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Research paper

Comparison of chemical treatment methods for loblolly pine to utilize as enzyme hydrolyzate feedstock[☆]

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ABSTRACT

The ground pine wood chips (GPWC) were examined through chemical treatment methods employing alkaline hydrogen peroxide treatment (AHP, consisted of 50 g L⁻¹ potassium hydroxide, and 50 g L⁻¹ hydrogen peroxide with added water at 78 °C for 24 h), and ethyl-hydro-oxides treatment (EHOs, consisted of 60% ethanol (of total solution), 50 g L⁻¹ potassium hydroxide, and 50 g L⁻¹ hydrogen peroxide with added water at 78 °C for 24 h). The effects of chemical treatments on GPWC were examined through combination of chemical composition followed by enzymatic hydrolysis (using Accellerase[®] 1500). The application of EHOs treatment removes the foaming issue that currently occurs due to AHP treatment at the elevated temperature. A removal of the foaming phenomenon increased the enzymatic glucan conversion (>70%) which is important in increasing the efficiency of biorefinery. The interaction of different variables in EHOs solvent formulations including ethanol concentration (0–60%), potassium hydroxide concentration (0–50 g L⁻¹), hydrogen peroxide concentration (0–50 g L⁻¹), and processing temperature (38 °–78 °C) were analyzed through four variables response surface methodology using glucan conversion and total polysaccharide conversion as responses. The glucan conversion and total polysaccharide conversion were analyzed to determine the specific and overall effects of Accellerase[®] 1500 on the amorphous polysaccharide contents of GPWC resulted through EHOs treatment formulations, respectively. The implications of all these findings are discussed with the available literature.

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1. Introduction

Softwood such as loblolly pine (*Pinus taeda*) is a fast-growing tree. Loblolly pine can reach a height of 18–30 m with a diameter of 0.3–1.5 m between 30 and 60 years. Softwoods such as pine and spruce consist of 42–45 g of cellulose, 17–22 g of hemicellulose, and 24–32 g of lignin per 100 g of biomass (dry basis) [1–6]. The high polysaccharides content of loblolly pine (approx. 63 g per

100 g of dried biomass) is crucial for increasing both transportation and development of bio-product efficiencies. The conversion of pine wood chips into bio-products is an energy intensive process due to a tight binding of polysaccharides matrix with lignin content. To enhance the release of polysaccharide contents of softwood, both physical and thermochemical treatments are required. A physical treatment involves the size reduction of particles, thereby increasing the surface area per unit volume. Pine wood chips require 1.7–3.8 times more energy compared to corn stover for the same size reduction [7]. The milling energy of pine wood chips increases with the decreasing particle sizes [7,8]. Whereas, thermochemical treatments are required to convert crystalline content to amorphous content with removal of lignin. Several different thermochemical treatments employing steam [2], sulfuric acid based reagents (such as Kraft [4], organosolv [3,9,10], and alkaline sulfite-anthraquinone-methanol (ASAM) [4]), alkaline hydroxide [5], and alkaline hydrogen peroxide (AHP) [6] have been reported for softwood conversion. The effects of thermochemical treatments on structural-chemical properties of softwoods can be measured through X-ray diffraction, scattering electron

Abbreviations: GPWC, Ground pine wood chips; AHP, Alkaline hydrogen peroxide; EHOs, Ethyl-hydro-oxides.

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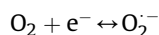
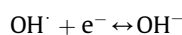
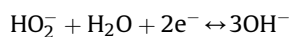
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microscopy, kappa number, and enzyme digestibility [2–6].

Water is the most polar solvent and form hydrogen bonding with cellulosic hydroxyl groups on interaction. However, the hydrophobic nature of lignin inhibits water molecule interaction with cellulose. To overcome the physical barrier of lignin in softwood conversion, steam treatment is utilized at a high temperature of 180 °C for 20 min [2]. Steam treatment at high temperature penetrates lignocellulosic biomass through formation of a hydronium ion [2]. The steam treatment promotes hemicellulose degradation and transforms lignin, thereby increasing access to cellulose content [2]. The application of steam treatment on softwood (particle size: 0.25–0.42 mm) completely removes xylan content and decreases 22.5% of phenolic compounds without affecting its cellulose content [2]. During enzyme hydrolysis, steam treated softwood converts up to 4% and 12.5% of total polysaccharide into fermentable sugars at substrate loadings of 50 g L⁻¹ and 200 g L⁻¹, respectively [2]. Sulfuric acid based reactants along with anthraquinone, organic solvents (such as ethanol and methanol) and alkaline hydroxide have been used with water to enhance softwood conversion [3,4,9]. The paper pulp industry utilizes sulfuric acid based reactants on softwood (size: particle (less than 5 mm) to chip (20 mm × 2 mm × 2 mm)) at temperature ranges of 160 °–180 °C for 1–3 h [3,4]. Compared to the conventional Kraft treatment, a significant improvement in both pulp brightness and yield have been reported with the application of ASAM treatment [4]. However, the use of carcinogenic anthraquinone in ASAM treatment formulation set back the process and its usage at commercial scale production [11]. Organic solvents (such as ethanol and methanol) are effective in the delignification of lignocellulosic biomass. Mantanis [12] has reported that the activation energy of softwood swelling (using spruce and Douglas-fir) ranges from 32.2 to 38.9.0 kJ mol⁻¹ and 57.1–60.4 kJ mol⁻¹ at the temperature of 23 °–100 °C using water and ethanol as solvents, respectively. The addition of –CH₃ group causes a subsequent increase in the activation energy of wood using ethanol compared to water [12]. The maximum swelling of wood in the aqueous organic solvent is accompanied by solvent basicity, molar volume, and hydrogen bonding capability [12]. In organosolv treatment, use of ethanol (50–80% of solution) along with mineral catalysts such as H₂SO₄ (1.0–1.1 g per g of biomass) at elevated temperature (160 °–200 °C) increases both delignification and enzymatic saccharification of softwood [10]. The application of organosolv treatment (65% ethanol of total solution and 1.1 g H₂SO₄ per g of biomass; processing temperature = 170 °C for 1 h) on softwood (particle size: less than 5 mm) removes 61.2% of phenolic compounds with 79% of glucose recovery, and increases enzymatic glucan conversion up to 70% [3]. Organosolv treatment involves the formation of hydro ion [H₃O⁺] similar to the acid treatment [10]. The generated lignin through organosolv treatment has a potential market value in the development of carbon fibers [10,13]. The use of organosolv treatment is limited in the biofuel industry due to a high price of solvent, high temperature processing, and an expensive infrastructure development. Moreover, the processing temperature at above 170 °C produces furfural and hydroxymethyl furfural [3]. The production of these inhibitors affect both a fermentation step (due to low conversion of sugars into ethanol) and a downstream processing step (due to low productivity).

