The Separation of Acetic Acid and Furfural from a Pre-hydrolysis Liquor Using Nanofiltration

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Abstract— As the use of paper and revenue for paper mills decrease, the need to recover valuable products such as acetic acid, furfural, lignin and oligomers from secondary process streams of the kraft process have become imperative. The main objective of this work was to investigate nanofiltration as a means to separate furfural and acetic acid and determine the influence of the feed composition and transmembrane pressure on the flux and selectivity of the membrane(s). Different concentrations of acetic acid and furfural were used in demineralized water at transmembrane pressures ranging from 5 to 15 bar. The NFS100-250 and NFX150-300 indicated favourable conditions for separation. Both membranes concentrated the acetic acid in the retentate for the binary mixtures of water and acetic acid, but separation of acetic acid and furfural was achieved with the ternary mixtures. A change in the feed composition significantly influenced the membrane flux and selectivity.

Keywords— Acetic acid, Furfural, Nanofiltration, Pre-hydrolysis liquor

I. INTRODUCTION

UNIVERSAL growth of digital media has become one of the primary concerns for pulping industries, as the use of paper and revenue for paper mills decrease. Paper mills contain many secondary process streams, such as the prehydrolysis stream from the kraft process that contains valuable products. Some of the valuable products include acetic acid, furfural, lignin and oligomers [1]. These products have multiple uses as building blocks in the chemical manufacturing industries and can significantly increase the economic efficiency of bio-refineries, when these products derived from wood and produced during the pulping process are recovered and used [2]. Woody biomass is one of the most abundant organic sources in the world [3] and primarily composed of cellulose, lignin and hemicellulose [4]. The structure of hemicellulose consists of different types of sugar units such as xylose, arabinose, glucose, rhamnose, galactose and mannose [5]. The structure, amount and composition of hemicellulose vary depending on the species present. Xylans are the main hemicellulose present in hardwoods, while glucomannans are mostly present in softwoods [6]. Lignin, the second most abundant bio-polymer besides cellulose found in soft woods, are almost entirely composed of guaiacyl, while in hardwoods, mixed lignins of syringyl, guaiacyl and trace amounts of para-hydroxyphenyl are found [5]. The kraft pulping process is one of the most widely used pulp producing processes, where approximately half of the original raw wood material is dissolved in spent pulping liquor [7], [8]. The separation, removal and recovery of the valuable products in the prehydrolysis stream can be done using a variety of methods, such as ion exchange resin to separate organic acids, however the resin requires regeneration with bases to remove the acid products; diffusion is usually slow and pressure drop across the filter bed is high [9]. Therefore, other methods such as vacuum evaporation, extraction, charcoal adsorption and neutralisation have also been used for the removal of products from hydrolysates [10].

An alternative technology however, apart from the methods mentioned, is membrane separation [10]. Membranes have become noteworthy in the field of alternative energy as well as the recovery of valuable products from process streams [10]. Membrane based separation methods are also generally better with regard to energy and capital efficiency, than traditional separation processes [10], and as the need to reduce the energy consumption and the impact on the environment, has become more important, the use of membrane separation to purify, fractionate and concentrate valuable products have become essential [11]. A wide range of different membrane processes are used for bio-energy and bio-refining production, of which pervaporation, ultrafiltration, microfiltration, membrane distillation, diafiltration and nanofiltration are just a few [12].

Nanofiltration and reverse osmosis have successfully been implemented in a variety of applications over the last twenty years including the removal of organic contaminants from water [13],[14], sugar fractionation and concentration [15], partial deacidification of vegetable oils [16], treatment of dairy by-products [17], and the recovery of cold solvents from lube oil [18]. Nanofiltration involves size exclusion with a molecular weight cut-off (MWCO) range of 0.01 kDa to 1 kDa [11]. Furfural and acetic acid have molecular weights of 96.09 g.mol⁻¹ and 60.05 g.mol⁻¹ and nanofiltration should thus be

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able to separate the two components. Recovery of acetic acid and furfural from the pre-hydrolysis kraft liquor is beneficial, as acetic acid is currently, exclusively used for the production of vinyl acetate monomers [11] and furfural can be converted to liquid bio-fuels [20], [21], as well as used as a bio-based alternative for the synthesis of paint, plastics, fertilizers and several other industrial applications [11].

