Adsorptive Membranes vs. Resins for Acetic Acid Removal from Biomass Hydrolysates

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Abstract

Acetic acid is a compound commonly found in hemicellulosic hydrolysates. This weak acid strongly influences the bioconversion of sugar containing hydrolysates. Previous investigators have used anion exchange resins for acetic acid removal from different hemicellulosic hydrolysates. In this study, the efficiency of an anion exchange membrane was compared to that of an anion exchange resin, for acetic acid removal from a DI water solution and an acidic hemicellulose hydrolysate. The results show that the membrane exhibited better performance in terms of dimensionless throughput and product loss.

Key words: dilute acid hemicellulose hydrolysate; ion exchange membrane; ion exchange resin

Introduction

Lignocellulosic residues represent a renewable, widespread and cheap source of carbohydrates that may be used as raw materials in bioconversion processes for the production of fuels, foods, medicines and enzymes [1]. Lignocellulosic residues are mainly composed of a mixture of polymerized carbohydrates (cellulose and hemicellulose) and lignin (complex phenolic macromolecule).

Prior to biological utilization, lignocellulosic biomass has to be hydrolyzed to release sugars from the polymeric matrix. Different processes have been developed to hydrolyze hemicellulosic sugars from lignocellulosic materials. Among them, dilute acid hydrolysis (mainly using sulfuric acid) is recognized as being effective for producing a xylose-rich hemicellulose hydrolysate liquor while enhancing cellulose enzymatic digestibility[2].

During hydrolysis, some inhibitory compounds are also produced which hinder the subsequent bioconversion of the solublized sugars into desired products, reducing conversion yields and rates during fermentation [3,4]. These inhibitory compounds include acetic acid and lignin derivatives (released from the lignocellulose) and furfural and hydroxymethylfurfural (from acid-catalyzed sugar degradation).

This investigation studied the removal of acetic acid from a hemicellulosic hydrolysate. The inhibitory effect of acetic acid (pKa = 4.75, 25°C) is strongly affected by the pH. When the pH of a hydrolysate is lower than 4.75, the protonated form of acetic acid is dominant in the solution. Since this form of the acid is lipophilic, it can diffuse through the cytoplasmatic membrane and detrimentally affect cell metabolism[5]. Although the effect of acetic acid can be effectively controlled by conducting the bioconversion at high pH (around 6.0), fermentation at this high pH can be suboptimal. Therefore, in many situations, removal of acetic acid from the hydrolysate is necessary.

Ion-exchange resins have been used to remove acetic acid from hemicellulosic hydrolysates[6-8]. However resin-based chromatography suffers from a number of limitations. The pressure drop across the bed is generally high and tends to increase during operation due to media deformation. Pore diffusion is often slow leading to increased processing time and possible degradation of fragile biological product molecules [9-13]. Scale-up of packed-bed columns is also difficult.

Adsorptive microporous membranes have surface functional groups attached to their internal pores. When the feed is pumped through the membrane pores, transport of the solute to the binding sites occurs predominantly by convection, and this can greatly reduce the required processing time. Furthermore, the pressure drop for flow through adsorptive membranes is significantly lower than in typical packed beds, since the flow path is much shorter, even using a stack of multiple membranes. An important practical advantage is that scale-up of membrane devices is easier than scale-up of packed beds[14-17]. Thus, adsorptive membranes may offer significant improvements over traditional ion-exchange resins.

Experimental

A corn stover hemicellulosic hydrolysate generated by dilute sulfuric acid pretreatment was obtained from the National Renewable Energy Laboratory (NREL). Prior to acetic acid removal, the hydrolysate was detoxified using two different procedures. In the first procedure, the pH of the hydrolysate was raised to 10 by the addition of $Ca(OH)_2$. After filtration using a 0.22 μm membrane, the pH of the hydrolysate was decreased to 6.0 by the addition of H_2SO_4. Finally, the hydrolysate was filtered again to remove particulate material. This process is referred to as overliming and has historically been used by NREL to improve hydrolysate fermentability; it will be referred to as the “NREL process” hereafter. In the second procedure, the pH of the hydrolysate was raised to 7.0 by the addition of CaO. After filtration using a 0.22 μm membrane, the pH of the hydrolysate was decreased to 5.5 by the addition of H_3PO_4 and the hydrolysate was filtered again to remove particulate materials. Then, the hydrolysate was mixed with activated charcoal (2.5 % w/v) at 30 °C and 200 rpm for 60 min and filtered again to remove the suspended charcoal and particulate matter. This process is currently used at Faenquil in Brazil, and hereafter will be described as the “Brazilian process.”

