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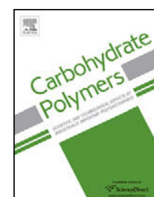

# Optimization of hot-compressed water pretreatment of bagasse and characterization of extracted hemicelluloses

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ABSTRACT

Developing optimum treatment and separation procedures for hemicellulose components of lignocellulosic biomass could be useful in ethanol fermentation processes and obtaining pure hemicelluloses as biopolymers. Sugarcane bagasse analyses indicate that xylose is the major hemicellulose component constituting 17.7% of dry bagasse weight. In this study the effects of treatment conditions such as time, temperature and pressure on the yields of extracted hemicelluloses were studied. The optimum conditions were achieved at 180 °C for 30 min and 1 MPa pressure, with the yield of xylose reaching to 85% and the concentrations of sugar degradation products such as HMF and furfural remaining minimal at 0.95 and 0.07 g/L, respectively. Further, isolation of hemicelluloses from extracted hemicelluloses solutions was performed using Alfa Laval M20 membrane filtration system in two steps: (1) concentration of high molar mass hemicelluloses by ultrafiltration; and (2) separation of low molar mass hemicelluloses and oligomeric sugars by nanofiltration. The isolated hemicelluloses with the optimum pretreatment conditions were characterized by FT-IR and $^{13}$C NMR techniques, resulting in agreement with typical spectra of xylan-type hemicelluloses.

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## 1. Introduction

The demand for using renewable resources for energy and chemicals has been increasing rapidly because of population growth. Lignocellulosic biomass is abundant, renewable, and cost effective sources of energy and chemicals (Demirbas, 2001; Zhu & Pan, 2010). Ethanol produced from biomass provides many advantages over fossil fuels, most of ethanol currently produced in the world comes from corn as a major feedstock and the extra demand created a tight supply of corn for food production and higher food prices. Therefore, research on using lignocellulosic biomass for production of ethanol has been intensely pursued (Sun & Cheng, 2002; Wyman, 1994).

Production of ethanol from biomass requires releasing of cellulose and hemicelluloses sugars through hydrolysis and carrying out of a fermentation process (Mielenz, 2001). Hydrolysis and fermentation of biomass are much more complex than just fermentation of sugars and, currently, biomass conversion to ethanol needs further technical developments to make it competitive, such as increasing the hydrolysis yields of sugars and improving the fermentability of mixed sugars (Zhu, Wang, Pan, & Gleisner, 2008). Pretreatment of biomass is the most common technical approach used to hydrolyzing recalcitrance lignocellulosic biomass (Galbe & Zacchi, 2007; Zhu & Pan, 2010), wherein the lignin seal is broken down and structures of cellulose and hemicelluloses are disrupted to allow their separation and, most often, followed by further hydrolysis to mixtures of monomeric sugars and lignin components. The monomeric sugars mixture can be separated from the lignin fraction and subjected to a fermentation process for conversion to ethanol (Mosier et al., 2005; Taherzadeh & Karimi, 2007). However, the presence of different sugars requires different enzymes for fermentation, making the process complicated, costly, and inefficient due to differences in enzyme selectivity and durability. Also, certain by-products derived from hemicellulose degradation such as furfural, formic and acetic acids suppress the enzyme activities and inhibit the fermentation process (Kumar, Kothari, Lee, & Gupta, Ram, 2011; Sun, 2008). Therefore, in addition to separation of lignin components, separation of hemicellulosic components can be a useful approach for increasing the efficiency of the fermentation process of main glucose components. Membrane filtration methods have been used successfully to separate hemicelluloses and inhibitor compounds such as furans and carboxylic acids from pretreatment hydrolyzate solutions (Mousavi & Moghdam, 2009; Sjöman, Mänttäri, Nyström, Koivikko, & Heikkilä, 2008; Weng et al., 2010). Membrane filtration techniques have the advantages of ease and high efficiency; low energy consumption, adjustable separation capability, and applicability under various conditions.

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Pretreatment of lignocellulosic biomass materials has been investigated by using several methods such as dilute acid hydrolysis, liquid hot-water extraction, steam explosion-based extraction, dilute acid steam explosion, alkaline extraction, ammonia fiber explosion, hydrothermal pretreatment, and many other methods (Mosier et al., 2005). Among these methods, the hydrothermal pretreatment method using hot compressed water showed promising separation of hemicelluloses polymers from biomass because of a low capital cost and no use of major chemicals. Also, this method allows recovering of hemicelluloses as oligomers rather than monomeric sugars (Saha, 2003). Hardwoods and woody biomass can be hydrolyzed with yields of more than 90% oligomeric sugars using the hydrothermal pretreatment method (Mosier et al., 2005). Agricultural residues such as corn stover, cornhusk, wheat straw and sugarcane bagasse has very similar chemical compositions to woody biomass and hardwood and represent an abundant, inexpensive, and readily available source of lignocellulosic biomass (Gould, 1984). Sugarcane bagasse is produced in large quantities from sugar industry in many countries including the United States. Approximately, 280 kg of bagasse are generated from 1 ton of sugarcane and 54 million dry tons of bagasse is produced annually throughout the world (Sun, Sun, Sun, & Su, 2004).

