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Intensification of hemicellulose hot-water extraction from spruce wood in a batch extractor – Effects of wood particle size

Jens Krogell [a,*], Ekaterina Korotkova [a], Kari Eränen [b], Andrey Pranovich [a], Tapio Salmi [b], Dmitry Murzin [b], Stefan Willför [a]

[a] Åbo Akademi Process Chemistry Centre, c/o Laboratory of Wood and Paper Chemistry, Porthansgatan 3, FI-20500 Åbo, Turku, Finland
[b] Åbo Akademi Process Chemistry Centre, c/o Laboratory of Industrial Chemistry and Reaction Engineering, Biskopsgatan 8, FI-20500 Åbo, Turku, Finland

HIGHLIGHTS

- Different wood particle sizes were studied for hemicellulose extraction at 170 °C.
- Smaller particle sizes gives faster extraction and slightly better yield.
- The reaction order was 1.5st for 0.5–2 mm and pseudo-first for 2–12.5 mm particles.
- Hemicellulose molar-mass dropped rapidly during the first 10 min of extraction.
- For maximum yield of high-molar-mass hemicelluloses 20 min extraction was optimal.

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ABSTRACT

The effect of five different wood particle size fractions between 0.5 and 12.5 mm on hot-water extraction of acetylated water-soluble hemicelluloses from spruce wood with a batch extraction setup at 170 °C was investigated. Extraction kinetics, with regard to particle size, was also studied. The purpose was to intensify the hemicellulose extraction for high molar mass hemicelluloses at high yield and purity. About 30% of the wood was dissolved and basically all the hemicelluloses could be extracted. The average molar masses of the extracted hemicelluloses decreased rapidly during the first 10 min of the extraction, but were not much affected by the difference in wood particle sizes. Smaller particles resulted in higher extraction rates. The reaction order was established to be of pseudo-first order for particles above 2 mm and 1.5st order for particles smaller than 2 mm. The effective diffusion coefficient was determined to be 9.11×10^{-10} m^2/s.

1. Introduction

The biorefinery concept aims at utilizing the whole biomass for different products. Refining the biomass in a biorefinery comprises of several steps; pretreatment, fractionation, biological, and/or chemical treatment in several steps depending on the end product. This calls for an initial separation of the different components in the biomass, e.g., wood, and converting them into value-added products such as biochemicals, renewable materials, and biofuels (Alén, 2011). With this approach, it is possible to improve the financial revenue for the existing forest-based industries. To replace petro-based chemicals and products with bio-based ones is of great importance and both environmentally and economically sustainable.

Wood is known to be high potential raw material for biorefineries because it is the most abundant and renewable source of lignocellulosic material in the world. Its three main components; cellulose (40–45%), hemicelluloses (20–30%), and lignin (20–30%) (Timell, 1967) can all be used for further processing to new products. Today, the cellulose is principally used for pulp and papermaking, and the other two are mainly burned for energy generation. Converting the pulp and paper industry into an even more biorefinery-oriented industry would mean that hemicelluloses and lignin should be utilized more efficiently. Hemicelluloses have attracted an increasing interest during the last decade as feedstock for bioethanol, biopolymers, emulsion stabilizers, and possible health applications (Xu et al., 2011; Willför et al., 2008; Mikkonen et al., 2009). Lignin, as a residue from a bioethanol plant, can also be used as raw material in a different kind of biorefinery (Zhang et al., 2013).

* Corresponding author. Address: Laboratory of Wood and Paper Chemistry, Åbo Akademi University, Porthankatu 3, 20100 Turku, Finland. Tel.: +358 2 215 4888; fax: +358 2 215 4868.
E-mail address: jekrogel@abo.fi (J. Krogell).

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Norway spruce is an important tree species for pulp and paper industries when producing mechanical pulp, especially in northern Europe. Spruce hemicelluloses consist mainly of acetylated galactoglucomannan (AcGGM). AcGGM has a backbone of β-D-(1→4)-glucopyranosyl and β-D-(1→4)-mannopyranosyl units in a linear or slightly branched chain. Single α-D-galactopyranose units are attached to the main chain by (1→6)-bonds. Also, *O*-acetyl groups are attached to the C-2 and C-3 positions in the main chain, on the average one group per 3–4 hexose units. An approximate ratio of galactose-to-glucose-to-mannose is around 0.5–1.1:1:3.5–4.5 for water-soluble AcGGM (Willför et al., 2003, 2008). The average weight molar mass M_w of native AcGGM has been reported to be between 20 and 50 kDa and the degree of polymerization varies from 100 to 400 (Timell, 1967; Sjöström, 1993; Willför et al., 2003). However, the molar mass and degree of polymerization is strongly dependent on the method of isolation and purification.

Over the years, several different methods for isolating hemicelluloses from wood have been studied. Microwave heat treatment has been applied for isolation of spruce hemicelluloses at different temperatures and times (Lundqvist et al., 2002) and also combined with steam explosion (Palm and Zacchi, 2003). Capek et al. (2000) extracted hemicelluloses from spruce sawdust with alkali to determine the fine structures of the hemicelluloses. GGM can also be extracted with plain water at room temperature or at elevated temperature below the boiling point, although at very low yields (Willför et al., 2003; Willför and Holmbom, 2004).

