Recovery of Acetic Acid from Prehydrolysis Liquor of Kraft Hardwood Dissolving Pulp using Ion-exchange Resin

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The growing demand for rayon and cellulosic products has resulted in the conversion of a number of kraft pulp mills into dissolving pulp mills in recent years. In fact, kraft-based dissolving pulp production fits well into the concept of an integrated forest biorefinery, in particular, the utilization of dissolved organics in the pre-hydrolysis liquor (PHL) for bio-materials and bio-energy purposes. In this study, the recovery of acetic acid, the second major component in the PHL of the kraft-based hardwood dissolving pulp production process, was investigated using amine-based resin adsorption. Activated carbon (AC) adsorption was adopted as the first step to remove the lignin, and six AC samples were evaluated for this purpose. Among them, CR325 W-Ultra Powder AC showed the best result and removed about 90% of lignin with a minimal loss of hemicellulosic sugars and acetic acid from PHL at a ratio of 1:20 (AC:PHL). Subsequently, the adsorption of acetic acid from AC-treated PHL (TPHL) was studied on tertiary and quaternary amine-based resins. The tertiary amine resin demonstrated better adsorption efficiency. Desorption of the adsorbed acetic acid from the amine resin using sodium hydroxide solution was also studied, and the results showed that 66 to 84% acetic acid desorption occurred using a 4% NaOH solution.

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INTRODUCTION

Pre-hydrolysis is an important step in the kraft-based hardwood dissolving pulp process to remove hemicelluloses from the raw materials. In the pre-hydrolysis process, a part of lignin is dissolved along with hemicellulose. Also, acetic acid is formed from acetyl groups bound to hemicelluloses. Separation and concentration of acetic acid from the prehydrolysis liquor (PHL) is essential for implementing a biorefinery concept in the kraft-based dissolving pulp production process. The presence of lignin in the PHL is detrimental for utilizing dissolved biomass. For example, lignin in the PHL hampers xylose/xylan fermentation for ethanol or xylitol production (Agbogbo and Coward-Kelly 2008; Sixta 2006). It can create a fouling problem when using membrane technology to concentrate the dissolved hemicelluloses/sugars (Shen *et al.* 2013). Lignin in the PHL even can increase side reactions during furfural production from the dissolved hemicelluloses/sugars (Liu *et al.* 2012). The presence of lignin also creates problems in separating and concentrating acetic acid from the PHL by reactive extraction with tri-

octyl amine (TOA) and octanol (Ahsan *et al.* 2013). Therefore, lignin must be removed for the successful exploitation of dissolved biomass.

Activated carbon (AC) adsorption is a popular physico-chemical treatment for the removal of dissolved organics from wastewaters (Juang *et al.* 2001; Lin *et al.* 2008). AC has a highly porous structure and high specific surface area, which makes it a strong candidate for adsorbing various organic and inorganic materials in liquid or gas media (Inal *et al.* 2009; Lua and Yang 2009). In this study, six types of AC were evaluated in terms of lignin removal from PHL.

Acetic acid is an important co-product in the pre-hydrolysis of biomass (Amidon and Liu 2009; Jahan *et al.* 2009; van Heiningen *et al*. 2006), and it is a commodity product that has many applications in the food and chemical industries. Conventional technologies, such as liquid-liquid extraction and distillation, are not commercially viable for recovering acetic acid from the PHL because its concentration is only about 10 g/L (Shen *et al.* 2013).

Because of its low concentration in the PHL, adsorption may be an attractive method for separation of acetic acid. Amine-based resins may serve this purpose well because acetic acid forms hydrogen bond complexes with amino groups on resins (Anasthas *et al.* 2001). Different types of resins have been reported to remove acetic acid from its dilute solution (Hasan *et al.* 2010; Anasthas *et al.* 2001; Cloete and Marais 1995; Bhandari *et al.* 1993; Takatsuji and Yoshida 1997; Juang and Chou 1996; Husson and King 1999). Tertiary amine-based resins adsorb more acetic acid than primary and secondary amine-based resins, and it was reported that about 98.5% of the acetic acid was recovered from a 1% acetic acid solution using Duolite A-375 (Cloete and Marais 1995). In the present study, three different weak base resins and a strong base resin were evaluated for acetic acid adsorption from the PHL.

