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Research Paper

Hemicellulose extraction and characterization for applications in paper coatings and adhesives

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ABSTRACT

Hemicellulose materials are arguably the second most abundant renewable component of lignocellulosic biomass after cellulose. They are relatively under-utilized hetero-polysaccharides present in lignocellulosic biomass. In this research an alkaline treatment was optimized for extraction of polymeric hemicellulose from fully bleached hardwood pulp (B-HWP) and partially delignified switchgrass (SWG). The hemicellulose extracted from B-HWP was relatively pure with zero percent lignin and 89.5% xylose content whereas the partially delignified SWG hemicellulose contained about 6-3% lignin and 72–82% xylose, depending on the NaOH concentration during extraction (3–17% NaOH solution). A maximum molecular weight of SWG hemicellulose of 64,300 g/mol was achieved for the 10% NaOH solution extraction, whereas the MW of B-HWP hemicellulose at 10% NaOH solution extraction was lower at 49,200 g/mol. We have demonstrated that the residual lignin in SWG hemicellulose lowered the system T_g and this might be utilized as a way to increase the applications of hemicellulose in high value biomaterials. Furthermore, the hemicellulose could be crosslinked with zirconium to develop a water resistant gel for coating or adhesive applications. Our results showed that the loading stress required to break an hemicellulose based adhesive connection between two paper surfaces was 0.89, 2.02, 2.75, 3.46, and 3.11 (MPa) for 2, 4, 6, 8 and 10% AZC samples, indicating that up to about 8% AZC crosslinker in the hemicellulose increases the adhesive behavior of the material.

1. Introduction

Currently, there is intense research activity targeted at the replacement of petroleum-based products with renewable lignocellulosic-biomass-based products in order to reduce the environmental impacts, provide new energy resources, and conserve petroleum resources. In addition, there is a great interest for the lignocellulosic biofuels industry to develop valuable co-products that can improve the overall economics of a biofuel production process.

Lignocellulosic biomass is a term referring to the woody and non-woody dry matter that is mainly composed of three polymers: cellulose, hemicellulose and lignin. Cellulose is a homogeneous polymer consisting of C6 glucose monomers, and hemicellulose is a heterogeneous polymer consisting of C5 and C6 monomeric residues (Anwar et al., 2014). Hemicellulose associates with lignin through covalent bonds known as lignin-carbohydrate complexes (LCC), of which comprise phenyl glycoside bonds, esters and benzyl ethers (Balakshin et al., 2011; Christopher, 2012). However the linkage between hemicellulose and cellulose has been assumed to be through H-bonding (Lodish et al., 2000). Hemicelluloses are carbohydrate polymers containing xylans (arabinoxylans and 4-O-methyl-glucuronoxylans), galactomannans, glucomannans, and xyloglucans (4-linked β-D-glucans with attached side chains). Indeed, upon acid hydrolysis, hemicelluloses are easily fragmented into their constitutional pyranoses and furanoses sugar units which include: xylose, mannose, arabinose, glucose, glucuronic acid and others (Sjöström, 1993). Structural and compositional differences in hemicellulose exist between different biomasses (Sjöström, 1993).

During conventional Kraft pulping the majority of hemicelluloses are degraded into low molecular weight isosaccharinic acids which, along with lignin and other pulping chemicals, dissolve in the black liquor (Al-Dajani and Tschirner, 2008). About 80% of the black liquor solids come from lignin and hemicellulose. The black liquor is usually burned to produce energy, however, since the heating value of hemicellulose (≈13.6 MJ/Kg) is much lower than that of lignin (≈27 MJ/Kg), its combustion represents an inefficient use of the feedstock

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resource (Kang et al., 2012). Thus it would be beneficial to pre-extract the hemicellulose prior to the pulping in order to develop a number of bioproducts such as biochemical and biomaterials to enhance the value extracted from woody and non-woody materials. Hemicelluloses can be used in value-added industrial applications including hydrogels, thermoplastics, coatings and additives in papermaking, in cosmetics, and in pharmaceutical applications such as drug carriers (Gabrielii et al., 2000; Jain et al., 2000; Fredon et al., 2002). Actually, hemicellulose is a green substitute for petroleum based polyols and is a non-food-based substitute for starch polyols. Therefore, extraction of hemicellulose would have great potential to supply raw materials for the coating industry.

Hemicellulose extraction from biomass is an essential step for the production of a wide range of fuels, biomaterials and chemicals (Farhat et al., 2017). Many different effective methods have been used to isolate hemicellulose from woody and non-woody tissues. Those methods include dilute acid pretreatments (Knappert et al., 1981), alkaline extraction (Egües et al., 2012), alkaline peroxide extraction (Doner and Hicks, 1997), liquid hot water extraction (Hasegawa et al., 2004; Saska and Ozer, 1995), steam treatment (Palm and Zacchi, 2003), microwave treatment (Azhar, 2015), ionic liquid extraction (Froschauer et al., 2013) and others (Mosier et al., 2005). Alkaline extraction is well studied, and it is known as a strong and efficient method for hemicellulose extraction (Cheng et al., 2011).

