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Fractionation of wheat and barley straw to access high-molecular-mass hemicelluloses prior to ethanol production

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ABSTRACT

The cost efficiency of the biorefining process can be improved by extracting high-molecular-mass hemicelluloses from lignocellulosic biomass prior to ethanol production. These hemicelluloses can be used in several high-value-added applications and are likely to be important raw materials in the future. In this study, steam pretreatment in an alkaline environment was used to pretreat the lignocellulosic biomass for ethanol production and, at the same time, extract arabinoxylan with a high-molecular-mass. It was shown that 30% of the arabinoxylan in barley straw could be extracted with high-molecular-mass, without dissolving the cellulose. The cellulose in the solid fraction could then be hydrolysed with cellulase enzymes giving a cellulose conversion of about 80–90% after 72 h. For wheat straw, more than 40% of the arabinoxylan could be extracted with high-molecular-mass and the cellulose conversion of the solid residue after 72 h was about 70–85%. The high cellulose conversion of the pretreated wheat and barley straw shows that they can be used for ethanol production without further treatment. It is therefore concluded that it is possible to extract high-molecular-mass arabinoxylan simultaneously with the pretreatment of biomass for ethanol production in a single steam pretreatment step.

1. Introduction

Interest in utilizing cereal straw and wood for high-value-added applications has increased during recent years and the term biorefinery is now frequently used. In order to meet future demands, biorefineries have to produce both biofuels and chemical products from lignocellulosic biomass (Ragauskas et al., 2006).

Bioethanol is a liquid transportation fuel that is likely to be an important product in the future, in reducing greenhouse gas emissions (Huang et al., 2008). The second generation of bioethanol, produced from lignocellulosic plant materials such as softwood (Söderström et al., 2003), hardwood (Sassner et al., 2006), cereal straw (Ballesteros et al., 2004; Chen et al., 2008; Linde et al., 2007, 2008) and corn stover (Öhgren et al., 2006), has, however, not yet been commercialised. These materials contain both hexose and pentose sugars, but the industrial fermentation of pentoses has not yet been achieved in a cost-efficient way (Ragauskas et al., 2006). This is a drawback, especially for the cost efficiency of the process when using lignocellulosic biomass containing a large amount of arabinoxylan, such as cereal straw and hardwood.

When producing bioethanol from a lignocellulosic feedstock, the biomass must be pretreated prior to enzymatic hydrolysis to improve the accessibility of the enzymes (Mosier et al., 2005). During pretreatment it is important to limit the formation of degradation products such as furfural and hydroxymethylfurfural (HMF), which inhibit the fermentation process (Palmqvist and Hahn-Hägerdal, 2000). Pretreatment can be carried out by a physical or a chemical method, or a combination of both.

Steam pretreatment can be performed on its own, or in an acidic or alkaline environment. Sulphuric acid and sulphur dioxide have been used as catalysts in several studies on the production of bioethanol (Linde et al., 2007, 2008; Sassner et al., 2006; Söderström et al., 2003), since acid hydrolyses both cellulose and hemicelluloses. Sodium hydroxide has been used as a catalyst when extracting hemicelluloses from softwood (Palm and Zacchi, 2004) and barley husks (Krawczyk et al., 2008; Persson et al., in press; Roos et al., 2009). Another common method of extracting hemicelluloses from biomass is alkaline extraction (Glasser et al., 2000; De Lopez et al., 1996; Ren et al., 2006, 2007; Sun et al., 1995; Sun and Sun, 2002). Alkaline conditions at elevated temperatures can also be used to pretreat biomass for bioethanol production, for example, ammonia recycled percolation (ARP) (Mosier et al., 2005) and wet oxidation (Klinke et al., 2002). Alkalis hydrolyse the ester linkages between plant polysaccharides and lignin, which increases the solubility of the hemicelluloses, without reducing their molecular mass, provided the conditions are not too severe.

The aim of the present study was to investigate the possibility of extracting hemicelluloses with high-molecular-mass and

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pretreating the biomass for ethanol production in a single alkaline steam-pretreatment step. The extraction of hemicelluloses prior to ethanol production is not a novel idea. However, several methods discussed in the literature (Huang et al., 2008; Wu et al., 1999) result in degradation of the hemicelluloses to oligomeric and monomeric forms, which significantly limits the possible applications of the hemicelluloses. In their oligomeric form, hemicelluloses can be used to produce health foods (Moure et al., 2006), and in their polymeric form to produce barrier films (Grönholm et al., 2004), hydrogels (Söderqvist Lindblad et al., 2001) and paper additives (Lima et al., 2003). The economic value of materials used for barrier film production today, such as ethylene vinyl alcohol (EVOH), is approximately 10 times higher than that of ethanol. Thus, to improve the cost efficiency of future biorefineries, the hemicelluloses should be extracted with high-molecular-mass for use in applications with high economic value. The improvement in cost efficiency may also promote the commercial production of bioethanol.

Steam pretreatment experiments were performed at different alkali concentrations, residence times and temperatures. The extracted arabinoxylan was evaluated regarding both yield and molecular mass. The cellulose conversion during enzymatic hydrolysis of the solid residues after steam pretreatment of wheat and barley straw was also investigated.