EXPERIMENTAL

Materials

Acetic acid (purity > 99%) was obtained from Fisher Scientific Canada. Industrial pre-hydrolysis liquor (PHL) was collected from dissolving pulp mills in Eastern Canada. The weak base resins Purolite A111S and PA103S were supplied by Purolite International Ltd. Other resin samples (WA30 and PA408) were supplied by DIAION. These were macroporous weak base anion resins and used without any treatment or purification. BL Powdered Activated Carbon (AC), PWA Powdered AC, and CANE CAL Granular AC were purchased from CALGON Carbon Corporation, and CR325AA-10, CR325W-Ultra, and CR610A samples were obtained from Carbon Resources.

Methods

AC treatment

The PHL was treated with AC at room temperature for 5 h. The ratio of PHL to AC was 20:1, and the shaking speed was 150 rpm.

Resin treatment

All resins and different volumes of 1% model acetic acid (MAA) solutions and AC-treated PHL (TPHL) were added at various ratios (1:5 to 1:20) to a thermostatic

shaker at 25, 35 and 45 °C for adsorption studies. Agitation was provided at 150 rpm for 1 h. The amount of adsorbate on the adsorbent and in solution at equilibrium can be represented as,

$$q_e \text{ (g/g)} = (C_o\text{-}C_e)V/W \tag{1}$$

$$X_e \text{ (g)} = C_e \text{ (g/L)}*V\text{(L)} \tag{2}$$

where C_o and C_e (g/L) are the initial and equilibrium acetic acid concentrations, respectively. V (L) is the solution volume, and W (g) is the weight of adsorbent used in the experiment. Regeneration/desorption was performed in a manner similar to adsorption with 4% NaOH at a 1:10 resin-to-alkali ratio, with 150-rpm shaking for 1 h.

Acetic acid analysis

The initial and equilibrium acid concentrations of furfural and acetic acid were determined using ^{1}H NMR spectroscopy (Ni and Kang 2007; Ni *et al.* 1996). Calibration curves were made with the standard solutions of each component to determine the unknown concentrations present in the PHL. Samples were prepared for NMR spectroscopy using a ratio of aqueous sample to D_2O of 4:1. All NMR spectra were recorded using a Varian Unity Inova 300 spectrometer operating at a frequency of 299.95 MHz for [1]H. Solvent suppression of the water signal was achieved using the DPFGSE method.

Lignin analysis

The lignin contents of the original PHL and TPHL were measured based on the UV/vis spectrometric method at a wavelength of 205 nm (TAPPI UM 250) (Liu *et al.* 2012).

Sugar analysis

The mono and oligo-sugar contents in the pre-hydrolysis liquor and the raffinate were determined using ion chromatography with a pulse amperometric detector and CarboPacTM PA1 column (Dionex-300, Dionex Corporation, Canada) (Ahsan *et al.* 2012).

RESULTS AND DISCUSSION

Adsorption of Lignocelluloses onto Different Activated Carbons

The specific surface area of activated carbon (AC) was varied from 950 to 1350 m^2/g. As shown in Table 1, the lignin and furfural adsorption was very high on AC. The adsorption of both lignin and furfural was directly related to the surface area of AC. CR325W-Ultra Powdered AC had the highest surface area, yielding 93.17% lignin and 92.75% furfural adsorption at a ratio of 1:20 (AC:PHL). These results were in agreement with those in the literature (Shen *et al.* 2013). It was observed that lignin and furfural adsorption from the model PHL onto AC was very high (Fatehi *et al.* 2013). In another study, hydrolysis liquor was prepared by steaming hardwood chips at 170 °C for 1 h and contained 3.62 g/L monosugars and 0.78 g/L furfural. The treatment of this hydrolysis liquor with 5% AC in a batch system at 50 °C and 180 rpm resulted in 97.5% furfural