An ion exchange membrane, Sartobind Q (Sartorius AG, Göttingen, Germany), was used to remove acetic acid from these two hydrolysate solutions. An ion exchange resin, Amberlyst A21, was also investigated and its performance compared to that of the Q membrane. A control study was also conducted to compare acetic acid removal from DI water using both the Q membrane and A21 resin.

The Q membrane module consisted of 25 mm diameter discs, surface area 75 cm^2, thickness 4 mm and nominal pore size larger than 3 μm. The experiments started with an equilibration of the membrane with water at pH 7.0. Then the membrane was loaded with acetic acid solution at pH 7.0 followed by a washing with water at pH 7.0. After that a 0.1 mol/L HCl solution was used to elute the acetic acid from the membrane. And finally the membrane was regenerated with water at pH 7.0. Flow rates of 0.375-5.0 mL/min were investigated.

For the Amberlyst A21 resin, the experiment was carried out in a small plastic column containing 5 mL of resin at room temperature and at flow rates of ranging from 0.375-5.0

mL/min. The resin was washed with water at pH 7.0; then loaded with acetic acid solution at pH 7.0, followed by washing with water at pH 7.0. Finally 1.0 mol/L NaOH was used to elute the acetic acid from the resin. Table 1 summarizes the two systems tested.

During both experiments, permeate samples were withdrawn every 1 mL and the acetic acid concentration was determined using a HP 1050 HPLC equipped with a HP 1047A refraction index detector and a Bio-Rad HPX87H column. The eluent was 0.005 mol/L H_2SO_4 flowing at a rate of 0.6 mL/min. The column temperature was 45 ºC. For the hydrolysate solution, the concentration of some of the sugars present was also measured.

Table 1 Comparison of Sartobind Q membrane and Amberlyst A21 resin

System	**Membrane**	**Resin**
Commercial name	Sartobind Q	Amberlyst A21
Material	Cross-linked regenerated cellulose	Polystyrene macroreticular
Configuration	Flat sheets	Opaque spherical beads
Functional groups	$R\text{-}CH_2\text{-}N^+\text{-}(CH_3)_3$	Styrenic group
pKa of functional groups	11	---
Characteristics	Strongly basic anion exchanger	Weak base anion exchanger
Capacity	29mg BSA/mL	≥ 4.6 eq/kg
Pore size (μm)	> 3	Particle size 0.49-0.69 mm Pore diameter 110 Å
pH stability	2-13	0-14
pKa of functional group	11	9
Surface area (m^2/g)	1.29	35
Porosity (pore volume)	---	0.10 mL/g
Dry density (g/L)	291	660

Results and Discussions

Figure 1 shows three curves depicting the variation of dimensionless acetic acid concentration expressed as the concentration in the permeate divided by the initial feed concentration as a function of permeate volume for the Q membrane. Results are given for flow rates of 0.375, 1.0 and 5.0 mL/min. Breakthrough is observed as a gradual rise in the acetic acid concentration in the permeate. The acetic acid concentration falls to zero during washing. A sharp peak is then seen during elution. These results show that the Q membrane adsorbs acetic acid from aqueous solutions. At pH 7, the acetic acid is dissociated, CH_3COO^- being the dominant species present. The membrane is positively charged as the pKa of the functional group on the membrane is 11. Therefore, the following reaction occurs between the functional groups on the Q membrane and CH_3COO^- molecules:

$$R\text{-}CH_2\text{-}\overset{+}{N}\text{-}(C_2H_5)_3OH^- + CH_3COO^- \rightarrow R\text{-}CH_2\text{-}\overset{+}{N}\text{-}(C_2H_5)_3CH_3COO^- + OH^- \qquad (1)$$

The Q membrane module used in this study has a thickness of 4 mm. SEM analysis indicates that the membrane pore size is not homogeneous. Rather, a pore size distribution is observed. Suen and Etzel[18] have shown that the presence of a pore size distribution can lead to a slow increase in the acetic concentration in the permeate after initial breakthrough. We believe that this accounts for the gradual rise in acetic acid concentration in the permeate as

breakthrough occurs. From Figure 1, it also can be seen that the elution of the acetic acid from membrane using 1 mol/L NaOH is very effective. Further, the acetic acid can be concentrated up to 9 times in the eluent. This could facilitate the possible recovery of eluted acetic acid.

