Industrial Crops and Products 59 (2014) 282–289

Contents lists available at ScienceDirect

Industrial Crops and Products

journal homepage: www.elsevier.com/locate/indcrop

Film-forming polymers from distillers' grains: structural and material properties

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ARTICLE INFO

Article history:
Received 5 February 2014
Received in revised form 10 May 2014
Accepted 18 May 2014

Keywords:
2D-NMR
Alkaline extraction
Animal feed
Distillers' grains
Hemicelluloses
Paper coating

ABSTRACT

Hemicelluloses are promising biopolymers for substituting petroleum-based polymers. Distillers' grains (DG), a residual product from the dry grind ethanol industry, has a high hemicellulose and low lignin content making it an interesting feedstock as a low-cost source of hemicelluloses. This study fractionated DG into an alkali-soluble hemicellulose-rich polymer (DG-HC) and an alkali-insoluble residue (DG-AI). Chemical and 2D-NMR analyses suggested that DG-HC was rich in arabinoxylans, whereas DG-AI was more rich in glucans, along with crude proteins and fat. The DG-HC was made into stand-alone films or thin film coatings on paper, and evaluated by DSC, TGA, FT-IR, corrected water vapor transfer rate and tensile strength. Created DG-HC films were stiff with a T_g of about 174 °C. When coated onto paper, DG-HC can effectively increase paper dry and wet tensile strength. The residual DG-AI was characterized showing good potential for animal feed, having approximately 95% *in vitro* true dry matter digestibility.

1. Introduction

The demand for sustainable and biodegradable polymeric materials has increased in recent years due to the concerns of non-degradable solid waste, greenhouse gas emission and petroleum crisis. The sustainable polymeric materials mainly come from plant sources of biopolymers including starch, cellulose, hemicelluloses, and protein that can be actively used in the packaging and coating industries. Hemicelluloses present in many types of biomass are underutilized and should be considered more bio-based products. This underutilization may be due to many plants having a high lignin content, 10–30 wt%, which hinders the hemicelluloses isolation and affects the properties of extracted materials, making delignification a necessary step for hemicelluloses extraction from most biomasses (Sun et al., 2011). Considering these issues, distillers' grains (DG), with their low lignin content, might be a potential suitable raw material for hemicelluloses extraction and conversion into useful bio-based materials.

Distillers' grains (DG) are the remaining residues after the distillation process from the corn ethanol process. They are typically dried and sold as animal feed at a relatively low price. Consequently, effective utilization of corn ethanol byproducts as a bio-based chemical could also further improve the corn ethanol plants' profitability and thus further lower the bioethanol price. DG typically consists of ~30% protein, ~20% hemicelluloses, ~15% cellulose, ~5% starch, ~10% crude fat and minimal amount of lignin (~1.5%), although the compositions vary among different manufacturers (Kim et al., 2010). The low lignin content of DG should facilitate extracting carbohydrates and producing bio-based materials. Extensive research has been carried out on converting DG-derived polysaccharides into monosaccharides (simple sugars) (Bals et al., 2006; Noureddini et al., 2009), fermenting them into ethanol in order to improve ethanol yield (Dien et al., 2008; Kim et al., 2008), and using protein-rich residues as animal feed (Tucker et al., 2004). However, hydrolyzing and fermenting the glucan and xylan components of the DG require different conditions and specialized enzymes than the starch portion of corn making it currently economically unfeasible (Gírio et al., 2010). Developing other ways to convert the DG carbohydrates into other high-value products is therefore of interest.

Abbreviations: DG, distillers' grains; DG-HC, alkali-soluble hemicellulose-rich polymer fraction extracted from DG; DG-AI, alkali-insoluble residue from DG; IVT-DMD, *in vitro* true dry matter digestibility; NDF, neutral detergent fiber; NDFD, neutral detergent fiber digestibility; WVTR, water vapor transfer rate; CWVTR, corrected water vapor transfer rate; TI, tensile index; SAB, strain at break; MOE, modulus of elasticity.

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http://dx.doi.org/10.1016/j.indcrop.2014.05.023
0926-6690/

Cellulose and hemicelluloses are two of the major components in most of the lignocellulosic plant tissues. Cellulose is composed exclusively of D-glucose linked through β-(1→4) linkages, and is a linear homopolymer with high molecular weights (Sjöström, 1993). Cellulose molecules aggregate into uniform and compact microfibrils acting as structural materials in plant tissues (Sjöström, 1993). Hemicelluloses are amorphous heteropolymers with a number of diversified types and structures incorporating many kinds of monosaccharide units. Enzymatic or acid hydrolysis will release primarily D-xylose, L-arabinose, D-galactose, D-mannose, and uronic acids.

Few studies have analyzed the detailed structures of hemicelluloses extracted from DG, although it should be similar to the hemicelluloses extracted from corn or corn hull, which have been extensively studied. Similarly to other cereal crops, the major hemicelluloses found from the corn endosperm and the bran is arabinoxylan (Gáspár et al., 2007). Arabinoxylan is a heterogeneous polymer with β-(1→4)-D-xylopyranose units being substituted at C-2 or/and C-3 position by α-L-arabinofuranose (Spiridon and Popa, 2008). If the arabinoxylan backbone is lightly substituted by D-glucuronic acid at C-2/C-3 position, these are termed glucuronoarabinoxylans, which is also one type of hemicelluloses common in corn kernel (Ebringerová and Heinze, 2000; Ebringerová et al., 2005). Another minor type in corn kernel are heteroxylans. Heteroxylans also have β-(1→4)-D-xylopyranose backbones, but are heavily substituted by side-chains with one or more monomers of α-L-arabinofuranose, D-galactopyranose, D-glucuronic acid, and some minor entities (Ebringerová and Heinze, 2000; Ebringerová et al., 2005). Similar to many other graminaceous plants, corn hemicelluloses are partially acylated by hydroxycinnamic acids, such as ferulic and *p*-coumaric acids (Allerdings et al., 2006; Hatfield and Marita, 2010).