removal (Lee *et al*. 2011). Therefore, it can be concluded that AC is a suitable adsorbent for furfural and lignin. The adsorption of lignocelluloses also depends on the charge interaction and hydrophobicity/hydrophilicity (Chinn and King 1999; Lee *et al*. 2011; Sulaymon and Ahmed 2008; Zhang *et al.* 2011). Furfural is a hydrophobic material and has a small size; thus, it can easily access the pores of AC. The pore accessibility/large available surface area and high hydrophobicity are the reasons for the high adsorption of furfural on AC (Table 1). Lignin could be adsorbed onto AC based on van de Waals and hydrogen bonding (Fatehi *et al.* 2013). About 20% acetic acid present in the PHL was also adsorbed onto AC, which did not vary significantly with surface area (Table 1).The results indicated that CR325W-Ultra Powdered AC was the best adsorbent for lignin and furfural removal from the PHL. The AC-treated PHL (TPHL) was subsequently treated with an amine-based resin to recover acetic acid.

Table 1. Lignocellulose Adsorption on Different Activated Carbons (25 °C, 1:20 AC:PHL, 5 h)

AC	Surface area (m^2/g)	Total pore volume (cm^3/g)	Mean pore diameter (nm)	Lignin (%)	Acetic acid (%)	Furfural (%)
BL Powdered AC	919	0.47	2.12	87.78	21.34	88.88
PWA Powdered AC	975	0.58	2.41	88.35	22.15	89.56
CR325AA-10 Powdered AC	1045	0.88	3.45	90.69	20.66	90.26
CR325W-Ultra Powdered AC	1350	1.21	4.06	93.17	20.11	92.75
CANE CAL Granular AC	1039	0.63	2.44	85.4	20.96	82.48
CR610A Granular AC	908	0.52	2.85	82.04	22.65	81.65

Adsorption of Acetic Acid onto Amine-Based Resin

At this stage, the main objective was to recover acetic acid from the TPHL. Three different weak base resins and a strong base resin were evaluated for acetic acid adsorption from the TPHL and MAA. As shown in Table 2, acetic acid adsorption from the MAA was 95 to 98% for tertiary amines, while it was only 45 to 57% for TPHL.

Table 2. Adsorption of Acetic Acid from Model Acetic Acid (MAA) Solution and Activated Carbon-treated Prehydrolysis Liquor (TPHL) onto Different Resins

Resin type	Adsorbent name	Capacity (meq/mL)	Recovery of acetic acid %	
			1% MAA	TPHL
Tertiary	A111S	1.70	97.94	46.26
	A103S	1.60	95.25	45.25
	WA30	1.50	97.48	45.25
Quaternary	PA408	0.90	26.66	22.34

The greater adsorption in the case of the tertiary amine resins may be attributed to the presence of sugars and lignin in addition to acetic acid in TPHL, which can hinder acetic acid adsorption. The highest amount of acetic acid adsorption for both MAA and TPHL was found with A111S, while the lowest adsorption was for quaternary PA408. The presence of more electronegative chloride ions in the quaternary resin hindered the exchange of acetate ions.

Effect of Time and Temperature on Acetic Acid Adsorption

The A111S resin had the highest acetic acid adsorption (Table 2); thus, further adsorption studies were carried out using the same resin but varying time, temperature, and the adsorbate-to-adsorbent ratio. As shown in Table 3, a higher temperature negatively affected the adsorption of acetic acid from the TPHL. The lower adsorption of acetic acid at higher temperatures indicates that this reaction is exothermic in nature (Saha and Chowdhury 2011). The treatment time did not change the acetic acid adsorption significantly in the range studied, indicating that the adsorption was very fast.

Table 3. Effect of Time and Temperature on the Adsorption of Acetic Acid from TPHL and MAA onto Resin A111S

Temperature (°C)	Time (h)	HAc removal from MAA (%)	HAc removal from TPHL (%)
25	1	97.94	46.26
	2	98.45	46.54
	3	98.50	46.66
	4	98.58	46.75
35	1	95.46	45.51
	2	97.99	45.82
	3	98.19	45.93
	4	98.25	45.98
45	1	92.77	44.13
	2	96.47	44.56
	3	96.50	44.76
	4	97.53	44.84