A study conducted by Kaur & Ni (2015) [22], to separate acetic acid and furfural from a pre-hydrolysis liquor using nanofiltration combined with reverse osmosis, reactive extraction and a monopolar or bipolar reactor system indicated that separation was indeed possible. Nanofiltration was used to concentrate the hemicellulose and lignin contained in the original prehydrolysis liquor in the retentate, while acetic acid was found in the permeate. Other studies conducted by Ozaki & Huafang (2002) [23] and Berg et al. (1997) [24] indicated that an increase in pH, increased the rejection of organic acids in the membrane. A study conducted by Ajao et al. (2015) [25] indicated that in order to improve the conversion process of the hemicelluloses prehydrolysate to furfural, a low pH was required. A study done by Ahmed et al. (2008) [26] indicated that the influence of pH was of greater significance with regard to the membrane rejection than on the permeate flux. The transmembrane pressure and feed compositions also greatly influence the performance of nanofiltration membranes and therefore, the main objective of this work was to investigate whether nanofiltration can be used to separate furfural and acetic acid as well as to determine the influence of the feed composition and transmembrane pressure on the flux and selectivity of the membrane(s).

II. MATERIALS AND METHODS

A. Membranes and Chemicals

Commercially available DOW FILMTEC™ NF90 and NF270 flat sheet nanofiltration membranes were purchased from Sterlitech, NFG600-800, NFW300-500, NFX150-300 and NFS100-250 flat sheet nanofiltration membranes were purchased from Synder Filtration™. Sigma–Aldrich furfural (99%) and ACE acetic acid (glacial 99.7%), as well as demineralized laboratory water with a conductivity of 0.055μS was used to conduct the experiments. An industrial prehydrolysis liquor (PHL), was used after all experiments were completed in order to determine the effect of the liquor on one of the membranes.

B. Absorption Experiments to Screen Membranes

Six membranes were used for determining the selectivity of the membranes towards furfural and acetic acid. Sorption experiments were done by weighing dry membrane pieces (3mm x 2mm) and then submerging them in known volumes of acetic acid or furfural. The increase in the mass of the membrane pieces were recorded at different time intervals until saturation was reached. Absorption experiments were repeated three times to obtain the experimental error.

C. Experimental Dead-End Nanofiltration Setup

All experiments were conducted at 19°C using a stainless steel dead-end pressure cell (see Fig.1). The cell had an inside diameter of 0.045m and therefore, the membrane had an active surface area of 15.9cm², with the active layer of the membrane facing the feed mixture. Ultra high purity nitrogen gas, purchased from Afrox Ltd., was used to pressurise the cell at pressures ranging from 5 to 15bar. The volume added to the cell with different feed compositions was kept constant at 110mL, except for the water permeability tests, where the feed volume was kept constant at 60mL.

D. Nanofiltration experiments

Prior to use in the nanofiltration cell, the preservative layer present on the membrane surface was removed by soaking it in demineralized water for 10 minutes. Steady-state operation was ensured by pre-swelling of the membranes in demineralized water. The permeability of pure demineralized water at different transmembrane pressures were done to test the membranes for osmotic pressure effects. The pure water permeability was measured at transmembrane pressures of 5 to 15bar with a constant feed volume of 60mL. The permeate mass was electronically logged to determine the flux and permeability through the membrane(s). Only the NFS100-250 and NFX150-300 nanofiltration membranes from Synder Filtration™ displayed reasonable water permeabilities with negligible osmotic pressure effects and was used further in the study.

