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Research paper

Effects of hot water extraction pretreatment on physicochemical changes of Douglas fir

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ABSTRACT

Hot water extraction (HWE) is an autocatalytic pretreatment that can be effectively integrated into most of the conversion technologies for extracting hemicelluloses from woody biomass. The objective of this study was to understand the influence of pretreatment factors on removal of hemicelluloses from Douglas fir chips. Compositional change in biomass was analyzed with ion chromatography and further confirmed with Fourier transform infrared spectroscopy (FT-IR). Highest hemicellulose extraction yield (HEY) was estimated to be 67.44% at the optimum reaction time (79 min) and temperature (180 °C) by using response surface methodology (RSM). Experimental results show that the HEY increased from 19.29 to 70.81% depending on the reaction time (30–120 min) and the temperature (140–180 °C). Effects of the severity factor (SF) on the mass removal and compositional changes were also evaluated. Hygroscopicity and thermal stability of wood were improved after HWE pretreatment. Colorimetric analysis showed that temperature has a greater influence on color of the wood chips during HWE pretreatment than dwell time. HWE pretreatment shows great potential for extracting hemicelluloses and altering physicochemical properties of wood in an integrated biorefinery for diversification of product portfolio.

1. Introduction

Recently, second generation biofuels from lignocellulosic materials have attracted substantial attention due to an increased demand for fuels, rising environmental concerns, and the decreased availability of fossil fuels [1]. Lignocellulosic materials are the most abundant organic source on earth, with an annual production in the biosphere of about 170 billion metric tons [2]. Softwoods are one of the major lignocellulosic resources available, and represent a potentially large source of biomass for bioconversion [3]. Softwoods have higher lignin content compared to hardwoods. They also have more hemicelluloses with a higher mannose content and lower xylose content [4].

A typical biochemical pathway in biofuel production involves three main steps: pretreatment, enzymatic hydrolysis, and fermentation. The cellulose microfibrils are assembled by crystalline polymer chains that are constrained by a highly organized Van-der-Waals force and hydrogen bonding, which cannot be swelled or dissolved by common solvents [5]. In addition, the cellulose microfibrils are embedded in a matrix of hemicellulose and lignin, which acts as an interface. This complex composite must be at least partially deconstructed by pretreatment so that the polysaccharide fractions (mainly cellulose) can become more accessible and amenable to enzymatic hydrolysis.

Over the past few decades, several pretreatment approaches have been developed to convert carbohydrates in lignocellulosic materials more efficiently into fermentable sugars. Generally, the approaches can be classified into biological, physical, chemical and physicochemical pretreatments, according to different forces or energy consumed in the pretreatment process [6]. Different pretreatment parameters alter several key properties of biomass. This appears to effect the recalcitrance of pretreated biomass, including resulting biomass constituents, cellulose crystallinity, ultrastructure, cellulose degree of polymerization, and accessibility [7]. However, there are still several unresolved issues in the pretreatment process. For instance, most existing pretreatments require energy-intensive size reduction from wood chips to particles of millimeters or less (fiber or powder) prior to or along with

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pretreatment in order to achieve satisfactory cellulose conversion efficiencies [8]. Typical size reduction energy consumption for fiberization wood chips is about 200–600 Wh electricity/kg oven dry wood [9]. Besides, hazardous chemical used during pretreatment increase the overall cost and can pose serious environmental problems.

One promising physico-chemical pretreatment is hot-water extraction (HWE), also described as autohydrolysis or autocatalytic. In this approach, biomass is treated with chemical-free and water-only media in a wide range of temperatures (130–230 °C) and pretreatment times (from a few seconds to several hours) [10]. It combines the hydrolytic properties of water with the actions of released organic acids to catalyze hydrolysis reactions [11]. The process causes hemicellulose depolymerization (mainly converted into soluble oligomers as a major reaction product) and lignin transformation due to the high temperature, thus increasing the potential of cellulose hydrolysis. Besides, the HWE pretreatment has great scalability, since the process can use existing infrastructures (such as digesters) in the pulp and paper industry.