Effect of Resin-to-Adsorbate Ratio on Adsorption

The adsorption of acetic acid increased with increasing adsorbent dose (Fig. 1). The mass ratios of TPHL or MAA solution to resin were 20, 10, 5, 4, and 3.3. For TPHL, the maximum adsorption was 57% at the resin-to-TPHL ratio of 1 to 3.3. At a resin dose of around 1 g to 10 g of aqueous sample, the adsorption capacity reached 98% for 10 g/L MAA, which is 1.5 meq/g of dry resin. For TPHL, the acetic acid adsorption was only 46%, which is 0.63 meq/g of dry resin at a 10:1 ratio of aqueous solution to resin dose. This may be attributed to the presence of sugars and lignin in addition to acetic acid in TPHL, which may hinder acetic acid adsorption.
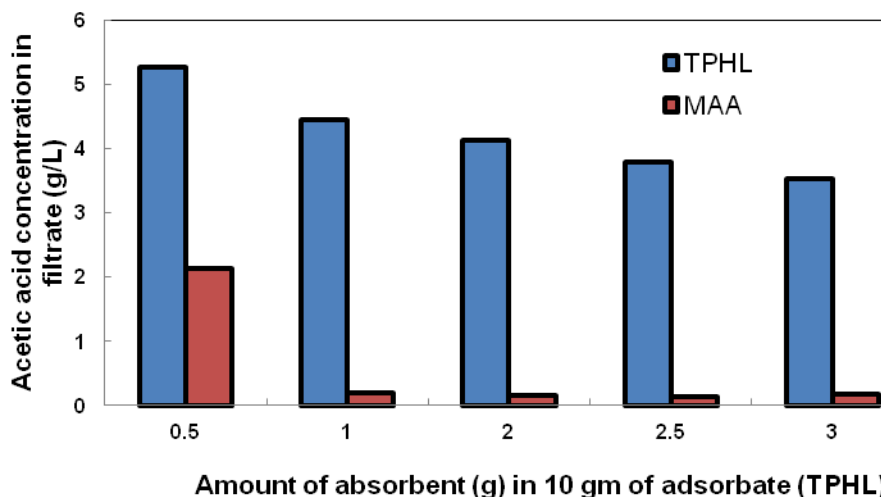
Fig. 1. Effect of adsorbent on the adsorption of acetic acid from TPHL and MAA at 25 °C for 1 h

Regeneration of Resin

From an economic perspective, the resin would have to be reused/ recycled. Table 4 shows the amount of acetic acid that was desorbed from the resin using 4% NaOH. It was also found that a higher alkali concentration was capable of removing more acetic acid from the resin, but this condition could hamper the properties of resin (Lv *et al.* 2012). Therefore, 2 to 4% NaOH was reasonable for this purpose. From Table 5 it is clear that desorption increased with increasing temperature. At room temperature, 78% and 66% acetic acid in MAA and TPHL were desorbed as sodium acetate from adsorbed resins, respectively, values that increased to 90% and 84% when increasing the temperature by 20 °C. The lower desorption for the TPHL was due to the presence of lignin and other dissolved organic materials, which were also adsorbed and block the resin pores.

Table 4. Desorption of Acetic Acid by 4% NaOH Solution at 1:10 Ratio of Resin to Alkali Solution for 1 h at 150 rpm

Feed stock	Desorption of acetic acid from resin					
	25 °C		35 °C		45 °C	
	% Desorbed	Concentration in filtrate (g/L)	% Desorbed	Concentration in filtrate (g/L)	% Desorbed	Concentration in filtrate (g/L)
MAA	78%	7.02	85%	7.65	90%	8.10
TPHL	66%	2.64	74%	2.96	84%	3.36

CONCLUSIONS

1. Activated carbon adsorption can be used to remove the dissolved lignin in the prehydrolysis liquor of kraft-based hardwood dissolving pulp. The adsorption is largely dependent on the surface area and pore volume of the activated carbon.

2. The recovery of acetic acid from the treated prehydrolysis liquor can be carried out by adsorption onto amine-based resins. Better adsorption was observed for weak base resin than for strong base resin. Resin A111S showed the best adsorption of acetic

acid. Acetic acid adsorption from the TPHL was lower than it was from MAA due to the presence of impurities.

3. A higher temperature negatively affected the adsorption of acetic acid from the MAA and TPHL.

4. A sodium hydroxide solution can be used to desorb acetic acid from resin, which can then be reused/recycled in the process.

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