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Rapeseed straw as a renewable source of hemicelluloses: Extraction, characterization and film formation

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ABSTRACT

Polymeric hemicelluloses were extracted by autohydrolysis and alkali from a biomass feed consisting of the stems of rapeseed straw according to a full statistical factorial screening design. Water extraction yielded fractions rich in galactoglucomannan, while alkaline extraction yielded primarily xylan. The extracted galactoglucomannan and xylans had similar molecular weights, while the yield of xylan was higher than the yield of galactoglucomannan. The extracted hemicellulose fractions also contained some lignin (7–15%) and traces of Ca, K, Na, and Si. Free-standing films were prepared from the hemicellulose fractions with different xylan:galactoglucomannan ratios. The rapeseed xylan films showed strain-to-break values >60% without any added plasticizers.

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1. Introduction

The biorefinery concept involves the fractionation and conversion of biomass feedstock into new streams of value-adding chemicals, materials and biofuels. Hemicellulose has long been of high interest as a resource in existing and future developing biorefineries and is most preferably obtained from sources previously considered low-cost waste and where there is no competition with existing food production (Ragauskas et al., 2006; FitzPatrick, Champagne, Cunningham, & Whitney, 2010). The extraction and isolation of hemicelluloses have been studied for decades (Yanovsky, 1939; Hägglund, Lindeberg, & McPherson, 1956) and have lately attracted increasing attention Willför et al., 2003; Benkö et al., 2007; Kabel, Bos, Zeevalking, Voragen, & Schols, 2007; Parajó, Garrote, Cruz, & Dominguez, 2004; Parsons, Cenkowski, Sorensen, Beta, & Arntfield, 2013; Carvalheiro, Duarte, & Gírio, 2008). Different agricultural wastes, such as wheat straw (Sun, Sun, Fowler, & Baird, 2005; Sun, Tomkinson, Wang, & Xiao, 2000a; Fang, Sun, Salisbury, Fowler, & Tomkinson, 1999; Sun, Lawther, & Banks, 1998; Sun, Lawther, & Banks, 1996; Sun, Lawther, & Banks, 1995; Ruiz et al., 2013), barley husks (Roos, Persson, Krawczyk, Zacchi, & Stålbrand, 2009), maize stems, rye straw, rice straw (Song, Pranovich, & Holmbom, 2012; Xiao, Sun, & Sun, 2001; Sun, Tomkinson, Ma, & Liang, 2000b), spent grain (Carvalheiro, Esteves, Parajó, Pereira, & Gírio, 2004; Nabarlatz, Ebringerová, & Montané, 2007), flax shives (Parsons et al., 2013; Jacobs, Palm, Zacchi, & Dahlman, 2003), sugarcane bagasse (Sun, Sun, Sun, & Su, 2004) and barley straw (Sun & Sun, 2002), among others, have been investigated in the last decade as hemicellulose sources for fuel, chemical and material production.

Hemicelluloses are important building components in the cell walls of higher plants and comprise roughly one-fourth to one-third of most plant biomass. They are branched polysaccharides composed of many different monosugars, including xylose, arabinose, glucose, galactose, mannose, fucose, and glucuronic acid, with a lower degree of polymerization than cellulose. The structures of hemicelluloses isolated from annual plants such as maize, rice, oats, sunflower, rye, barley and wheat straw differ from the structures of hemicelluloses isolated from wood and are generally more complex with more side-groups (Ren & Sun, 2010). Hemicelluloses are generally divided into four groups: (1) xyloglycans (xylans); (2) mannoglycans (mannans); (3) xyloglucans (XG); and (4) mixed-linkage β-glucans (Ebringerová, Hromádková, & Heinze, 2005). Xylan is the main type of hemicellulose in herbaceous plants, while the mannan type occurs to a lesser extent (Ren & Sun, 2010).

Hemicelluloses are, after cellulose, the most abundant plant polysaccharides and are promising raw materials for renewable films with good barrier and mechanical properties. (Albertsson, Edlund, & Varma, 2011; Hansen & Plackett, 2008) Hemicelluloses from different sources have been investigated and utilized

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to make barrier films (Edlund, Ryberg Zhu, & Albertsson, 2010; Ruiz et al., 2013; Benkö et al., 2007; Hartman, Albertsson, & Sjöberg, 2006a; Hartman, Albertsson, Söderqvist Lindblad, & Sjöberg, 2006b; Gröndahl, Eriksson, & Gatenholm, 2004; Goksu, Karamanlioglu, Bakir, Yilmaz, & Yilmazer, 2007; Zhang & Whistler, 2004; Mikkonen et al., 2009; Saadatmand et al., 2013; Ibn Yaich, Edlund, & Albertsson, 2012; Ibn Yaich, Edlund, & Albertsson, 2014; Ibn Yaich, Edlund, & Albertsson, 2015; Zhu Ryberg, Edlund, & Albertsson, 2011).

Hemicelluloses can be extracted from the plant cell wall in many ways, including acid hydrolysis, autohydrolysis, alkaline pretreatments and organic solvents. However, none of the available methods liberate 100% yields of hemicelluloses without dissolution of other components from the cell wall. The hemicellulose will degrade partially or completely depending on the severity of the extraction conditions (Carvalheiro et al., 2008; Garrote, Domínguez, & Parajó, 1999). Extraction parameters such as temperature, pH and time will ultimately influence the possible applications of the extracted fractions, such as fuel or packaging and coatings (Carvalheiro et al., 2008; Hansen & Plackett, 2008; Gírio et al., 2010). Glucomannan has been shown to dissolve with a preserved polymeric structure in the hot aqueous liquor during thermomechanical pulping (Willför et al., 2003; Song, Pranovich, Sumerskiy, & Holmbom, 2008; Benkö et al., 2007; Lundqvist et al., 2002; Lundqvist et al., 2003; Teleman, Nordström, Tenkanen, Jacobs, & Dahlman, 2003). The extraction of hemicelluloses using alkaline reagents and water from plant material is also well established (Carvalheiro et al., 2008). Alkaline extraction conditions have been shown in previous studies to yield a xylan-rich fraction (Ren & Sun, 2010, sid. 78; Kabel, Schols, & Voragen, 2002a; Kabel et al., 2002b; Nabarlatz et al., 2007; Parajó et al., 2004). Past and present research has focused on the separation and use of hemicelluloses from wood as a source of bio-ethanol for fuel and material production.

