



Production of furfural from an industrial pre-hydrolysis liquor



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ABSTRACT

Pre-Hydrolysis Liquor (PHL) produced from the prehydrolysis kraft-based (PHK) dissolving pulp production process can be considered as a potential source for the production of biomaterials and biochemicals. Several dissolved organics such as hemicelluloses, lignin and acetic acid can be recovered and converted to valuable products. Xylan/xylose, a 5-carbon sugar and the major component of the hardwood PHL can be utilized to produce furfural. Pretreatment is necessary to increase the furfural yield, mainly by removing lignin, facilitating processing and minimizing the side reactions. In this research, adsorption by activated carbon, ion exchange resin treatment, and concentration by membrane filtration were utilized as pretreatments of PHL for furfural production. It was found that a furfural yield of 57% was achieved from the PHL at 190 °C, using sulfuric acid as a catalyst. An overall process, integrated into the existing PHK dissolving pulp production process, was proposed to produce furfural from the PHL which fits well to the Integrated Forest Biorefinery concept.

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1. Introduction

Biorefinery is a multi-disciplinary concept that targets the production of value-added chemicals and materials, energy and fuels from biomass [1]. Applying the biorefinery concept in the pulp and paper industry can result in the production of value-added chemicals and fuels, in addition to pulp, which can increase the revenue of the mills. Dissolving pulp production is one of the practiced pulping processes in the pulp and paper industry, aiming to produce high purity cellulose for applications such as textile manufacturing. In this process, two major biomass components, hemicelluloses and lignin, are removed through pre-hydrolysis and pulping stages, respectively, as critical steps to produce high quality dissolving pulp [2–4]. The hemicelluloses are extracted and dissolved in water, forming the Pre-Hydrolysis Liquor (PHL) which is currently considered as waste, being mixed with black liquor and burnt in the mills for energy production [5,6]. However, the high water content of PHL (>90%) and the low heating value of hemicelluloses (13.6 MJ/kg) in comparison to lignin (27 MJ/kg) [6–8] renders PHL burning an inefficient method of utilizing it. PHL contains sugars (polysaccharides), which can be considered as potential raw materials for the production of a variety of value-added products [9,10]. Furfural has been considered as one of the key green chemicals produced from lignocellulosic feedstock of a biorefinery [11]. Furfural and its derivatives are strategic

platform chemicals due to their large number of applications, and are likely to have a growing demand in different fields, such as oil refining, pharmaceuticals, plastics, liquid alkanes and diesel fuels, furan resins, foundry sand binders and adhesives [12–15].

Producing biochemicals from biomass depends on economical feasibility and efficiency of the pretreatments and processing. Removal of lignin from PHL in the pretreatment stage could be a challenging unit process. Lignin, due to its high molecular weight, may have high potential to cause fouling on adsorbent/membrane surfaces and reduction in furfural yield because of involvement in side reactions. In the literature, different strategies have been used to remove lignin, namely acidification, flocculation, over-liming and adsorption [5–10,16]. Activated carbon (AC) treatment was found as the most efficient process for lignin removal [16,17]. High surface area and hydrophobic attraction are the key factors in effective adsorption and removal of lignin from PHL by AC. Mohan and Karthikeyan [18] removed more than 90% of lignin from laboratory-prepared solutions simulating kraft pulp mill effluents. Andersson et al. [30] were able to remove up to 90% of lignin from an industrially produced waste water sample from a thermo-mechanical pulp (TMP) process. Therefore, adsorption by activated carbon was chosen as the method to remove lignin in this work.

After lignin removal, acetic acid (HAc) can be recovered as a co-product of the process. Potential processes for recovering and upgrading acetic acid from aqueous solutions are: distillation, liquid–liquid extraction, and adsorption by ion-exchange resins. The low concentration of acetic acid (around 1%) in PHL is an obstacle

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for an economic distillation and/or liquid–liquid extraction process. Isolation and recovery of acetic acid from aqueous medium using ion-exchange resins has been studied. Hassan et al. [19] used anion exchange resins to separate and concentrate acetic acid from palm oil mill effluent for the production of polyhydroxyalkanoate. They effectively removed HAc and increased its concentration by a factor of 4 through desorption by HCl. Shen et al. [16] were able to remove 70% of HAc from PHL using the resin Purolite A103S for 5 h with a resin/PHL ratio of 1:10 (g/g). A very similar treatment was practiced in this research, with changes in experimental conditions and resin type to investigate further improvement in HAc removal.

PHL has a very high water content (>90%), and at industrial scale, handling such quantity of water increases capital and operational costs. Hence, removal of excess water is a promising strategy toward the reduction of such costs. Two conventional methods of concentrating solutions are evaporation and membrane filtration. Evaporation would be a highly energy-demanding process considering the large quantity of water in PHL. Membrane filtration, however, is less energy-demanding, finding a growing number of applications in the pulp and paper industry. Shen et al. [16] used nanofiltration membranes for concentration of treated and untreated PHL and achieved more than 22% of sugar concentration. In this research, only AC + resin treated (double treated) PHL was used in order to minimize fouling on the membrane and improve the permeate flux.

