



Recovery of acetic acid from pre-hydrolysis liquor of hardwood kraft-based dissolving pulp production process by reactive extraction with triisooctylamine



G. Yang^{a,b,*}, M. Sarwar Jahan^{b,c,*}, Laboni Ahsan^b, Linqiang Zheng^b, Yonghao Ni^{b,*}

^a Key Laboratory of Pulp & Paper Science and Technology (Shandong Polytechnic University), Ministry of Education, Jinan 250353, Shandong, China

^b Limerick Pulp and Paper Centre, University of New Brunswick, Fredericton, New Brunswick, Canada E3B 5A3

^c Pulp and Paper Research Division, BCSIR Laboratories, Dhaka, Dhaka 1205, Bangladesh

HIGHLIGHTS

- Acetic acid was recovered from the PHL by reactive extraction with triisooctylamine.
- Diluent played an important role in recovering acetic acid from the PHL.
- Temperature and pH negatively affected the acetic acid extraction.
- Acetic acid concentration positively affected the acetic acid extraction.

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ABSTRACT

Acetic acid was one of the main compositions of the pre-hydrolysis liquor (PHL), which was recovered by reactive extraction with triisooctylamine (TIOA) diluted with decanol. Dilution of TIOA played an important role in extracting acetic acid from the PHL. The recovery of acetic acid from the PHL by TIOA was increased from 10.34% to 66.60% with the dilution of TIOA to 20% by decanol at the HAc to TIOA molar ratio of 1, consequently, the equilibrium distribution coefficient K_D increased. The effects of time, temperature and pH on the extraction process were also studied. The extraction process was very fast. The acetic acid extraction decreased from 65.13% to 57.34% with the rise of temperature to 50 °C from 20 °C. A higher pH increased the dissociation of acetic acid, as a result, decreased acetic acid extraction. The hemicelluloses in the PHL were unaffected on the extraction process of acetic acid.

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1. Introduction

Pre-hydrolysis is carried out in the kraft-based dissolving pulp process to remove hemicelluloses from the lignocellulose. The pre-hydrolysate liquor (PHL) contains both mono- and oligo-sugars, lignin, acetic acid (HAc), furfural and some degradation products (Shen et al., 2011; Liu et al., 2011; Shi et al., 2012). Effectively recovering these components will make it viable for the biorefinery concept of dissolving pulp production process. Acetic acid is generated by the cleavage of acetyl groups in wood, and it is an important industrial commodity chemical with a total production of 6.94 million tons in 2009 ([http://www.marketave-](http://www.marketave-nue.cn/upload/ChinaMarketReports/REPORTS_1212.htm)

[nue.cn/upload/ChinaMarketReports/REPORTS_1212.htm](http://www.marketave-nue.cn/upload/ChinaMarketReports/REPORTS_1212.htm)). The largest use of acetic acid is as a feedstock for the manufacture of vinyl acetate monomer (VAM), followed by terephthalic acid (TPA) which is used for the manufacture of polyethylene terephthalate (PET) bottle resins and polyester fiber (Mirasol, 2009). Presently, acetic acid is mainly produced (65%) through methanol carbonylation using non-renewable feedstock. Therefore, recovery of acetic acid from the PHL as a valuable product, certainly fits into the forest biorefinery and can open a window for producing acetic acid from a renewable resource.

Many methods for separating acetic acid from different industrial waste liquor have been reported such as solvent extraction, membrane separation, adsorption (Tamada and King, 1990a,b; Hou et al., 2008). Activated carbons and polymeric resins with functional groups were also used in the recovery of acetic acid (Husson and King, 1999); however, the adsorption capacity was limited. In the conventional solvent extraction process, the equilibrium distribution coefficient, K_D for acetic acid extraction is 1 or

* Corresponding authors. Address: Limerick Pulp and Paper Centre, University of New Brunswick, Fredericton, New Brunswick, Canada E3B 5A3. Tel.: +1 5064516860 (G. Yang).

E-mail addresses: ygh@spu.edu.cn (G. Yang), sarwar2065@yahoo.co.uk (M.S. Jahan), yonghao@unb.ca (Y. Ni).

less, therefore, was not economically attractive (Saha et al., 2000). The distribution coefficient, K_D , is defined as the ratio of organic acid in the two phases by:

$$K_D = \frac{[HA]_{org}}{[HA]_{aq}} \quad (1)$$

It is known that ethyl acetate has a high dissolving power for acetic acid in comparison with other solvents, and many studies were carried out on acetic acid extraction using ethyl acetate (Garner and Ellis, 1953). But these process needs lot of solvent for a diluted HAC feed, such as PHL, therefore, regeneration of solvent is energy intensive. Another drawback of ethyl acetate is its partial miscibility with water.

