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Hydrolysis of sweet blue lupin hull using subcritical water technology

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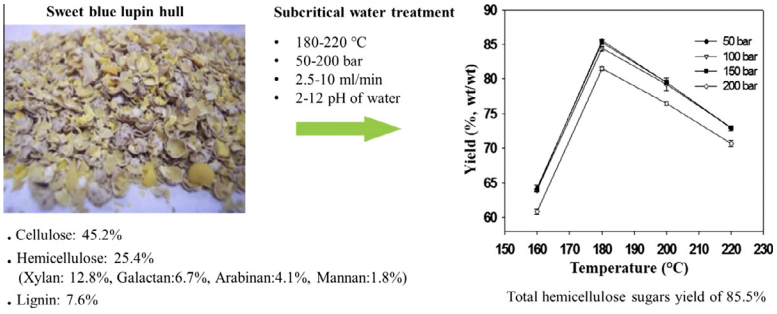
HIGHLIGHTS

- Subcritical water (sCW) was used to obtain hemicellulose sugars of lupin hull.
- The highest yield of 85.5% was obtained at 180 °C, 50 bar, 5 mL/min, and pH 6.2.
- Crystallinity and thermal stability of lupin hulls improved after sCW treatment.
- sCW is a promising technology to obtain hemicellulose sugars from lignocellulose.

GRAPHICAL ABSTRACT



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ABSTRACT

Hydrolysis of sweet blue lupin hulls was conducted in this study using subcritical water technology. Effects of process parameters, such as pressure (50–200 bar), temperature (160–220 °C), flow rate (2–10 mL/min), and pH (2–12), were studied to optimize maximum hemicellulose sugars recovery in the extracts. Extracts were analyzed for total hemicellulose sugars, phenolics and organic carbon contents and solid residues left after treatments were also characterized. Temperature, flow rate, and pH had a significant effect on hemicellulose sugar removal; however, the effect of pressure was not significant. The highest yield of hemicellulose sugars in the extracts (85.5%) was found at 180 °C, 50 bar, 5 mL/min and pH 6.2. The thermal stability of the solid residue obtained at optimum conditions improved after treatment and the crystallinity index increased from 11.5% to 58.6%. The results suggest that subcritical water treatment is a promising technology for hemicellulose sugars removal from biomass.

1. Introduction

Lignocellulosic biomass (LCB) refinery approach is currently gaining significant prominence not only for the minimization of environmental impact, but also for the rational utilization of natural biomass resources. This implies the fractionation of major LCB components (cellulose, hemicellulose and lignin) to yield a wide range of valuable products that can replace oil-derived products. Among the major components, the hemicellulose fraction which may find broader use for chemicals, fuel, and food applications has been proposed as the first stage of LCB refineries.

Hemicelluloses are branched polysaccharides, associated in plant cell walls with cellulose and lignin. They are formed by a wide variety of sugar residues, such as xylose, arabinose, glucose, galactose and mannose depending upon the source. The expanding range of hemicellulose sugar applications includes products for the food industry and the pharmaceutical industry as novel sweeteners, prebiotics, gels, films, coatings, adhesives, stabilizers and viscosity-enhancing additives (Ebringerova, 2005). Bioconversion of hemicelluloses into ethanol by fermentation is another valuable application (Krishna and Chowdary, 2000). Several processes have been continuously developed to fractionate hemicellulose from LCB. These processes include dilute acid hydrolysis, alkaline treatment, organosolv process, steam explosion, and subcritical water treatment.

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Subcritical water treatment, also known as hot-compressed water, liquid hot water, hydrothermolysis, aquasolv or autohydrolysis, using pressure to maintain the water in the liquid state at elevated temperatures is attracting considerable attention as an environmentally friendly technology because it avoids the use of chemicals and neutralization of high volumes of sludges (Brunner, 2009). Subcritical water has unique properties of dielectric constant, ionic product, density, viscosity, diffusivity, electric conductance, and solvent ability. Increase in the ionic product and decrease in the dielectric constant, viscosity, and density of water in the subcritical region makes it an excellent medium for fast, homogeneous and efficient reactions (Kruse and Dinjus, 2007). This technology leads to a liquid phase rich in hemicellulose sugars and a solid residue rich in cellulose and lignin. Depending on the processing conditions and biomass employed, possible compound concentration in the liquid phase (oligosaccharides, monosaccharides, acetic acid and sugars decomposition products) may differ. Many researchers have attempted to fractionate hemicellulose from various LCB with subcritical water technology (Mok and Antal, 1992; Perez et al., 2008; Pronyk and Mazza, 2010, 2012). Mok and Antal (1992) found that almost 100% of the hemicellulose of various wood and herbaceous plants was hydrolyzed at 230 °C and 34.5 bar for 2 min using subcritical water treatment. Around 90% of hemicellulose was recovered as monomeric sugars. Perez et al. (2008) applied subcritical water at 188 °C, 1/10 solid to liquid ratio and 40 min in a batch system to treat wheat straw and obtained maximum hemicellulose-derived sugar recovery of 80%, with minimum sugar degradation products like furfural. Pronyk and Mazza (2010) studied optimization of the fractionation of triticale straw using subcritical water technology to obtain a cellulose rich fraction. They reported that subcritical water was successful in removing 73–78% of the hemicellulose, leaving a cellulose rich residue (65% glucose concentration). The optimum reaction conditions for efficient hemicellulose yield were 165 °C, with a flow rate of 115 mL/min, and a solvent-to-solid ratio of 60 mL/g. At these optimum conditions, they fractionated five cereals (triticale, durum wheat, CPS wheat, feed barley, and oats) and two oilseed (canola and mustard) straws with subcritical water using a flow-through reactor (Pronyk and Mazza, 2012). More than 90% of the xylan was extracted, and there was no significant effect on yield due to crop species utilized.