The results shown in Figure 1 are replotted in Figure 2 to show the variation in acetic acid concentration in the permeate as a function of relative mass throughput prior to washing. The relative mass throughput is defined as[19]:

$$T = (C_0 + K_d)Q_f t/(Q_m V_m) \quad (2)$$

where T is the relative mass throughput, C_0 the feed concentration of acetic acid, K_d the equilibrium dissociation binding constant, Q_f the flow rate, Q_m the maximum adsorbed ligate concentration at equilibrium, t the time, and V_m the membrane volume. From Figure 2, it can be seen that although the flow rates used vary over an order of magnitude, the breakthrough curves almost collapse onto each other. Thus, an approximately self-similar behavior can be observed by plotting dimensionless concentration as a function of relative mass throughput.

Figures 3 and 4 compare results for the membrane and resin. Figure 3 shows the dimensionless acetic acid concentration in the liquid stream leaving the membrane module or column plotted as a function of chromatographic bed volume. The Q membrane module has a very different geometry to the A21 resin column. For the Q membrane module, the total volume is 1 mL with a thickness of 4 mm, while for the column, the resin volume is 5 mL with a bed thickness of 20 mm. In order to make a reasonable comparison, Figure 3 is developed by comparing the systems based on a chromatographic bed number, which is defined as the ratio of the cumulative flow through the volume to that of the chromatographic bed volume. In Figure 4, the comparison is based instead on the mass throughput per chromatographic bed volume, and so only presents results up to breakthrough. From Figure 3, it can be seen that although the bed thickness of the resin is much larger than that of the membrane, earlier breakthrough is observed for the resin system. This behavior can be seen even more clearly in Figure 4. Beyond these differences, the elution peak obtained using the resin is broader than for the membrane, which leads to a less concentrated acetic acid eluent.

Figures 5 shows the variation of acetic acid in the flow through using hydrolysate feed streams. As described previously, the hydrolysate was pretreated using either the NREL or Brazilian conditioning processes. For comparison, acetic acid removal from DI water is also depicted. It can be seen that the different conditioning methods do not have a significant effect on acetic acid removal for the membrane or resin systems. However, for the same chromatographic matrix, earlier breakthrough is observed for the hydrolysate solutions as compared to DI water, i.e., the adsorption capacity of the matrix is decreased for the hydrolysate solution. Unlike acetic acid in DI water, the hydrolysate solution contains a large number of components, some of which are likely to also adsorb on to the ion exchange matrix leading to a decreased adsorption capacity. From Figure 5, it also can be seen that the Q ion exchange membrane has a comparatively higher capacity than the A21 ion exchange resin.

Figure 6 compares the adsorption of glucose, xylose and arabinose on the membrane and resin. It is essential the loss of these sugars be minimized. Comparing Figures 3 and 6, it is evident that very little adsorption of these sugars occurs.

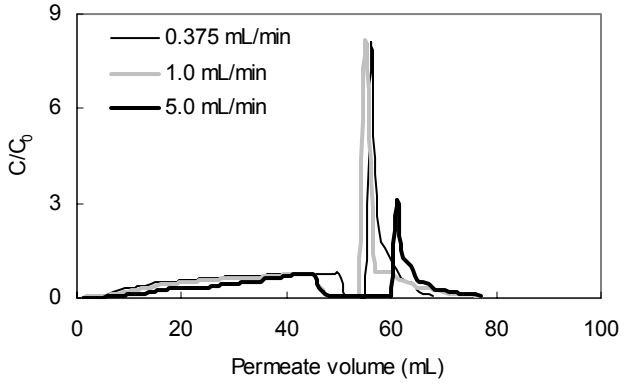

Figure 1. Concentration of acetic acid in DI water in the permeate from the membrane module as a function of permeate volume.

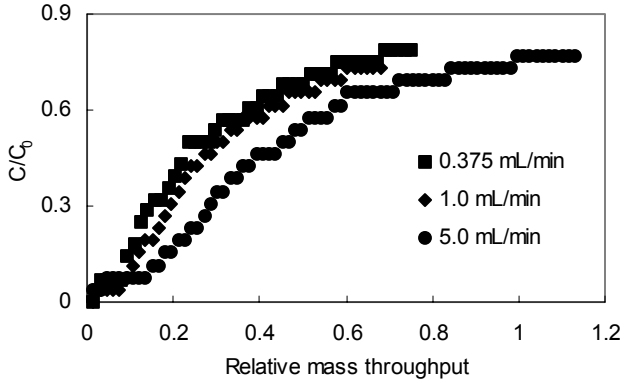

Figure 2. Breakthrough curves plotted versus relative throughput of acetic acid in DI water. Results are shown for Q membranes at different flow rates.