In a recent study (Boussarsar, Roge, & Mathlouthi, 2009), the hydrothermal pretreatment of bagasse was optimized in a temperature ranging from 170 to 190 °C, resulting in an optimum reaction time of 2 h at 170 °C. This pretreatment time appears to be long and, therefore, the major aim in this study was to investigate the pretreatment conditions for sugarcane bagasse at the same temperature range but using shorter reaction time of less than 1 h. The second aim was isolating of hemicellulose components from the pretreatment solutions using ultra and nanoflitration techniques, characterizing and investigating them as biopolymers.

## 2. Experimental

### 2.1. Chemicals

All chemicals used in this study were purchased from commercial resources and used without further purification. Calcium carbonate ≥99%, sulfuric acid 98%, certified ethanol, methanol and HPLC water were purchased from Fisher Scientific. Sugars used for HPLC analysis, D-glucose, D-mannose, D-galactose, D-arabinose and D-xylose, and dextran (1000, 5000, 12,000, 25,000, 50,000 and 80,000 Da) standards used for average molecular weight determinations were purchased from Sigma–Aldrich.

### 2.2. Raw material

De-pithed sugarcane bagasse used was provided by Sustainable Fuels LLC, New Iberia, LA. First it was air dried, then ground in a Wiley mill, and sieved through 40–80 mesh size sieve. Bagasse (15 g) was extracted with ethanol/benzene (1:1) mixture in a Soxhlet apparatus for 6 h to remove extractives and wax. Then bagasse was dried off from the solvent under the hood at room temperature for 24 h, and stored in plastic bag for moisture conditioning.

The chemical composition of the extracted bagasse sample was determined according to a known procedure (Sluiter et al., 2008b). Summary of this method is as follows: 0.3 g of sample was hydrolyzed by treating with 3 mL of 72% sulfuric acid for 1 h at room temperature by agitating and crushing constantly with glass rod. Then, 84 g deionized water (DI) was added to obtain 4% sulfuric acid solution and the mixture autoclaved at 121 °C for 1 h in a pressure tube to completely hydrolyze all oligomeric sugars into monomers. Then, the sugar solution was neutralized with calcium carbonate to pH 5.5 and filtered with 0.2 μm syringe nylon membrane (Millex-GN) for removal of fine particles. The solution was then analyzed by high performance liquid chromatography (HPLC) using an Agilent 1200 instrument equipped with a refractive index detector and Biorad column HPX 87P (7.8 mm × 300 mm) at 80 °C. Deionized water was used as an eluent at flow rate of 0.6 mL/min and the run last 50 min. Quantification of the sugars was done by comparing the peak integration values with those of chromatograms made with known sugar standards and presented in percentages based on dry bagasse weight. The acid soluble lignin content of the hydrolyzed sample was determined by Cary 100 Bio UV–vis Spectrophotometer (Varian Australia, Australia). The Klason lignin content of the hydrolyzed sample was determined by NREL/TP-510-42623 method. Ash content of bagasse was determined by NREL/TP-510-42622 technique by burning at 600 °C for 4 h.

### 2.3. Pretreatment procedures

The hot compressed water (HCW) pretreatment of bagasse was carried out in a high pressure Parr Reactor, series 4550 (Parr Instrument Company, Moline, IL) with a total volume of 450 mL. The reactor was loaded with bagasse (10 g) and water (100 g) in a 1:10 solid:liquid ratio and sealed. Then, the reactor was flushed with nitrogen for 10 min to remove the air and then filled with nitrogen until targeted pressure reached. Subsequently, heating and stirring at 200 rpm was applied until the desired reaction condition was reached. The pretreatment condition was varied: temperature, 170, 180, 190 °C; time, 10, 20, 30, 40, and 50 min, and pressure, 1, 2, 3, 4 and 5 MPa, resulting in 20 pretreatment samples in total. The pretreatment time began when the selected temperature was reached (approximately 20–30 min) and when the targeted time attained, the reaction was stopped by quenching the reactor in cold water. The liquid and solid portions were separated by vacuum pump filtration.

### 2.4. Acid hydrolysis and sugar analyses of hemicelluoses in pretreatment filtrates

Pretreatment filtrates were weighed and aliquots of them were hydrolyzed. The sugar contents were detected to determine the pretreatment efficiencies according to the standard NREL method (Sluiter et al., 2008a). Summary of this method is as follows: 20 mL of aliquots was placed in a pressure tube and certain amount of 72% of sulfuric acid was added to obtain a 4% sulfuric acid solution using the pre-calculated value reported in the appendix of the method. The, the sample mixture was autoclaved for 60 min at 121 °C, neutralized, filtered, and the sugar contents were determined by the same HPLC method described in Section 2.2. The sugar content weight values were then converted to those based on dry bagasse weights and then to percentage values based on each sugar types.

### 2.5. Determination of lignin components in pretreatment filtrates

The content of dissolved lignin in the extract was determined by scanning the aliquot on the UV–vis spectrophotometer as described in Section 2.2.

### 2.6. Molecular weights determination for extracted hemicelluloses

Average molecular weights of extracted hemicelluloses were determined by gel permeation chromatography (GPC). Aliquotes

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