Binary mixture separation was conducted using feed compositions of 2.6 wt.% to 9.5 wt.% acetic acid in demineralized water. Tertiary mixture separation was conducted at a fixed acetic acid concentration of 5wt.% and varying furfural concentrations form 1wt.% to 5wt.% in demineralized water. An industrial PHL was spiked with furfural and tested for separation using nanofiltration with the NFX150-300 membrane and transmembrane pressures of 5 to 15bar.

E. Chemical Analysis

The change in pH between the retentate and permeate was used to determine the amount of acetic acid that permeated the membrane during binary mixture experiments. Refractive index (RI) was used to determine the concentration of furfural and acetic acid in the permeate mixture during the ternary feed
mixture experiments. Quantification was done using calibration curves with a dilution factor of 50 using 0.005M H$_2$SO$_4$. The PHL was analysed using an ICP-OES in order to determine metals present in the mixture that crystalized on the nanofiltration membrane during the experiment.

III. RESULTS AND DISCUSSION

A. Sorption Results

Sorption saturation was reached for all the membranes within 10 minutes. The saturation mass was used to calculate theoretical fluxes for all the membranes using (1).

\[ J = \frac{m}{A \cdot t} \] (1)

Where J is the flux in (L·m$^{-2}$·h$^{-1}$), m is the mass of liquid absorbed, A is the membrane surface area and t is the time to reach sorption equilibrium. All six membranes absorbed more acetic acid than furfural indicating a preference towards separation of acetic acid. With an increase in the molecular weight cut-off values of the different membranes, an increase in the sorption saturation capacity was observed for both furfural and acetic acid in all the membranes screened. The experimental error obtained for the theoretical flux of acetic acid was between 3% and 12% and for the furfural between 7% and 21%.

B. Water Permeability and Membrane Selection

The results of water permeability obtained through four membranes at different transmembrane pressure are given in Fig.2.

![Fig.2 Influence of transmembrane pressure on pure water permeability of four membranes (● - NFS 100-250, ■ - NFS 150-300, ▲ - NFW 300-500, × - NFG600-800)](http://dx.doi.org/10.15242/IIE.E1115003)

Based on the straight line fits seen in Fig.2, all the membranes displayed some form of osmotic pressure and the permeabilities were not linear with TMP, indicating that there is an interaction between water and the membranes. The NFS100-250 and NFX150-300 membranes however displayed the least amount of interaction with water and were used further in the study.

C. Binary Feed Mixtures

C.1 Binary Feed Mixtures - NFX150-300 membrane

The influence of feed concentration and transmembrane pressure on the total flux and partial flux through the NFX150-300 membrane was found to increase linearly with an increase in transmembrane pressure for each concentration of acetic acid used (see Fig.3), these fluxes ranged from 0.0241L·m$^{-2}$·h$^{-1}$ to 0.540L·m$^{-2}$·h$^{-1}$.

![Fig.3 Influence of transmembrane pressure on the total flux at different concentrations of acetic acid (● - 9.5% Acetic acid, ■ - 7.3% Acetic acid, ▲ - 5% Acetic acid, × - 2.6% Acetic acid)](http://dx.doi.org/10.15242/IIE.E1115003)

Selectivity towards water and acetic acid is show in Fig. 4.

![Fig.4 Influence of feed concentration on the selectivity of water and acetic acid at a transmembrane pressure of 10 bar (● - Acetic acid selectivity, ■ - Water selectivity)](http://dx.doi.org/10.15242/IIE.E1115003)

The membrane was found to be selective towards water with selectivities in the range of 1.089 to 1.390. The water selectivity increased with an increase in the transmembrane pressure, but did not change significantly with concentration.