Overall, the HWE process has been considered as a simple, low-cost and environmental friendly pretreatment technology. It has great potential to be integrated into a biorefinery processes, as presented in Fig. 1. After HWE pretreatment, there are two main product streams: residual chips and extracted aqueous solution. The structural components of residual chips (mostly cellulose and lignin) remain largely intact during and after HWE, but become more chemically reactive and more energy-dense (Btu/ton), lower in ash content and substantially less hydrophilic [12]. There properties improvements have significant implications for HWE in the manufacture of conventional wood-derived products such as paper, fiberboard, particleboard, wood plastic composites (WPCs) and fuel pellets [13–16]. Removal of hemicelluloses increases the mean pore size of the substrate and therefore increases the accessibility and the probability of the cellulose to be hydrolyzed. Recovery of nanocellulose can also improve due to relatively increased cellulose content, along with more accessible regions of amorphous cellulose. The extracted aqueous solution, on the other hand, contains primarily saccharides from hemicelluloses and a small portion of inhibitory byproducts such as furfural, acetic acid and other organic acids. From this stream, the dissolved hemicellulose can be further converted to commodity chemicals and materials after separation and recovery steps. C-5 and C-6 sugars, which can be separated from the dissolved oligomer sugars, are essential feedstock sources for fermentation.

Many studies have been carried out on effects of HWE on hardwoods species such as aspen [17], maple [18] and oaks [19]. Limited research has been conducted on the effects of HWE on softwoods [13–15,20]. Softwoods are more challenging due to their unique characteristics such as greater difficulty of delignification due to the composition of hemicellulose (higher proportions of mannose and galactose units) and the intimate association between the polysaccharide and lignin part of the cell wall [21]. Douglas fir is a refractory species, which is difficult to impregnate with water even under pressure. The main objective of this research is to investigate the effects of the severity factor (SF) on compositional changes and physicochemical (hygroscopic, thermal and colorimetric) properties of Douglas fir. This study highlights the potential of using the HWE technique for lignocellulosic materials to facilitate downstream processing for production of various co-products and biofuels.

2. Materials and methods

2.1. Raw materials

Douglas fir wood chips were acquired from Vaagen Brothers Lumber Inc. (Colville, WA) and screened with a Black-Clawson Gyratory screening machine to sizes from 4.75 mm to 25.40 mm. The screened chips were dried to 15% moisture content (MC) in a forced air dryer and stored in the conditioned room (equilibrium MC = 12%) before further processing. Screened chips were used directly for HWE pretreatment without further size reduction or separation. Particle size analysis showed that 90.1 wt% of the wood chips ranged between 15.88 and 4.75 mm, and 9.9 wt% ranged from 25.40 to 15.88 mm.

2.2. Protocol of hot water extraction pretreatment

HWE pretreatment was conducted in a 2 L Parr batch pressure reactor (controller model 4842). Each batch of HWE consisted of 50 g oven-dry (OD) wood chips. The moisture content of wood chips was measured before weighting and subtracted from the liquid–solid ratio (LSR) calculation. The reactor took 20–30 min (warming-up time) to reach the target temperature. HWE pretreatment was carried out for a selected time, excluding the warm-up time. The reactor was immediately cooled down by soaking in a water bath at the end of the desired reaction time. Liquid and solid fractions were separated by filtration using vacuum pump equipment. Liquid fractions (hydrolysate) were refrigerated for further analysis. Solid fractions were washed with deionized water several times and then oven-dried overnight at 103 ± 2 °C. Oven dry weight (ODW) of the solids was recorded and used to calculate mass removal as follows:

$$\text{Mass removal} = \left(W_{before} - W_{after}\right) \Big/ W_{before} \times 100\% \quad (1)$$

Where W_{after} is the ODW of solids after pretreatment, and W_{before} is the ODW of solids before pretreatment. Effectiveness of HWE process was evaluated using the severity factor (SF) in order to summarize in one variable the effects of main parameters (reaction time and temperature). SF value ($\log(R_0)$) were calculated as shown in Equation (2) [22], where t is the reaction time (min), T is the

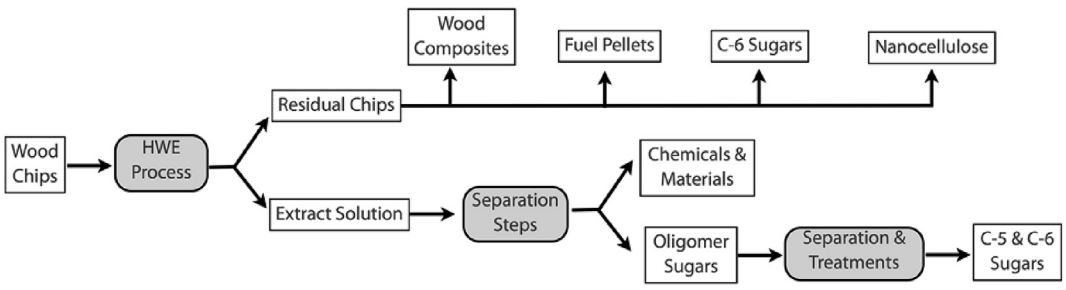

Fig. 1. Scheme of biorefinery with the integration of HWE process [12].