



A process to produce furfural and acetic acid from pre-hydrolysis liquor of kraft based dissolving pulp process



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ABSTRACT

Pre-hydrolysis Liquor (PHL) is an aqueous stream containing dissolved organics, produced in the pre-hydrolysis kraft (PHK)-based dissolving pulp production process. Hemicelluloses (6 wt.%) and acetic acid (1 wt.%) present in the PHL can be used or recovered as valuable products, instead of being used as fuel for recovery boiler operation. In this work, hemicelluloses in the PHL were concentrated about 3 times by membrane nano-filtration (NF), while simultaneously separating acetic acid in permeate. NF permeate was subjected to reverse osmosis (RO) to obtain concentrated acetic acid which was subsequently extracted with tertiary amines and polar organic diluents. The concentrated sugars/hemicelluloses in the NF concentrate were converted to furfural using monophasic and biphasic reactor systems. Overall, a sequential bio-refining process to recover organics from PHL was developed.

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1. Introduction

The pre-hydrolysis kraft (PHK) dissolving pulp production process is a variation of the typical Kraft pulping process with the addition of a pre-hydrolysis stage required to remove the hemicelluloses prior to cooking [1]. During the pre-hydrolysis stage of the process, hemicelluloses and other organics are dissolved in the pre-hydrolysis liquor, hereafter known as PHL [2]. The industrially obtained PHL usually contains dissolved components comprising of lignin, hemicelluloses, acetic acid and furfural [3]. Currently, the concentrated solids obtained from evaporation of PHL are burned in the recovery boiler to meet the energy requirements in the mill, even though the heating value of hemicelluloses is only about 13.6 MJ/kg [3,4]. The hemicelluloses dissolved in PHL are a valuable source of hexose and pentose sugars, therefore, extraction and then conversion of hemicelluloses to value added products like ethanol, furfural, xylitol etc. would be more economical [3,5]. The acetyl groups bound to the lignocelluloses can also be used to generate acetic acid, which itself has significant market value [6,7].

Membrane separation processes can play an essential role for fractionation, purification and concentration of valuable intermediate and final products. NF membranes have been investigated in the past for hemicellulose concentration and simultaneous acetic acid

separation from treated PHL, which is essential for better hemicellulose utilization as well as acetic acid recovery [3,8,9]. The concentrated hemicelluloses in NF concentrate can be converted to furfural by hydrolysis and dehydration of pentosans at elevated temperatures in the presence of acid catalyst in either monophasic or biphasic reactor systems [10–14]. The acetic acid in NF permeate can also be upgraded to higher purity acetic acid product, using previously studied techniques like reactive extraction [15]. In the last few decades, several studies focused on concentration and recovery of acetic acid by using membrane separation processes, typically by using reverse osmosis (RO) [16–19].

This study focussed mainly on the development of a continuous sequential process using PHL as feed, in order to obtain furfural and acetic acid as end products. The proposed process flow diagram shown in Fig. 1 comprised of: 1. Nano-filtration of original PHL for concentration of sugars/hemicelluloses and lignin in the retentate, and simultaneous release of acetic acid in permeate; 2. Utilization of concentrated hemicelluloses from NF concentrate to produce furfural; and 3. Concentration and purification of acetic acid from NF permeate using reverse osmosis and reactive extraction.

2. Materials and methods

2.1. Materials

The industrially produced PHL of the kraft-based dissolving pulp production process was collected from a mill located in

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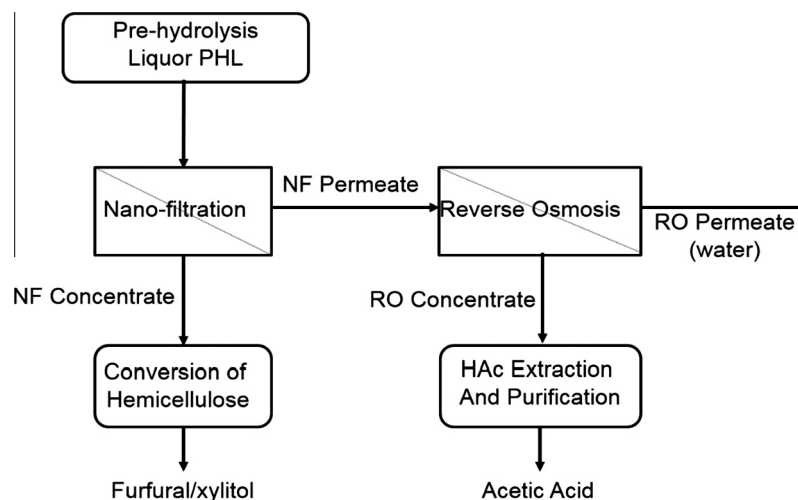


Fig. 1. Proposed process flow diagram for biorefinery.

