



In-line high-temperature pH control during hot-water extraction of wood



Jens Krogell^{a,*}, Kari Eränen^b, Andrey Pranovich^a, Stefan Willför^a

^a Åbo Akademi Process Chemistry Center, c/o Laboratory of Wood and Paper Chemistry, Porthansgatan 3, FI-20500 Åbo Turku, Finland

^b Åbo Akademi Process Chemistry Center, c/o Laboratory of Industrial Chemistry and Reaction Engineering, Biskopsgatan 8, FI-20500 Åbo Turku, Finland

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ABSTRACT

An in-line pH control system for hot-water extraction of wood was developed and tested for optimal extraction of high-molar-mass hemicelluloses from spruce wood. Automated alkali addition was achieved by combining a controller and HPLC pump with a solid ZrO₂-based high-temperature and high-pressure pH electrode and a high-temperature and high-pressure Ag/AgCl reference electrode. Three different set points were tested; 600 mV, 575 mV and 550 mV corresponding to a pH at 170 °C of 4.3, 4.6, and 4.85, respectively. An extraction with no pH control was conducted for reference. The extracts were analyzed for total dissolved solids, non-cellulosic carbohydrates, monomeric sugars, average weight molar mass of the hemicelluloses and free acetic acid. The results show that higher extraction pH increases the molar mass but decreases the total yield of dissolved hemicelluloses and also inhibit sugar monomer formation.

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1. Introduction

For a biorefinery to be economically feasible it is important to utilize all or as much as possible of the used biomass for high-value products. Separation of the different components is naturally a first step in utilization of the biomass. However, the pulp and paper industry is still currently focused primarily on cellulose extraction for either high-volume or high-value products. The other components are more or less considered waste or low-value energy material. Conventional paper mills use the cellulose in the wood for papermaking and convert the other major wood components (non-cellulosic carbohydrates *i.e.*, hemicelluloses and lignin) into energy (as steam) in the recovery boiler to be used in the process. Although the energy is vital for the papermaking process, the total turnover of the plant would increase if the now burned wood components could be separated, isolated and refined to high-value end products.

The most common product from hemicelluloses today is ethanol *via* chemical- and/or enzymatic hydrolysis and fermentation (Gírio *et al.*, 2010). Although bio-ethanol is a desired product today and could be produced in fairly large volumes (Ragauskas *et al.*, 2005) it requires a pre-treatment method to degrade the hemicellulose

chains into monomers. With this degradation the possibility of producing high-molar-mass hemicelluloses based products such as bio-based barrier films, hydrogels, emulsion stabilizers, and possible health-promoting agents (Kisonen *et al.*, 2012; Maleki *et al.*, 2014; Mikkonen *et al.*, 2010; Pan *et al.*, 2012; Stevanic *et al.*, 2014; Willför *et al.*, 2008; Xu *et al.*, 2010) are lost.

Hot-water extraction of hemicelluloses is a well-known method for separating hemicelluloses from wood. Many different ways of hot-water extraction have been investigated; with plain water in batch mode (Grénman *et al.*, 2011; Krogell *et al.*, 2013; Song *et al.*, 2008), with flow-through mode (Kilpeläinen *et al.*, 2012; Leppänen *et al.*, 2010), with steam explosion (Martin-Sampedro *et al.*, 2014), with microwave heat-fractionation (Lundqvist *et al.*, 2003) or with mild acid- or alkali addition (Al-dajani and Tschirner, 2010; Capek *et al.*, 2000; González-Muñoz *et al.*, 2011; Söderström *et al.*, 2003), to name a few and all with different pros and cons considering the end products and economics of the whole process.

If the native molar-mass of the hemicelluloses could be preserved during the extraction more options regarding different end products would be possible. High-molar-mass starting material provides an opportunity to choose whether to produce high-molar-mass demanding end-products such as films *etc.* or to produce ethanol or other platform chemicals with controlled degradation after the extraction. To synthesize polymeric carbohydrates from sugar monomers is at present a very demanding task, especially heteropolysaccharides with similar molar-masses similar to those

* Corresponding author. Tel.: +358 40 0690029; fax: +358 2 215 4868.
E-mail address: jekrogel@abo.fi (J. Krogell).

that can be recovered from biomass by extraction (Ekholm et al., 2012). That kind of synthesis is extremely demanding, if not impossible, and definitely not economical feasible.

Due to the water auto-ionization at the high temperatures (normally 160–180 °C) (Zumdahl and Zumdahl, 2007) used in the hot-water extractions and acetic acid formation from detached acetyl groups from the hemicelluloses (the *O*-acetyl-galactoglucosylmammans in spruce wood used in this study) (Borrega et al., 2011; Jacobs et al., 2002; Song et al., 2008), pH drops rapidly during the extraction. This decrease in pH will induce an autohydrolysis of the hemicellulose chains with a loss in molar mass of the hemicelluloses and increase of monomeric sugars in the extracts. Also, splitting of acetyl groups will result in re-precipitation of spruce hemicelluloses back to the fibers, with lower extraction yield as a consequence (Hannuksela et al., 2003).