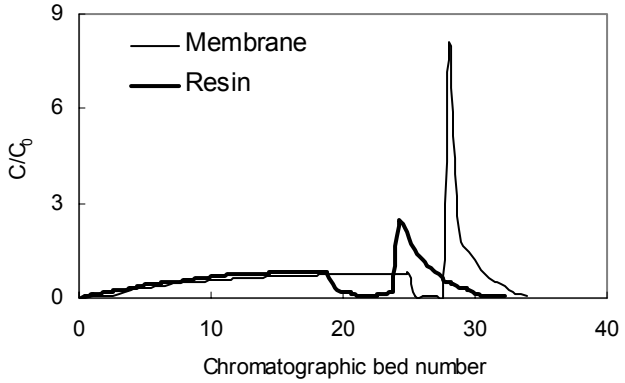

Figure 3. Comparison of acetic acid concentration in the flow through for the membrane and resin. Results are shown at a flow rate of 0.375 mL/min.

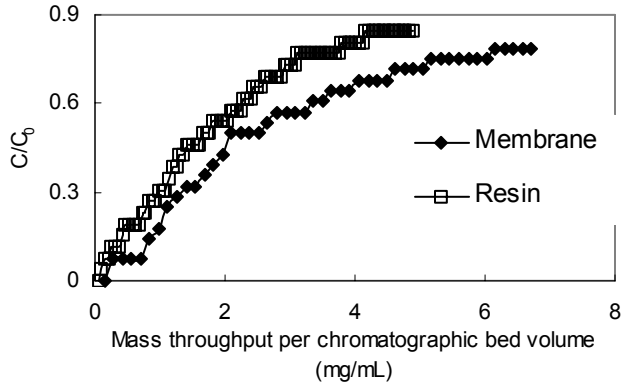

Figure 4. Comparison of acetic acid breakthrough curves for the membrane and resin. Results are shown at a flow rate of 0.375 mL/min.

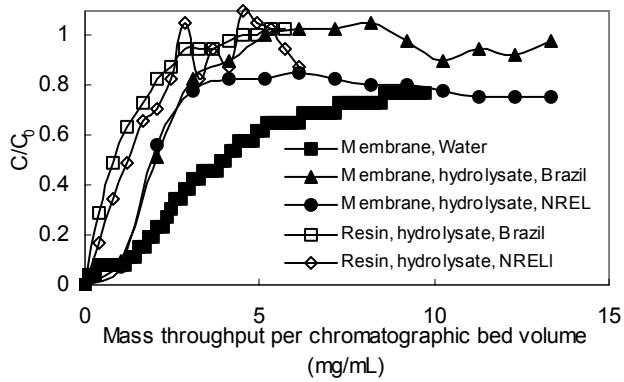

Figure 5. Comparison of acetic acid breakthrough curves for the membrane and resin. Results are shown at a flow rate of 5 mL/min. Results are shown for both DI water and hydrolysate.

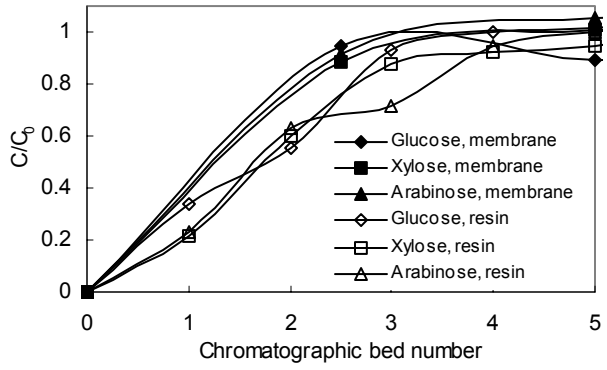

Figure 6 Breakthrough curves for glucose, xylose and arabinose present in the hydrolysate for the membrane and resin. The flow rate was 5 mL/min.

Conclusions

An ion exchange membrane and resin were compared for removing acetic acid from DI water and conditioned hemicellulosic hydrolysate. The results show that the acetic acid capacity of the ion exchange membrane is higher than that of the ion exchange resin using both acetic acid in DI water and actual hydrolysate. The ion exchange membrane was better able to concentrate the eluted acetic acid than the resin. Sugar losses appeared to be low. These preliminary results suggest that ion exchange membranes hold promise for providing a more efficient means of removing acetic acid from biomass hydrolysates.

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