Sweet blue lupin (*Lupinus angustifolius*) is a representative of the legume family among 450 species. Lupin seeds contain high protein and are used as valuable additives mainly in bakery products as well as in dietary and functional food products. The hull comprises about 25% of the seed weight, which has a high fiber content. One unique aspect of lupin hull is its low lignin content, which facilitates access to the hemicellulose fraction (Bailey et al., 1974). Thus, lupin hull can be used as an ideal feedstock for hemicellulose sugar production. To the best of our knowledge, there is no reported study on the hydrolysis of lupin hull using subcritical water technology. Research on fractionation of lupin hulls is needed for their exploitation according to the LCB refinery concept. Therefore, the main objective of this study was to optimize the process conditions for maximum hemicellulose sugar yield from lupin hull using subcritical water technology. Effects of process parameters, such as pressure (50–200 bar), temperature (160–220 °C), flow rate (2–10 mL/min) and pH (2–12) on hemicellulose removal were studied. X-ray diffraction, thermo-gravimetric and scanning electron microscopy analysis of subcritical water treated lupin hulls at optimum conditions were performed to investigate the impact of treatment on the structure.

2. Methods

2.1. Raw material

Sweet blue lupin hulls were kindly provided by Ceapro Inc. (Edmonton, AB, Canada). Hulls were ground in a centrifugal mill (Retsch, Haan, Germany) to obtain a powder with maximum 1 mm particle size, then vacuum packed and stored at −20 °C.

All sugar standards (D(+)glucose, D(+)xylose, D(+)galactose, L(+)arabinose, and D(+)mannose with purity ⩾ 96%) were obtained from Sigma Aldrich (St. Louis, MO, USA). All other chemicals and solvents, including sulfuric acid were of analytical grade and obtained from Fisher Scientific (Fair Lawn, NJ, USA).

2.2. Proximate compositional analysis

Moisture content was determined gravimetrically by drying the hulls in an air oven at 105 °C for 16 h. The ash content of the hulls was determined according to the National Renewable Energy Laboratory (NREL) procedure. The protein content was determined using a Leco nitrogen analyzer (Model FP-428, Leco instruments Ltd., Mississauga, ON, Canada). The fat content was determined by Soxhlet extraction using hexane for 6 h.

2.3. Hydrolysis in subcritical water

A semi-continuous flow type subcritical water system similar to the one reported by Singh and Saldaña (2011) was used in this study. The system consisted of an HPLC pump (Gilson 307, Villiers-le-Bel, France), a pre-heater, a stainless steel high pressure vessel, a digital pressure gauge, a cooling system (Swagelok, Edmonton, AB, Canada), an oven (Binder, Bohemia, NY, USA) and a back pressure regulator (Tescom, Elk River, MN, USA). Distilled water was first degassed and then delivered with the HPLC pump at varying flow rates to the preheating section. Then, it was passed through the vessel (2.54 cm ID × 10 cm length, capped with a 20 μm stainless steel frit at the inlet and outlet) preloaded with the sample (3 g) and glass beads (39 g). The pressure of the system was maintained constant using the back pressure regulator. The system was heated by the oven and its temperature was monitored by a digital thermometer. The extracts (200 mL) were collected in vials after flowing through the cooler placed after the vessel. The experiments were conducted at temperatures of 160–220 °C, pressures of 50–200 bar, flow rates of 2–10 mL/min, and initial pH levels of 2–12. The desired initial pH of water supply was achieved by the addition of small amounts of acetic acid or sodium hydroxide for the acidic or basic pH conditions, respectively. The changes in pH values after treatments were also recorded. All experiments were performed at least in duplicates. The solid residue left in the high pressure vessel after each experiment was dried in an oven at 40 °C. Liquid extracts and solid residues were then stored at −20 °C for further analysis.

2.4. Analytical methods

2.4.1. Total phenolic content

Total phenolic content of extracts was determined by Folin–Ciocalteau method (Singleton and Rossi, 1965) that measures the capacity of a compound to reduce the Folin reagent. Briefly, 40 μL of sample was mixed with 3.1 mL of water. Then, 200 μL of Folin–Ciocalteau reagent was added and allowed to withstand for 5 min. Sodium carbonate (20% w/v; 600 μL) was then added to the mixture. After shaking, the mixture was incubated for 90 min in dark. The absorbance of the samples at 765 nm was measured