



Research paper

Rapid one-step solvent-free acid-catalyzed mechanical depolymerization of pine sawdust to high-yield water-soluble sugars



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ABSTRACT

One-step absolute solvent-free acid-catalyzed mechanical depolymerization of pine sawdust (PSD) and commercially available α -cellulose to water-soluble sugars was carried out using ball milling. For comparison purposes, the commonly reported “solvent-free” mechanocatalytic depolymerization of lignocellulose method, which normally involves three steps (acid impregnation in solvent, vacuum drying, and mechanical depolymerization of lignocellulose), was performed. The 3,5-dinitrosalicylic acid (DNS) method was used to measure the total reducing sugar (TRS) of the obtained sugar solution, and major monosaccharides in the solution were analyzed by capillary electrophoresis (CE). More than 90% of the PSD became water-soluble through milling. Furthermore, most of the PSD was converted into TRS in approximately 30 min, and the highest TRS yield obtained was 31%, based on the dry mass. Interestingly, the TRS solutions obtained from the processed PSD were much darker than those obtained from α -cellulose due to the chromophores that formed during the depolymerization of lignin.

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1. Introduction

Lignocellulose-based solid residuals, such as sawdust, bark, and peat, have long been used as major wood fuels in the forest industry in Finland [1,2]. Cellulose, hemicellulose, and lignin, which consist of 60–70% carbohydrates/sugars, account for about 90% of the dry matter in lignocellulose. The conversion of lignocellulose into bio-fuel and more available chemicals have been widely reported [3].

Mechanocatalytic depolymerization of lignocellulose into sugars, mainly C₆ and C₅, using a ball mill has emerged as a novel “solvent-free” approach in the last decade [3,4]. The widely used method of acid-impregnated mechanocatalytic depolymerization (AIMD) of biomass involves three steps: 1) acid impregnation of the biomass in diethyl ether, 2) removal of the solvent by vacuum evaporation, and 3) a ball mill process involving the depolymerization/decrystallization of lignocellulose and conversion of water-

insoluble lignocellulose into water-soluble oligosaccharides and lignin at room temperature (RT) [5,6].

In this study, we introduced an absolute solvent-free process through direct acid-catalyzed mechanical depolymerization (DAMD) of pine (*Pinus sylvestris*) sawdust (PSD) that converted lignocellulosic biomass into sugars without requiring a prior pre-treatment step. The focus of the study is to explore the industrial potential of such a methodology for the valorization of forest industry waste into reducing sugars that can be used for further production of bioenergy and valuable chemicals.

Experiments were performed with different acid/substrate (A/S) concentrations and milling times. DAMD of commercially available α -cellulose was carried out as a reference sample. For a comparison with the DAMD method, the commonly used “solvent-free” AIMD method was also performed. DAMD and AIMD of PSD were performed with a fixed (0.3 mol kg⁻¹) A/S concentration to provide a comparable overview of these mechanocatalytic depolymerization processes. The major monosaccharides obtained from the depolymerization of lignocellulose were analyzed by capillary electrophoresis (CE). The sum of disaccharides, oligosaccharides, and

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certain polysaccharides was analyzed according to the 3,5-dinitrosalicylic acid (DNS) method, in addition to which analysis of the produced total reducing sugars (TRS) was carried out.

2. Materials and methods

2.1. Samples

PSD was obtained from the Biofuel Technology Centre in Umeå. It was derived from approximately 30-year-old pine tree stumps (*Pinus sylvestris*) that originated from the coastal area of Västerbotten in northern Sweden. The collected stumps were crushed and transferred to chipper. The chipped sample was then sieved with 1 mm sieve.

The composition of the PSD is given in Table 1. Commercially available α -cellulose powder was obtained from Sigma-Aldrich and used as a reference sample for PSD. The major difference between cellulose and PSD in composition is the presence of additional lignin and hemicellulose in PSD.

2.2. Methods

DAMD and AIMD of PSD were performed (Fig. 1) in a planetary micro mill (FRITSCH Planetary Micro Mill PULVERISETTE 7 premium line). Fig. 1 provides an overview of the two different methods.