On the contrary to high temperature chemical treatment processes, moderate temperature treatment processes using alkaline hydroxide [5,6] and AHP [6] have also been reported for softwood conversion. Using alkaline hydroxide treatment (0.075 g of NaOH per g of biomass; processing temperature = 80 °–100 °C for 2 h) on softwood (particle size: less than 0.8 mm) had no significant effect on the delignification, and the enzymatic glucan conversion stayed below 25% [5]. Furthermore, the change in processing conditions of

alkaline hydroxide treatment (80 g L⁻¹ of NaOH, equivalent to 0.8 g NaOH per g of biomass; processing temperature = 70 °C for 20–21 h) on softwood (particle size: 0.125–0.50 mm), removed up to 25% of the phenolic compounds and the enzymatic glucan conversion stayed up to 37.5% [6]. However, the use of AHP treatment (80 g L⁻¹ of NaOH (equivalent to 0.8 g NaOH per g of biomass) and 204 g L⁻¹ of H₂O₂ (equivalent to 2.04 g H₂O₂ per g of biomass); processing temperature = 70 °C for 20–21 h) on softwood (particle size: 0.125–0.50 mm), increased the delignification efficiency up to 60% with the enzymatic glucan conversion up to 60% [6]. Using herbaceous feedstock, AHP treatment can increase the enzymatic saccharification efficiency up to 90% [14]. In alkaline condition, hydrogen peroxide produces hydroxyl radicals (OH[•]), superoxide anions (O₂^{•-}), hydroperoxide anions (HO₂⁻), solvated electrons (aq. e⁻).



and atmospheric oxygen (O₂) [15–18]. The generated hydrogen peroxide reactive species play a critical role in the delignification of lignocellulosic feedstock, thereby increasing subsequent enzymatic saccharification [14,19]. The scope of AHP treatment is limited to certain feedstock due to crystallinity, volatility of reaction with the increasing temperature, and safety concerns with a scale-up of the process [6,19,20]. AHP treatment can be performed using potassium hydroxide (KOH), sodium hydroxide (NaOH), calcium hydroxide (Ca(OH)₂), and ammonium hydroxide (NH₄OH). The efficacy of NH₄OH with H₂O₂ decreases with the increasing crystallinity of lignocellulosic biomass [19]. KOH has both environmental and health benefits compared to NaOH. The recovery of potassium ion (K⁺) in the form of potassium chloride (KCl) and potassium citrate salts have applications in fertilizer, food and beverages, and pharmaceutical products development [21,22].

The objective of the present study was to compare the effect of solvent polarities of EHOs treatment (60% ethanol + 50 g L⁻¹ KOH + 50 g L⁻¹ H₂O₂ with added deionized water), and AHP treatment (50 g L⁻¹ KOH + 50 g L⁻¹ H₂O₂ with added deionized water) using GPWC. The generated pulps were analyzed through chemical composition and enzymatic saccharification efficiency. Furthermore, the four variables response surface methodology was examined to understand the effect of temperature, ethanol, KOH, and H₂O₂ in the enzymatic saccharification of GPWC.

2. Materials and methods

2.1. Pine wood chips preparation

Pine woods chips were received from Arbogen (Ridgeville, SC). The received pine wood chips were oven dried for 6 days at 40 °C. The moisture content of 10.5 ± 0.6% of total biomass was measured. The dried chips (2 cm × 2.5 cm × 0.75 cm) were reduced to 0.5–1.0 mm size particles using a laboratory Wiley mill (Thomas Model 4 Wiley[®] Mill). The moisture content of the sieved GPWC was 0.1 ± 0.0% before further analyses.

2.2. Chemical treatments

Chemical treatments formulation consisted of hydrogen peroxide (350 g L⁻¹ H₂O₂, BDH), potassium hydroxide (85% KOH purity, Alfa Aesar), ethanol, and deionized water. For chemical

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