A widely studied extraction method for polymeric hemicelluloses from plants is steeping in alkali or alkaline peroxide. Alkaline or alkaline peroxide extraction of hemicelluloses has been substantially researched for corn fiber (Hespell, 1998; Doner and Hicks, 1997), corn cob (Hromádková et al., 1999), woody biomass (Sun et al., 2011; Yuan et al., 2010) and cereal straws or sugarcane bagasse (Sun et al., 2000; Sun et al., 2002; Sun et al., 2004). Few studies, however, have performed similar extractions on DG, which represents a low-cost source of hemicellulosic materials. Additionally, the low lignin content of DG would facilitate the hemicellulose extraction process (Sun et al., 2000). Considerable proteins and carbohydrates are expected to remain even after extracting hemicelluloses, so the residue may still retain the potential to be utilized as animal feed. Consequently, to maximize the utilization of DG as biomass, a compositional understanding and value recovery of those residual components is required.

Recently, hemicelluloses have been researched for the potential uses in food packaging, edible film for food, food coating, and some pharmaceutical and biomedical application (Hansen and Plackett, 2008). However, those applications only represent a small collection of potential utilization of hemicelluloses and far more areas can be explored. Paper coating is a possible use of polymeric hemicelluloses (Laine et al., 2013). Paper coatings are either used to provide smoothness and optical properties to the paper, or barrier coatings helping prevent permeation by water, solvents and greases, and providing better ink holdout. Hydroxyl-rich hemicellulose polymers can be modified as paper coatings allowing proper hydrophilicity and ink wettability. Current paper coatings are typically derived from petroleum-based chemicals, making natural coatings desired due to environmental concerns.

In this study, our goals are: (1) to extract polymeric hemicelluloses from DG by alkaline solution, (2) to evaluate their quality as films forming material, either as standalone films or cast onto paper as coatings, and (3) to test the possible animal feed value of the protein-rich alkaline extraction residue. We propose a novel utilization of polymeric hemicelluloses and a biorefinery process that may be incorporated into a current dry-grind corn ethanol production process, resulting in valuable products beyond ethanol and animal feed.

2. Experimental

2.1. Fractionation of DG

DG was obtained from Didion Milling Inc. (Cambria, WI). For alkaline extraction, triplicate runs were performed. For each run, about 30 g DG and 600 ml of 3% NaOH solution at 50 °C (1:20 solid to liquid weight ratio) were mixed. The mixture was maintained at 50 °C and stirred at 170 rpm in an Excella E24 incubator shaker (New Brunswick Scientific) for 3 h. The mixture was then separated into alkaline soluble and insoluble fractions by centrifugation at 3900 rpm for 10 min. The collected alkaline insoluble fraction (DG-AI) was washed with water and freeze-dried for further characterization. The alkali-soluble part was adjusted to pH 5.5 by 6 M HCl, concentrated to about one third of its original volume on a rotary evaporator at reduced pressure, and slowly poured into a three-time volume of 95% ethanol with constant stirring. The precipitated solid was separated and washed with 95% ethanol through filter paper to give an alkali-soluble hemicellulose-rich fraction (DG-HC). The ethanol-soluble fraction was also collected as a solid after evaporating at reduced pressure.

2.2. Compositional analyses

Samples being determined for neutral sugar contents were hydrolyzed according to the procedure described previously (Min et al., 2011). Approximately 100 mg of DG samples were reacted with 1.5 mL 72% H_2SO_4 at room temperature for 1.5 h. The mixture was then diluted to a 3% H_2SO_4 concentration and autoclaved at 121 °C for 1.5 h. The hydrolysate was separated by centrifugation, which was then analyzed through a Dionex ICS-3000 Ion Chromatography (IC) System for carbohydrates. Each liquid sample injected to the system was filtered through Phobic PTFE 0.20 μm filter (Millipore). The analysis was performed through a Dionex Carbopac PA20 ion-exchange analytical column (3 × 150 mm, Thermo Scientific) accompanied by a Dionex Carbopac PA20 guard column (3 × 50 mm, Thermo Scientific). Detection was performed by an integrated amperometric detector with a disposable gold electrode. The column compartment was maintained at 30 °C. NaOH (0.5 M) was used to mix with water or 0.1 M NaOH to maintain the ion-exchange analytical column at pH ~12. The Milli-Q water and 0.1 M NaOH were used as eluent at a rate of 0.3 mL/min with the following gradient: 0–30 min: 100% Milli-Q water; 30–45 min: 75% 0.1 M NaOH; 45–55 min: 100% Milli-Q water.

The uronic acid concentration in the hydrolysate was estimated by a photometric method according to Filisetti-Cozzi and Carpita (1991). Crude protein content was determined according to AOAC official method 990.03. The ash content was determined according to the NREL procedure (NREL/TP-510-42622, 2008). Crude fat content was determined according to AOAC official method 2003.06. Lignin content was determined according to AOAC official method 973.18.

2.3. Nuclear magnetic resonance (NMR) spectroscopy

NMR spectra of raw DG, DG-HC, and DG-AI were acquired on a Bruker Biospin (Billerica, MA) AVANCE 700 MHz spectrometer fitted with a cryogenically-cooled 5-mm TXI gradient probe with inverse geometry (proton coils closest to the sample). Finely ball-milled samples of DG and DG-AI (~50 mg) were swelled