study provided a efficient method for the extraction of hemicelluloses from sugarcane bagasse which can be utilized for various industrial applications.

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