Oil-rapeseed has long been cultivated, with many existing commercial hybrids to produce seeds for the production of oil and rapeseed methyl ester. The rapeseed woody stem has a diameter of 1–4 cm and a height of 1.5 m. The stem is not suitable for cattle feed but is left in the field as nutrients after harvest. Research on oil-rapeseed straw valorization has so far only focused on fuel applications (Ryden et al., 2014; Wood et al., 2014; Mathew, Chaney, Crook, & Humphries, 2011a; Mathew, Chaney, Crook, & Humphries, 2011b; Lu, Zhang, & Angelidaki, 2009; López-Linares et al., 2014; Lu, Zhang, & Angelidaki, 2011; Jeong, Um, Kim, & Oh, 2010). Oil rapeseed has many important applications, and in the interest of applying the biorefinery concept, it will be important to find value-added applications of the straw, which is currently considered a waste.

Our aim was to extract polysaccharide-rich fractions from oil-rapeseed straw, to evaluate the influence of extraction conditions on the structure, composition and yield of the recovered fractions, and to utilize the fractions in the design of renewable plastic films. The extraction protocol is purposely designed to provide a scalable and straight-forward method that generates extracts that can be used without subsequent purification.

2. Experimental

2.1. Materials and extraction

2.1.1. Materials

Rapeseed straw with a dryness of 91% was kindly provided by Svensk Raps and stored in the dark until use. A NaOH stock solution with a concentration of 10.25 mol/L was prepared by dissolving NaOH pellets (VWR International, 99.7% dryness, CAS nr: 1310-73-2) in deionized water, and the concentration was determined by titration. Sulfuric acid (72%, LabService AB, Sweden) was used for acid hydrolysis. L-(+)-Arabinose (99.9%, CAS nr: 5328-37-0, Sigma), D-(+)-galactose (99.9%, CAS nr: 59-23-4, Sigma-Aldrich), D-(+)-glucose (99%, CAS nr: 50-99-7, Sigma), D-(+)-xylose (99%, CAS nr: 58-86-6, Sigma), D-(+)-mannose (99%, CAS nr: 3458-28-4, Sigma) was used as standard in the HPLC-PAD. For NMR analysis, deuterium oxide (D, 99.9%, CAS nr: 7789-20-0, Cambridge Isotope laboratories, Inc., USA) and dry dimethyl sulfoxide-d_6 (D, 99.9% and 0.05% TMS as an internal standard, CAS nr: 2206-27-1, Cambridge Isotope laboratories, Inc., USA) from ampoules was used. Ethanol (96 vol%, CAS nr: 64-17-5, VWR Chemicals) was used for precipitation of polysaccharides. A 10 mM NaOH(aq) solution was prepared by dilution of 1 mol/L NaOH (Chem solute, Th Geyer, Germany). Carboxymethyl cellulose sodium salt (CMC) (medium viscosity of 400–1000 m Pa s, 2% in water, degree of substitution of 0.3 and weight average molecular weight (M_w) of 550,000 g/mol, CAS number: 9004-32-4, Sigma Aldrich) was used in film preparation.

Table 1
Extraction conditions selected according to a statistical full factorial screening design.

Extraction	Temperature (°C)		NaOH (mol/L)		Time (min)	
A	105	–	0	–	20	–
B	105	–	0	–	60	+
C	105	–	0.5	+	20	–
D	105	–	0.5	+	60	+
E	140	+	0	–	20	–
F	140	+	0	–	60	+
G	140	+	0.5	+	20	–
H	140	+	0.5	+	60	+
Center points (center 1, center 2)	120		0.1		30	

2.1.2. Extraction

The effect of time, temperature and pH on the extraction process outcome was evaluated according to a statistical full factorial screening design. Eight extractions (A–H) were performed in which the time, temperature and pH were varied simultaneously from a low (–) to a high (+) level, as described in Table 1. Two reference extractions were also performed, so called center points, center 1 and center 2, with conditions intermediate between the high and low levels.

Extractions were performed in 2.5 L steel autoclaves, charged with 50 g or 100 g dried rapeseed straw and evacuated for 30 min. NaOH extraction solutions at 0.1 M and 0.5 M were prepared by dilution from a 10.25 M NaOH stock solution with deionized water. The extraction liquid, either deionized water or NaOH(aq), was then introduced into the autoclaves by vacuum suction to reach a liquid-to-straw ratio of 10:1. The autoclaves were subsequently immersed in a steam-heated ethylene glycol bath with the autoclaves set slightly inclined to induce mixing by rotation. To compensate for the temperature ramp in the autoclaves, 10 min was added to the extraction time to allow the contents of the autoclaves to reach the extraction temperature. The extractions were terminated by removing the autoclaves from the steam-heated ethylene glycol bath and placing them in a water cooling bath for 20 min. The extraction liquids were collected by pouring and by pressing the straw and rinsing once with distilled water and then stored cold. To concentrate the extraction liquids, water was removed in a rotatory evaporator at 40 °C. The remaining extracts were then freeze dried for 24 to 72 h.

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