Eastern Canada. In this mill, the stream pre-hydrolysis of wood chips consisting of 70 wt.% maple, 20 wt.% poplar, and 10 wt.% birch, was conducted at 170 °C via the VisCBC process.

The PHL obtained was found to contain 9.22 g/L lignin, 51.4 g/L hemicelluloses, 10.11 g/L acetic acid and 1.43 g/L furfural [3].

2.2. Nano-filtration of original PHL

Nano-filtration of original PHL was carried out using a negatively charged thin film spiral wound membrane (NTR 7450) with sulfonated polyethersulfone as surface layer. The membrane was a tight ultra-filtration membrane with molecular weight cut off (MWCO) of 1000 Da and was obtained from Hydranautics, Nitto Denko. The retention mechanism through this membrane was both molecular sieving as well as Donnan exclusion of the negatively charged molecules [20,21]. The zeta potential of NTR 7450 at a pH of 4 (pH of PHL) is about -20 mV [22].

A stirred cell from Sterlitech (HP4750), which is a high-pressure chemically resistant dead end filtration cell was used for membrane filtration. It was made of 316 stainless steel (maximum operating pressure of 1000 psig), and used with a flat sheet membrane of 47 mm diameter. The cell contained a removable PTFE stir bar for mixing of filtration feed during operation. All nano-filtration experiments were performed at a pressure of 400 psig.

The extent of nano-filtration was expressed in terms of volume reduction factor (VRF), Where, $VRF = \text{Initial feed volume } (V_0) / \text{Volume of concentrate or retentate } (V_R)$.

2.3. Furfural production

NF concentrate was obtained from nano-filtration of original PHL using NTR 7450 membrane, and used as the aqueous feed containing pentose sugars for both mono and biphasic systems. Methyl isobutyl ketone (MIBK) was purchased from Fisher Scientific and used as organic solvent for biphasic reaction process. Sulfuric acid (37%) was used for the acidification of NF Concentrate before reaction.

Stainless steel tubes with Swagelok caps were used as reactors for both monophasic and biphasic systems. For the biphasic system, equal amounts of acidified NF Concentrate and MIBK (Weight ratio of 1:1) were added to the reactor and tightly capped. The reactors were placed in a Parr reactor (4843, Parr Instrument Company) which was equipped with temperature limit controller and

pressure transducer module, and the conversion to furfural was carried out in a single step at a desired temperature.

2.4. Reverse osmosis

The Sterlitech stirred cell used for nano-filtration was used for reverse osmosis as well. A pre-cut thin-film composite reverse osmosis membrane from Alfa Laval (RO99), with operating conditions of pH 3–10, temperature 5–50 °C, and pressure 200–600 psig was used. Reverse osmosis was carried out at 500 psig till VRF of 4.24 was achieved.

2.5. Reactive extraction of acetic acid

A 5% model acetic acid (MAA) solution, RO Concentrate obtained from reverse osmosis, and aqueous phase from biphasic furfural production, were used as 3 different feed aqueous.

A tertiary amine, Trioctylamine (ToA, 98%), and a polar diluent 1-Octanol (99.99%) were obtained from Fisher Scientific and Alfa Aesar, respectively. The extraction was carried out using Erlenmeyer flasks, magnetic stirrers, stir plate, separatory funnels, etc. Equal weights of organic solvent (at various mixture ratios of ToA and Octanol) and aqueous feed solution were separately charged in Erlenmeyer flasks. The experiments were carried out at different stoichiometric ratios between the acid (acetic acid in feed) and amine (ToA). The mixture was stirred by a magnetic bar at 500 rpm for 30 min at 25 °C, followed by centrifuging at 3000 rpm for approximately 5 min to separate the two phases and collected using a separatory funnel.

2.6. Quantitative determination of dissolved organics

Quantitative determination of dissolved organics, i.e., oligomeric sugars, monomeric sugars, acetic acid, furfural, and lignin, in various aqueous streams was carried out using ion chromatography (DIONEX), proton NMR, and UV/Vis spectrometric absorption methods, and the procedures have been published previously [6,23].

The concentration of furfural produced in the MIBK organic phase during biphasic reaction was also determined by proton NMR by using solvent suppression method with CDCl_3 to MIBK in a ratio of 1:1. Calibration curves were established for furfural by dissolving furfural reagent (Fisher Scientific) in MIBK, then

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