As described above, the pH level is important during extraction of carbohydrates from wood, particularly when long-chain hemicelluloses are desired. If the pH could be controlled during the hot-water extraction it could reduce or even prevent the hemicellulose chain degradation. Some work has been done with passive pH control during hot-water extraction using different buffers. (Song et al., 2011a) added different concentrations of NaHCO₃ to the water prior to the extraction to avoid too low pH-levels and hydrolytic cleavage reactions. The same authors also tried to influence the extraction pH and determine an optimal extraction pH by adding phthalate buffers with different pH to the extraction and thus trying to preserve high-molar-mass hemicelluloses extracted (Song et al., 2011b). In both cases the end-pH after extraction was higher than without NaHCO₃ and phthalate buffer addition, but the decrease in pH could not be avoided. Their results showed that the molar mass of the extracted hemicelluloses could be preserved to some extent with this passive pH control, but at the expense of the total hemicellulose yield (Song et al., 2011a,b). Another attempt to control pH during hot-water extraction was made with a flow-through extraction system and sodium acetate/acetic acid buffer (Kilpeläinen et al., 2013). It was also found that the degradation of hemicellulose chains could somewhat be reduced, but then the hemicellulose yield decreased. Both Song et al. (2011a,b) and Kilpeläinen et al. (2013) found an optimum of extraction pH around 4 regarding high molar-mass and yield. Since the optimal extraction pH seems to be a rather narrow interval a more precise controlling method is highly needed.

As stated earlier, pH is important and thus monitoring the extraction pH by measuring it is of great importance. Unfortunately, conventional glass pH electrodes cannot withstand temperatures over 80–100 °C (Galster, 1991; Morf, 1995), so pH can only be measured after the samples has cooled down. Therefore, in case of real hot-water extractions it has not been possible to perform precise pH adjustments in the reactor. And since pH-measurement is very temperature dependent, using conventional glass electrodes at room temperature gives an incorrect value of the actual in-line pH at the high temperature during the extraction. However, since both the dissolution of the hemicelluloses from the wood matrix and the hydrolysis of the hemicellulose chains occur at the high temperature, it is desirable to measure and also control the pH-level with the extraction setup.

In an earlier study, a high-temperature pH-measuring system was developed which can be used to measure in-line pH during hot-water extractions of wood (Krogell et al., 2014). In this present work the in-line pH-measuring system was further equipped with a controller and a pump to control the flow rate of added alkali. The objective for the current work was to build and evaluate a setup that would be able to control the in-line pH at different set pH-values during hot-water extraction of spruce wood in order to study the yield and molar mass of the extracted hemicelluloses at different extraction pH.

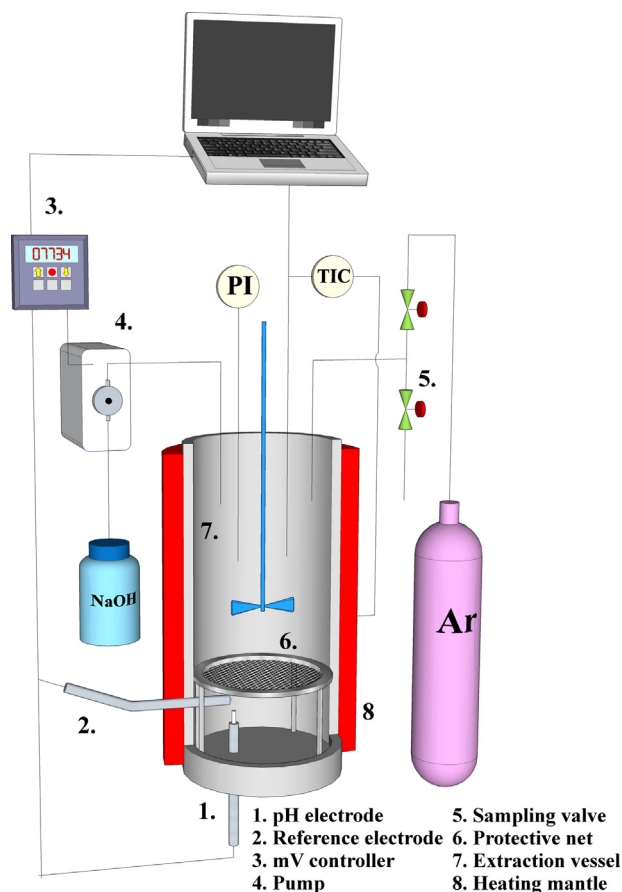


Fig. 1. Batch extraction setup with pH measuring electrodes and automated alkali addition setup. PI, pressure indicator; TIC, temperature indicator and controller.

2. Materials and methods

2.1. Materials

The NaOH pellets used for the solution were of analysis grade (J.T. Baker, Deventer, The Netherlands). The wood used in the extractions was knot-free sapwood from a healthy Norway spruce tree, felled in southern Finland, ground with a Fritsch Universal cutting mill “pulverisette 19” (Idar-Oberstein, Germany) and sieved to a particle size of 2–4 mm with a Retsch Vibratory Sieve Shaker AS 200 basic (Haan, Germany)

2.2. Methods

2.2.1. Reactor setup

The experiments were carried out in a 1000 mL modified batch reactor system (Autoclave engineers, PA, USA) (Fig. 1). The system was equipped with a Dispersimax™ turbine stirrer, heating mantle, and a sampling valve. The temperature was controlled by a Eurotherm 2416 temperature controller (Eurotherm, VA, USA) and logged to a computer with PicoLog TC datalogger and PicoLog software. In addition, the system was equipped with a solid ZrO₂-based high-temperature and high-pressure pH electrode and a high-temperature and high-pressure Ag/AgCl reference electrode (Corr Instruments, TX, USA). The pH electrode was an yttria-stabilized Zr/ZrO₂ membrane electrode with a Queon™ seal and a pressure range of 0–136 bars and temperature range of 90–305 °C. The reference electrode was a 0.1 N KCl filled internal pressure-balanced Ag/AgCl electrode with a ceramic frit as a junction partly based on ZrO₂, Queon™ seal and a pressure range of 0–136 bars and

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