2. Methods

2.1. Raw material

The wheat (cultivar Gnejs) and barley (cultivar Ortega) straw were supplied by local farmers in the south of Sweden. The dry matter (DM) content of both the wheat and the barley straw was 90 wt%. The carbohydrate content of both kinds of straw was determined according to NREL (National Renewable Energy Laboratory) analytical methods (Sluiter et al., 2007). The compositions are given in Table 1. Lignin, extractives, protein and ash are the main constituents of the non carbohydrate part, which was about 30% in wheat and about 38% in barley straw on dry weight basis.

2.2. Steam pretreatment

Steam pretreatment was performed in a 10-L steam explosion unit, which has been described elsewhere (Palmqvist et al., 1996). The substrate loading in each batch was 300 g of dry straw that had previously been chopped into pieces approximately 6 cm long. At least 30 min prior to steam pretreatment, the straw was sprayed, during agitation, with 675 g of a sodium hydroxide (NaOH) solution at various concentrations (1–5 wt%). The addition of a NaOH solution of 1 wt% corresponded to 23 g NaOH/kg dry straw. The DM content after spraying was 30%. The residence time during steam pretreatment was varied between 5 and 50 min, and the temperature between 180 and 190 °C. The temperatures range was selected from a previous study where it was shown that lower temperature and longer residence time is beneficial to higher temperature and shorter residence time when extracting hemicelluloses from barley husks (Persson et al., in press).

Table 1
Composition of wheat and barley straw on dry weight basis.

	Wheat straw (g/100 g)	Barley straw (g/100 g)
Glucan	41.8	36.3
Xylan	25.4	21.7
Arabinan	2.5	2.6
Galactan	0.7	1.0

2.3. Enzymatic hydrolysis

The steam-pretreated material was dewatered in a manual 3-L filter press. The filter cake was washed with deionised water to remove all water-soluble components. The sugar content of the washed filter cake was analysed according to the standardised NREL method prior to enzymatic hydrolysis (Sluiter et al., 2007).

The weight of each batch in enzymatic hydrolysis was 800 g, containing 2 wt% (16 g) washed filter cake, enzymes and 0.1 M sodium acetate buffer. The enzymes were added at the following amounts: 3.7 g Celluclast 1.5 L (60 FPU/g, 30 β-glucosidase IU/g) (Novozymes A/S, Bagsværd, Denmark), 0.8 g Novozyme 188 (500 β-glucosidase IU/g) (Novozymes A/S) and 0.8 g Multifect Xylanase (43 g protein/ml) (Genencor International Inc., Rochester NY, USA). Each batch was sterilized at 121 °C for 20 min prior to the addition of the enzymes. Enzymatic hydrolysis was performed in stirred 1-L flasks at 40 °C, and samples were withdrawn after 2, 4, 6, 8, 24, 48 and 72 h. The samples were immediately filtered through a 0.2 μm sterile filter and frozen to prevent further hydrolysis. Duplicate batches were run to verify the results.

2.4. Analysis

The dry matter content was determined by drying samples in an oven (105 °C) until constant weight was obtained. The UV absorbance was measured at a wavelength of 280 nm, using a Shimadzu UV-160 spectrophotometer (Kyoto, Japan). Before measurement, the samples were diluted with 0.5wt% NaOH.

Furfural and HMF were analysed using high-performance liquid chromatography (HPLC), using a refractive index (RI) detector (Shimadzu, Kyoto, Japan) and an Aminex HPX-87H column (Bio-Rad, CA, USA). Millipore water with 5 mM H_2SO_4 was used as eluent at a flow rate of 0.5 ml/min, at 65 °C. The injection volume was 20 μl. Furfural (Merck, Darmstadt, Germany) and 5-hydroxymethyl-2-furfural (Alfa Aesar GmbH, Karlsruhe, Germany) were used as standards.

The molecular mass distribution of the extracted arabinoxylan was determined using a size-exclusion chromatography system. The chromatograph was equipped with a pump and a system controller (600, Waters, Milford, MA, USA), an autosampler (717plus, Waters), a RI detector (410, Waters), an ultraviolet (UV) detector operating at 280 nm (486, Waters) and a column (16 mm I.D.), packed with 30 cm of Superdex 30 and 30 cm of Superdex 200 (both from GE Healthcare, Uppsala, Sweden). The injection volume was 2000 μl. The flow rate of the 0.5 wt% NaOH solution was set to 1 ml/min. The system was calibrated with polyethylene glycol standards with peak molecular masses of 400, 4000, 10,000 and 35,000 Da (Merck, Darmstadt, Germany). Nine fractions, each of 10 ml, were collected between 39 and 119 min. The xylan concentration in the fractions was used to determine the molecular mass distribution.

The concentration of dissolved xylan was analysed by hydrolysing the polysaccharide to monomeric sugars by acid hydrolysis, according to the standardised NREL method (Ruiz and Ehrman, 1996). The concentration of monomeric sugar after both acid hydrolysis and enzymatic hydrolysis was analysed by high-performance anion exchange chromatography coupled to pulsed amperometric detection, using an ED40 electrochemical detector (Dionex, Sunnyvale, CA, USA). The chromatograph was equipped with a GP40 gradient pump, an AS50 autosampler and a Carbo Pac PA10 column (all from Dionex). The injection volume was 10 μl, and deionised water with 2 mM NaOH was used as eluent, at a flow rate of 1 ml/min. D-Mannose, D-glucose, D-galactose, D-xylose and L-arabinose (Fluka Chemie AG, Buchs, Switzerland) were used as standards.