Food Hydrocolloids 80 (2018) 53–59

Contents lists available at ScienceDirect

Food Hydrocolloids

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

Molecular and conformational properties of hemicellulose fiber gum from dried distillers grains with solubles

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ARTICLE INFO

Article history:
Received 5 October 2017
Received in revised form
4 January 2018
Accepted 15 January 2018

Keywords:
NMR
Arabinoxylan
Molecular structure
Hemicellulose
Dried distillers grains with solubles

ABSTRACT

Hemicellulose fraction from dried distillers grains with solubles (DDGS) was isolated and its molecular structural and conformational properties were elucidated by using partial acid hydrolysis, methylation analysis and NMR spectroscopy. Using 0.3 M sodium hydroxide (120 °C), a purified water soluble hemicellulose molecules (HFG) was isolated from de-oiled and de-starched DDGS. The yield of HFG was up to 27% (w/w). Results from monosaccharide composition, methylation analysis indicated that HFG comprised three types of sugar residues: arabinose based sugar residues including t-Ara*f* (28.6 mol%) and 1,3-Ara*f* (4.9 mol%); xylose based sugar residues including t-Xyl*p* (14.1 mol%), 1,4-Xyl*p* (18.6 mol%), 1,3, 4-Xyl*p* (20.8 mol%), and 1,2,3,4-Xyl*p* (6.8 mol%); and galactose based sugar residue including t-Gal*p* (6.1 mol %). Partial acid hydrolysis combined with high performance size exclusion chromatography (HPSEC) indicated that protein (4.69%) was covalently linked with carbohydrate portion in HFG, which can be potentially used as food emulsifiers. Although HFG had a high substitution degree (75%), it was a more rigid molecule compare to gum arabic, indicating a shorter branching chain of HFG. 1D and 2D NMR spectroscopy confirmed the presence of t-xyl*p*, 2,3,4-β-D-xyl*p*, t-α-L-ara*f*, 3-α-L-ara*f* and 4-β-D-xyl*p* and several linkage fragments were deduced: t-ara*f*→2-ara*f*→2-*O*-(1,2,3,4-xyl), t-ara*f*→2-ara*f*→3-*O*-(1,2,3,4-xyl), t-ara*f*→2-ara*f*→3-ara*f* and t-gal→2-ara. The information gained from this study could help us to better understand the properties of hemicellulose and its performance in applications.

1. Introduction

Dried distillers grains with solubles (DDGS) are a by-product from corn-ethanol production. The raw DDGS contains about 17% (w/w) of hemicellulose, 28–32% (w/w) protein, 10–13% (w/w) oil and 19% (w/w) of other carbohydrates such as cellulose and starch (Kim, Amezcua, Utterback, & Parsons, 2008). In ethanol production, each bushel of corn (25.4 kg) produces about 11.8 L of ethanol and 7.7 kg of DDGS (Lyons, Kelsall, & Murtagh, 1995). The production of DDGS in United States reached 42.9 million tons in 2014–2015 (Wisner, 2014). Most of DDGS are used as low-value animal feed (Spiehs, Whitney, & Shurson, 2002).

Recently, the value-added utilization of protein, hemicellulose, and oil in DDGS have attracted rising attention but most of the research focused on extraction and functional study of these components (Brehmer, Bals, Sanders, & Dale, 2008; Reddy, Zhang, & Yang, 2013; Singh & Cheryan, 1998; Wolf & Lawton, 1997; Xu, Reddy, & Yang, 2009). To our knowledge, no literature exists about the studying of physicochemical and structure properties of hemicellulose from DDGS. Corn fiber gum, which is extracted from corn bran, has been reported to have excellent emulsification properties (Jin et al., 2017; Yadav, Cooke, Johnston, & Hicks, 2010a; Yadav, Fishman, Chau, Johnston, & Hicks, 2007a; Yadav, Johnston, & Hicks, 2009, 2008a,; Yadav, Johnston, Hotchkiss, & Hicks, 2007b; Yadav, Moreau, Hotchkiss, & Hicks, 2012a; Yadav, Moreau, Johnston, & Hicks, 2007c; Yadav, Nunez, & Hicks, 2011; Yadav, Parris, Johnston, & Hicks, 2008b; Yadav, Parris, Johnston, Onwulata, & Hicks, 2010b; Yadav, Strahan, Mukhopadhyay, Hotchkiss, & Hicks, 2012b; Yadav, Zhang, Luan, Ding, & Zhang, 2013). However, DDGS is a fermented product of corn. During the fermentation process, very complicated reactions could happen, new compounds were produced, and carbohydrate might react with other compounds or be broken down by some enzymes, etc. The objectives of this study were to determine the monosaccharide composition, molecular structure, and if protein and hemicellulose are covalently linked. It is important to understand the key structural elements that are essential for optimal emulsification

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https://doi.org/10.1016/j.foodhyd.2018.01.019
0268-005X/

properties. The information gained from this study could enable us to better understand the properties of hemicellulose from DDGS, and its performance in applications.

2. Materials and methods

2.1. Materials

Dried DDGS was supplied by MGP Ingredients Inc. (Atchison, KS). All chemicals were of reagent grade unless otherwise specified. Alpha-amylase (Termamyl 120L) was provided by Novozymes Corp (Franklinton, NC). The enzyme activity was 120 KNU/g (KNU = Kilo Novo Units alpha-amylase, the amount of enzyme which breaks down 5.26 g starch per hour at Novo Nordisks standard method for determination of alpha amylase). Dialysis membrane tubing with 6000–8000 Da molecular cut-off was purchased from Fisher Scientific (Lenexa, KS).