Pressurized hot-water extraction (PHWE) is nowadays a promising method under investigation for extracting hemicelluloses and sugars from wood and an interesting method, because the solvent used is water. Comparing to other industrially used solvents, water is inexpensive, easy to handle and non-toxic and thus making it a very good solvent for the chemical industry. Generally, a lot of studies on hemicellulose extraction with hot-water have been made and depending on the extraction method, the extraction equipment and, maybe most importantly, the wood species or material used makes them different. Depending on the desired end products or apparatus used, different methods have different areas of use. Several studies have been done with batch accelerated solvent extraction (ASE) (Song et al., 2008, 2011a,b). In these studies, the authors tried to preserve the hemicellulose structure by regulating the pH during extraction with different buffers and found out that a pH level around 4 was optimal at a temperature of 170 °C. Leppänen et al. (2011) used a continuous flow-through system with temperatures ranging from 120 °C to 240 °C. They also concluded that an extraction temperature of 170–180 °C is the most promising range to obtain high-molar-mass hemicelluloses from spruce wood. Extensive extraction time and higher temperatures lead to the degradation of the hemicelluloses due to autohydrolysis (Borrega et al., 2011). At elevated temperatures, water auto-ionization generates hydronium ions (Zumdahl and Zumdahl, 2007) and cleaving of acetyl groups from the AcGGM starts. This lowers the pH in the extract and thus catalyzes the cleavage of more acetyl groups. The formed acetic acid and other anionic compounds eventually causes cleavage of the glycosidic bonds between the sugar units, with a decrease in the molar mass of the hemicelluloses as a result (Lai, 2001; Fengel and Wegener, 1984).

The aim of this study was to evaluate the effect of wood particle size on hot-water extraction of long-chain acetylated water-soluble hemicelluloses from spruce wood with a batch extraction setup, while minimizing the extraction of other wood components, especially lignin. Furthermore, the extraction kinetics for different particle sizes was of interest. The ultimate goal is to control the extraction to get the desired hemicelluloses at high yield and purity with as high as possible molar mass.

2. Experimental

2.1. Material

A healthy 38-year-old Norway spruce tree was felled in southern Finland and a part of the stem was sawn out at 0.7–1 m above the ground. The heartwood and sapwood were separated by hand and ground with a Fritsch Universal cutting mill "pulverisette 19" (Idar-Oberstein, Germany). Five different particle size fractions from 0.5 mm to 12.5 mm (Fig. 1a) were then obtained by sieving the knot-free sapwood through different sieves with a Retsch Vibratory Sieve Shaker AS 200 basic (Haan, Germany).

2.2. Extraction setup

The extractions were carried out in a batch extractor setup (Fig. 1b). The setup consisted of an autoclave (1) (500 mL, Autoclave Engineers, PA, USA) equipped with a Dispersimax™ turbine stirrer (2) and a heating mantle (3). A pre-heating vessel (300 mL) (4) equipped with heating elements was connected to the autoclave adding the possibility to pre-heat the water before extraction. A sampling valve (5) made it possible to take the aliquots of samples during the extraction. Argon gas was coupled to the system for purging the inside of the autoclave as well as the tubing (6). The extraction temperature was controlled by a Eurotherm 2416 temperature controller (Eurotherm, VA, USA) and logged to a computer with PicoLog TC08 datalogger and PicoLog software (7).

2.3. Extraction

Approximately 9 g of air-dry (93% dry content) ground spruce sapwood and 100 mL distilled water was filled into the autoclave and the system was sealed off. Argon gas was used to purge the autoclave and the tubing. The pre-heating vessel was filled with 200 mL distilled water, purged with argon gas and heated to the extraction temperature. When the desired temperature was reached in the pre-heater, the heating mantle on the autoclave was switched on. When the temperature inside the autoclave reached approximately 100 °C the hot water from the pre-heater was fed into the autoclave. The pre-heater was purged with argon gas to ensure that all water was transferred into the autoclave. This increased the temperature in the autoclave rapidly and shortened the pre-heating time to the desired extraction temperature to about 15–20 min. A zero sample was taken when the extraction temperature (170 °C) was reached inside the autoclave and stirring was turned on. Then six samples were taken from the reactor through a 0.7 μm filter within the period of 120 min. No significant external pressure was applied during the extraction leaving the extraction pressure at about 8 bar. The pH of the samples was measured after the extracts cooled down to room temperature. Parallel experiments were made for all the different wood particle sizes.

2.4. Analysis

2.4.1. Total dissolved solids (TDS) and pH

Two mL of each sample was freeze-dried and weighed to determine the total dissolved solids extracted. The pH was measured with a SHOTT® Instruments handylab pH 12 meter (SI Analytics GmbH, Mainz, Germany) directly after the samples had cooled down to room temperature.

2.4.2. Non-cellulosic carbohydrates

2.4.2.1. Raw wood and residues after extraction. The total amount and sugar composition of non-cellulosic carbohydrates in the wood