In view of these limitations of the conventional process, it is appropriate to explore an efficient extraction process that will provide high K_D value. Some literature explored the use of some organophosphorous compounds and high-molecular-weight alkyl amine, which were found to have higher efficiency than the conventional solvent extraction for the extraction of diluted carboxylic acids (Wardell and King, 1978; Mahfud et al., 2008; Vitasari et al., 2012). The amine is dissolved in a diluent that dilutes the extractant to desire composition and control the viscosity and density. It has been found that the type of diluent and the solvent to diluents ratio can affect the extraction of carboxylic acid by amine (Bizek et al., 1993). Polar diluents have been shown to be more effective diluents than non polar ones due to high partitioning coefficients (Kumar and Babu, 2009). Polar diluents such as alcohols have been shown to be most suitable for amines because they give the highest distribution coefficients resulting from formation of solvents through specific hydrogen bonding between the proton of diluent and acid amine complex. Li et al. (2003) studied on the reactive extraction of aqueous solutions of different carboxylic acids with trioctylamine in various diluents, and the degrees of extraction of the medium-strong carboxylic acids with trioctylamine were in the order of 1-octanol \geq chloroform > tetrachloromethane > hexane. The strong acid provides a larger loading of trioctylamine than the weak acid.

Tertiary amines, such as trioctyl amine (TOA) or triisooctyl amine (TIOA), appeared to be the better choice for the extraction process. In this study, TIOA was chosen as the extractant for the recovery of acetic acid and decanol was selected for diluting the extractant. TIOA was chosen due to its lower price than the TOA. Many factors such as nature of the acid extracted, concentrations of the acid and the extractant, and the type of diluent used can influence the extraction process. The industrially produced PHL sample is a unique source for HAC and it is different from those studied on the extraction of acetic acid from waste stream/fermentation broth, in particular, the HAC concentration is only at 1%.

In this study, the recovering of HAC from the PHL was investigated by following the reactive extraction process using TIOA/ decanol. The different factors such as time, temperature, pH, dilution of TIOA with decanol and acid concentration have been studied for the extraction of acetic acid from the activated carbon (AC) pre-treated pre-hydrolysis liquor (PHL). The characteristics of PHL after acetic acid extraction have also been studied.

2. Experimental

2.1. Materials

The industrially produced PHL samples were collected from the bottom of digester (draining the whole digester after depressurizing) at a dissolving pulp mill in Eastern Canada. The PHL was filtered with Whatman qualitative filter papers (GE Healthcare UK Limited, UK) and Nylon 66 membrane with a pore size of

0.45 μm (Supelco analytical group, USA) for removing large particles and impurities. TIOA and decanol were purchased from Sigma-Aldrich Co. (USA). CR325 W activated carbon was obtained from Carbon Resources Inc. (CA). Sulfuric acid (4 N) was purchased from Fisher Scientific Inc. (USA) and diluted to 4 wt.% prior to use. Sodium hydroxide (60 wt.%) was obtained from Ricca Chemical Company (USA) and diluted to 5 wt.% for use.

2.2. Activated carbon treatment

In removing/recovering the lignin present, the PHL was treated with activated carbon (AC) at room temperature and in a sonication bath for 30 min. The weight ratio of PHL to AC was 20:1.

2.3. Sugar analysis

The hydrolysis condition was 1.78% (w/w) sulfuric acid concentrations in the PHL at 130 °C for 20 min (Yang et al., 2012). Hydrolysis of PHL was carried out in a Parr reactor. Required amount of sulfuric acid was added to PHL in an ample and sealed. Sealed ample was placed inside the parr reactor contained water which was put in an oil bath (Neslab Instruments, Inc., Portsmouth, NH, USA) to convert oligosaccharide to monosaccharide. The sugar concentrations were determined by using an Ion Chromatography unit equipped with CarboPac TM PA1 column (Dionex-300, Dionex Cooperation, Canada) and a pulsed amperometric detector (PAD). The sugar content in the PHL before the acid hydrolysis represented the monomeric form while the polymeric sugars were calculated from the difference with and without the acid hydrolysis.

2.4. Acetic acid and furfural analysis

A Varian 300 NMR-spectrometer was employed for determining the furfural and acetic acid concentrations as described earlier (Ni and Kang, 2007). Calibration curves were made with the standard solutions of each component to determine the unknown concentration for each of these present in the PHL. The sample was prepared with D₂O to sample volume ratio of 1:4.

2.5. Lignin analysis

The lignin content in the PHL was determined following Tappi Useful Method (Tappi UM250).

2.6. Reactive extraction

Required amount of the organic phase (extractants) and aqueous solution (PHL samples) were charged in flasks separately. The extraction was performed by stirring with magnetic bar at 200 and 400 rpm. The extraction time and temperature were varied from 2 to 20 min and from 20 to 50 °C, respectively. The pH value of the PHL-amine mixture was adjusted by adding a diluted NaOH solution. Then the extraction mixture was centrifuged at 3000 rpm for 5 min to assist separation of organic and aqueous phases, followed by 20 min in separating funnel. The two phases were analyzed immediately after the separation. Then the concentration of HAC in the organic phase was determined by mass balance (Eq. (2)).

$$([HA]_{org})_{eq} = \frac{([HA]_{aq}V_{aq})_{initial} - ([HA]_{aq}V_{aq})_{eq}}{(V_{org})_{aq}} \quad (2)$$

where V_{aq} : volume of aqueous phase (mL) and V_{org} : volume of organic phase (mL).

For the evaluating extraction efficiencies of different runs, HAC recovery (%) and distribution coefficient (K_D) were determined. The

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