2.3. DAMD of PSD

DAMD of the PSD was performed using different concentrations (0.45 mol kg⁻¹, 0.3 mol kg⁻¹, and 0.2 mol kg⁻¹) of sulfuric acid (A, mol)/substrate (S, kg). Approximately 2 g of PSD, equal to 15 cm³ (measured in a measuring cylinder), was roughly premixed with H₂SO₄ in a 45 cm³ stainless steel bowl. The premixed sample was then milled with approximately 8 cm³ (46.4 g) of 3 mm diameter grinding balls [7]. The temperature of the milling process was controlled by a “1-min milling/1-min pause” alternation mode at 13.3 Hz (Fig. 1a). The sample was then transferred to a further hydrolysis process at 100 °C for 1 h. The water solubility of the processed PSD was determined at RT, as described in Section 2.6.

2.4. AIMD of PSD

The AIMD of the PSD (Fig. 1b) was performed according to the procedure of Schüth et al. [8]. It involved three steps: 1) acid impregnation in a mixture of H₂SO₄ and diethyl ether, 2) vacuum evaporation drying, and 3) mechanocatalytic depolymerization. The PSD was immersed in the solution of H₂SO₄/diethyl ether, with

an A/S concentration of 0.3 mol kg⁻¹. The resulting mixture was shaken in an incubator at 3.3 Hz at RT for 2 h, followed by drying in a rotary evaporator at approximately 50 kPa, and 40° C for 2 h. Mechanocatalytic depolymerization and the same procedures as followed in the DAMD process were then carried out (Section 2.3.).

2.5. Determination of the remaining acid in the acid-impregnated PSD

To obtain data on the effect of the acid impregnation on the biomass, acid impregnation of PSD and α -cellulose was performed using the same A/S concentration of 0.8 mol kg⁻¹. Three layers, based on the color differences, were observed in the rotary evaporator flask after the vacuum evaporation drying. The processed PSD was carefully collected in a round flask, according to the color of the PSD on the top, middle, and bottom. The acid concentration of each layer was then determined by classical acid-base titration using 0.1 mol dm⁻³ sodium hydroxide (NaOH).

2.6. Determination of the water solubility of processed PSD at RT

The temperature of the grinding balls was measured immediately by connecting to a K type thermocouple after depolymerization. The water solubility of the processed PSD was determined by adding 15 cm³ of distilled water in a 500 mg sample, followed by shaking the resulting aqueous mixture in an incubator at RT at 3.3 Hz for 1 h. The water solubility of the processed sample was then calculated based on the dried remaining solid residuals [7].

2.7. Determination of total reducing sugars (TRS)

The DNS method was used to determine the TRS produced during DAMD and AIMD [2].

2.8. Determination of monosaccharides by capillary electrophoresis (CE)

The samples were filtered with a 0.45 μ m GHP Acrodisc syringe filter (Pall Corporation, USA) prior to the CE analysis. Monosaccharides were analyzed using a CE method modified from the original method [9] with a P/ACE MDQ CE instrument (Beckman-Coulter, Fullerton, CA, USA) and diode array detection at 270 nm. Uncoated fused-silica capillaries with an I.D. of 25 μ m and a length of 30/40 cm (effective/total length) were used. The samples were injected at a pressure of 105 kPa for 10 s. The used separation voltage was +16 kV, and it was raised linearly within a 1-min ramp time, followed by a separation time of 15 min. Calibration curves for the external quantification of monosaccharides were prepared using standard solutions. In addition, each sample was spiked with standard solution for reliable identification of peaks in the electropherogram. All samples were duplicated.

3. Results

3.1. Yields of remaining acid in the acid-impregnated PSD

Three different colored layers appeared after acid impregnation and vacuum drying. Approximately equivalent amounts of light brown and yellow (natural color of PSD) colored PSD appeared on the top and middle layers of the flask, respectively. In addition, a small amount of dark brown PSD accumulated at the bottom of the flask. The three colored layers were collected separately from the flask, and the remaining acid in each layer was determined by classical acid-base titration (Fig. 2).

The highest acid concentration was found in the darkest colored

Table 1
Elemental analysis and physical properties of the pine sawdust (PSD).

PSD	
Cellulose (%), d.s.	42–44
Hemicellulose (%), d.s.	25–26
Lignin (%), d.s.	27–29
Carbon (%), d.s.	52.8
Hydrogen (%), d.s.	5.95
Oxygen (%)	< LOD
Nitrogen (%), d.s.	0.22
Sulphur (%), d.s.	< LOD
Ash (%), d.s.	0.47
Moisture (%),d.s.	6.4

% d.s., Mass fraction calculated from dry material (substance).
LOD, limit of detection.

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