Hemicelluloses can be liberated by alkaline extraction since alkaline treatment can completely or partially cleave ester bonds between lignin and hemicellulose in the cell walls, resulting in the dissolution of hemicelluloses. Moreover, it is known that hydroxide ions cause swelling of cellulose, hydrolysis of ester linkage, and disruption of intermolecular hydrogen bonds between cellulose and hemicellulose, thereby bringing a portion of the hemicellulosic material into solution. Alkaline extraction is compatible chemically with the kraft pulping process, which is well established processing annually 100 s of millions of tons of wood and its associated hemicellulose.

Extraction of hemicellulose from non-delignified biomass (lignocellulosic materials) yields polysaccharides that may be contaminated with high proportions of lignin, whereas its extraction from bleached pulps results in a relatively pure hemicellulose (Puls and Saake, 2004).

This study identified an efficient alkaline extraction of hemicellulose from a woody and non-woody biomass source − bleached hardwood pulp (B-HWP) and partially delignified switchgrass (SWG) − using extraction conditions of 3, 7, 10, 13 and 17% NaOH w/w solutions at 50 °C for 3 h. The physicochemical properties and the structural features of these hemicellulosic samples were investigated. Hemicellulose extracted from SWG by 10% NaOH was studied for its ability to be used in coating or binder material crosslinked with a water-soluble zirconium salt. The importance of this study are reflected in being the first report that investigated the differences between pure hemicelluloses and partially purified hemicelluloses. Also this is the first study that reports the possibility for lignin to have a role of plasticizer for hemicellulose. In addition to that, improved understanding of hemicellulose/zirconium crosslinking will allow for further improvement of the material for paper coating, surface sizing, adhesives and other applications.

2. Experimental section

2.1. Materials

Switchgrass (SWG) was harvested in August 2011 from Cherry Research Farm in Goldsboro, North Carolina, State Department of Agriculture, and bleached hardwood pulp (B-HWP), with an origin from the southeastern United States, was provided by International Paper. The materials were stored indoors and the moisture content allowed to equilibrate for 4 weeks prior to use. Moisture content of the air-dried materials was measured by oven drying at 105 °C until constant moisture content was achieved.

2.2. Delignification of switchgrass

The SWG was processed into powder in a Wiley mill to pass through a 1-mm mesh size screen attached to the mill. The powder was sieved on a 60-mesh screen (250 μm openings). SWG fractions were de-lignified by adding a solution consisting of 30% by weight of an aqueous NaOH solution (2% by weight of NaOH) and 70% anhydrous ethanol (96% by weight ethanol) at 75 °C (40:1 liquid to solid ratio) and stirred for 2.5 h with a mechanical stirrer to solubilize some of the lignin. The suspension was allowed to cool to room temperature under ambient conditions before filtration with a house vacuum on Whatman Filter Paper (Whatman International Ltd., Maidstone, England, Catalog Number 1004 150, quantitative number 4, 150 mm diameter). The obtained solid (partially delignified SWG) was used for downstream hemicellulose extraction

2.3. Hemicellulose extraction from partially delignified switchgrass and bleached hardwood pulp

Hemicellulose was isolated from partially delignified SWG and B-HWP by an alkaline extraction method. The partially delignified SWG samples were transferred to a NaOH solution at concentrations of 3, 7, 10, 13 and 17% by weight and stirred for 3 h at 50 °C to solubilize hemicellulose. However, after being processed by pulping in a 200 gallon pilot plant hydrapulper, the B-HWP was subjected to hemicellulose extraction by 10% NaOH solution (based on optimum SWG results, see later) and stirred for 3 h at 50 °C which was the same as the extraction conditions applied for hemicellulose extraction from SWG. At the end of the 3-h period, the suspension was filtered with a house vacuum on Whatman GF/A glass microfiber filter paper to remove the filtrate containing hemicellulose. The filtrate pH was adjusted to 5–6 by adding 25% acetic acid and then transferred to 96% ethanol (2x ethanol volume relative to the filtrate) at 4 °C. The mixture was left for two days to allow the hemicellulose to precipitate (no stirring) and settle to the bottom. The clear liquid above the precipitate layer was carefully removed by vacuum suction. The hemicellulose precipitate was washed 3 times with 70% ethanol. The hemicellulose material was freeze-dried to yield hemicellulose powder. (Each extraction condition was repeated 4 times and the yield average and standard deviation were calculated). The hemicelluloses are labeled as indicated in Table 1.

2.4. Sugar compositional analysis and lignin quantification

The sugar compositions of SWG and B-HWP, as well as hemicellulose extracted from both biomasses were determined by high performance liquid chromatography (HPLC) analysis of monomeric sugars (glucose, xylose, galactose, arabinose and mannose). Briefly, 0.3 g oven-dried, ground sample was taken and hydrolyzed by 72% (w/v) sulfuric acid followed by 4% (w/v), sulfuric acid hydrolysis (Ehrman, 1996). The hydrolysate was then filtered to remove solids from the liquid (the filter paper and solids were kept in the oven at 105 °C for 2 days to quantify the acid insoluble lignin and ash content). The

Table 1
Hemicellulose Extraction Conditions Nomenclature.

Hemicellulose	Sodium hydroxide concentration (%)	Biomass
SWG-HC3	3	Switchgrass
SWG-HC7	7	Switchgrass
SWG-HC10	10	Switchgrass
SWG-HC13	13	Switchgrass
SWG-HC17	17	Switchgrass
HW-HC10	10	Bleached hardwood pulp