The majority of literature work on furfural production has been done with solid biomass, similar to the industrial processes of producing furfural [12,20–22]. Feed stocks, similar to PHL, such as wood extracts and hydrolysates have also been used for such a purpose. Harris and Smuk [27] simulated an industrially produced wood extract in the lab by hot water extraction of hemicelluloses from hard wood chips, and a 90% furfural yield was achieved in a biphasic system, using tetrahydrofuran (THF) as an organic phase for immediate removal of furfural from the reaction medium. Liu et al. [2] utilized original (untreated) and activated carbon (AC) treated PHL samples for furfural production. However, due to side reactions caused by lignin presence and low acidity in different samples, furfural yield reached up to only 32%. In this work, AC and resin treated PHL was used in a single-phase aqueous system for furfural production, using sulfuric acid as the catalyst.

2. Materials and methods

2.1. Materials

The Pre-Hydrolysis Liquor (PHL) sample was provided by a mill in Eastern Canada producing dissolving pulp based on the kraft technology. The mill uses a mixture of 70 wt.% maple, 20 wt.% poplar, and 10 wt.% birch as raw materials. Two filtration steps were carried out with Whatman filter papers (GE Healthcare UK Limited, UK) and Nylon 66 membrane with a pore size of 0.45 μm (Supelco Analytical Group, USA), in order to remove particulates and impurities. Wood based powdered activated carbon (AC) CR325W-Ultra sample was obtained from Carbon Resources. The ion-exchange resin samples used in this work were macro-porous weak-base anion-exchange resins with tertiary amine functional groups, namely Diaion[®]WA30 and Purolite A111S from Sigma Aldrich. To concentrate the sugar solution of PHL, DL nanofiltration membrane (molecular cut off 150–300, pH range 2–10) was used from GE Osmonics.

2.2. Activated carbon treatment

Original PHL was first treated with activated carbon at 1:25 of AC:PHL for 1 h and 200 rpm. The mixture was vacuum filtered

using a vacuum pump and funnel through a 0.45 μm microfiltration membrane ($D = 47$ mm). The activated carbon treated PHL was collected in a flask, while AC was retained on the membrane.

2.3. Ion-exchange resin treatment

The resin treatment procedure was very similar to AC treatment. Mixtures of resin and AC-treated PHL (1:10) were prepared in Erlenmeyer flasks, and shaken at 200 rpm and 25 °C for 1 h. After the desired residence time, the mixture was filtered through 0.45 μm micro-filter (similar to AC treatment), and double treated PHL was collected in a container.

2.4. Membrane filtration

After AC and resin treatments, the PHL may be used for furfural production. However, concentration of dissolved solids (mainly sugars) is very low in PHL (<5%). Since furfural production process needs high temperatures (>170 °C) and low pH (acid addition is needed), high water quantity would make handling difficult, and increases the costs. Therefore, a part of the double treated PHL sample was used for concentration by membrane filtration, before furfural production. The permeate was collected in a flask with a known weight, located on the balance for a continuous monitoring of the permeate weight. A stopwatch was used to record the time needed for the collection of a specific weight of permeate. After the desired quantity of permeate was collected, the filtration module was disassembled and the concentrate was collected. All the experiments were conducted at a constant pressure of 600 psi, and with a stirrer speed of 500 rpm.

2.5. Furfural production

Double treated PHL, in both original concentration (5% sugar) and concentrated (10% sugar) forms, was used for the production of furfural in a batch system. For each experiment, 200–250 g of double treated PHL was added to a reactor (Parr Instrument Company), pH was decreased to 2 by adding sulfuric acid and the temperature was set to 190 °C for 30 min. After reaching the required temperature, liquid samples were taken as the reaction progressed, using a tube that was immersed in the solution. Samples were immediately cooled down by cold water to prevent further side reactions.

2.6. Furfural and acetic acid analysis

The initial and sample concentrations of furfural and acetic acid were determined using ¹H NMR spectroscopy [23,24]. Samples were prepared for NMR spectroscopy using an aqueous sample to D₂O ratio of 4:1. All NMR spectra were recorded using a Varian Unity Inova 300 spectrometer operating at a frequency of 299.95 MHz for ¹H. Solvent suppression of the water signal was achieved using the DDPGSE method.

2.7. Lignin analysis

The lignin content of the samples were measured based on the UV/vis spectrometric method at a wavelength of 205 nm (Tappi UM 250) [25].

2.8. Sugar analysis

The sugars concentration in PHL was measured by an ion chromatography unit equipped with CarboPac[™] PA1 column (Dionex-300, Dionex Corporation) and a pulsed amperometric detector (PAD). The PAD settings were $E_1 = 0.1$ V, $E_2 = 0.6$ V, and

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