2.2. Extraction and purification of hemicellulose from DDGS

The extraction and purification procedure was shown in Fig. 1. DDGS (100 g) was ground, passed through 40 mesh sieves, and de-oiled by 300 mL of hexane under 2 h agitation for five times. The air-dried, de-oiled residue was treated with α-amylase solution (pH 6.2, 92 °C, 5 h) to remove the starch molecules. The mixture was centrifuged (12406 g for 25 min) to remove the supernatant and washed with 200 mL of water for 4 times to thoroughly remove the degraded starch. The oven dried de-oiled, de-starched DDGS (40 g) was then mixed with 400 mL 0.3 M NaOH in a Parr reactor at 120 °C for 1 h. After centrifugation, the supernatant was collected and the pellet (residue) was discarded. The pH of the alkaline supernatant was adjusted to 4.0 by adding acid to precipitate acid insoluble fractions. This precipitate is called Hemicellulose A (Hemi. A). The precipitated Hemi. A was collected by centrifugation at 12406g for 25 min. Three volumes of ethanol were gradually added to the supernatant with stirring to precipitate the major arabinoxylan fraction, Hemicellulose B, or Hemi. B. This hemicellulose B is called "hemicellulose fiber gum" (HFG) in this article. The HFG was allowed to settle out as a white flocculent precipitate at the bottom of the beaker overnight at 4 °C. The clear alcohol/water mixture above the precipitate was removed by decantation. The white flocculent precipitate was transferred into another beaker, suspended in water and freeze-dried.

2.3. Chemical composition of HFG

Total sugar and monosaccharide composition analysis was conducted according to the procedure of Kang et al. (2011) with slightly modification. The sample was hydrolyzed by 1 M H_2SO_4 and diluted 50 times. The diluted samples were passed through a 0.45 μm filter and injected to a high-performance anion exchange chromatograph with pulsed amperometric detection (HPAEC-PAD) (Dionex Corporation, Sunnyvale, CA). Separations were achieved with isocratic eluent (15 mM NaOH) on a CarboPac PA1 column (250 × 3 mm I.D., Dionex Corporation) and a guard column (3 × 50 mm, Dionex Corporation) at 25 °C with a flow rate of

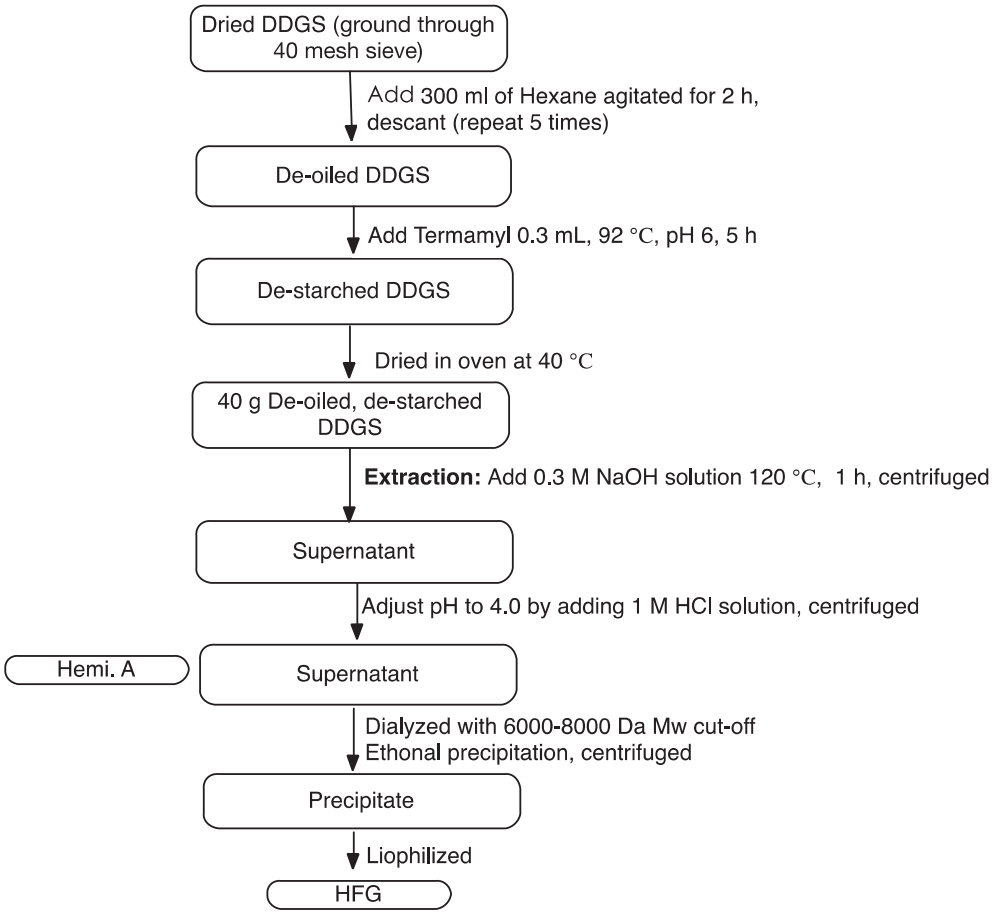

Fig. 1. Scheme for extraction of hemicellulos fiber gum (HFG) from DDGS.