C.2 Binary Feed mixtures - NFS100-250

The influence of feed concentration and transmembrane pressure on the flux through the membrane is given in Fig.5.
Fig. 5 Influence of transmembrane pressure on the total flux at different concentrations of acetic acid (◆ - 9.5% Acetic acid, ■ - 7.3% Acetic acid, ▲ - 5% Acetic acid, □ - 2.6% Acetic acid)

From Fig. 5 it can be seen that the total flux increased linearly with an increase in the acetic acid concentration in the feed. The pH was used to calculate the concentration of the acetic acid and water in the mixtures in order to calculate the acetic acid and water selectivities for each membrane. The selectivity was calculated using (2).

\[ \alpha_{A/w} = \frac{y_A}{y_w} \left( \frac{x_A}{x_w} \right) \]  

where \( \alpha_{A/w} \) is the selectivity, \( y_A \) and \( y_w \) is the mass fractions of acetic acid and water in the permeate and \( x_A \) and \( x_w \) is the mass fractions of acetic acid and water in the feed mixture. The selectivity of the membrane towards water and acetic acid is shown in Fig. 6. The experimental error determined for selectivity values at a 95% confidence level ranged between 0.02% and 6.93% for the different feed concentrations and transmembrane pressures.

Fig. 6 Influence of feed concentration on the selectivity of water and acetic acid at a transmembrane pressure of 10 bar (◆ - Acetic acid selectivity, ■ - Water selectivity)

From Fig. 6 it can be seen that the membrane is selective towards water up to a feed concentration of approximately 5wt.% acetic acid. At higher concentrations of acetic acid in the feed, the membrane selectivity is reversed and the membrane becomes selective towards water. This is a significant result, as it indicates that dilution can be used to selectively separate acetic acid from industrial waste water streams. An increase in transmembrane pressure had a positive effect on water selectivity at high concentrations of acetic acid in the feed, but a negative effect on acetic acid selectivity at low concentrations of acetic acid in the feed. Scanning Electron Microscopy images of the membranes after treatment with water and acetic acid indicated that both membranes were unstable in the presence of mixtures containing more than 5wt.% acetic acid and therefore 5wt.% acetic acid was used for further experiments (see Fig. 7).

D. Ternary Feed Mixtures

D.1 Ternary Feed Mixtures-NFS100-250 membrane

The total flux obtained at different transmembrane pressures and feed compositions are given in Fig. 8. The acetic acid concentration was kept constant at 5wt.% for all the experiments.

Fig. 8 Influence of transmembrane pressure on the total flux at different concentrations of furfural (◆ - 2% Furfural, ■ - 5% Furfural, ▲ - 4% Furfural, □ - 1% Furfural)

It was found that the transmembrane pressures greatly influenced the permeate fluxes through the membranes at 4wt.% and 5wt.% furfural mixtures, as the flux increased from 0.425L·m⁻²·h⁻¹ to 26.982L·m⁻²·h⁻¹ for the 5wt.% furfural mixture and from 0.0567L·m⁻²·h⁻¹ to 6.657L·m⁻²·h⁻¹ for the 4wt.% furfural mixture with an increase in the transmembrane pressure. It was however seen that the transmembrane pressure had little influence on the flux when the concentration of furfural in feed was low (1wt.% to 2 wt.%).

The selectivity of the membrane towards furfural and acetic acid was calculated and is given in Fig. 9. It was found that transmembrane pressure had a negligible influence on the selectivity. From Fig. 9 it can be seen that the membrane was highly selective towards furfural at low concentrations of...
furfural, but rapidly decreased with an increase in furfural in the feed mixture. From this results it is seen that furfural can be separated from a mixture of water and acetic acid if the furfural is present in sufficiently low concentrations.

Fig.9 Influence of furfural concentration on the selectivity towards furfural and acetic acid at a transmembrane pressure of 10 bar (● - Furfural selectivity, ■ - Acetic acid selectivity)

D.2 Ternary Feed Mixtures-NFX150-300 membrane

The influence of transmembrane pressure on total flux through the NFX150-300 membrane at different concentration of furfural in the feed is shown in Fig.10.

Fig.10 Influence of transmembrane pressure on the total flux at different concentrations of furfural (× - 1% Furfural, ● - 2% Furfural, ▲ - 4% Furfural, ■ - 5% Furfural)

It was found that the transmembrane pressures greatly influenced the permeate fluxes through the membranes at 4wt.% and 5wt.% furfural mixtures, as the flux increased from 2.83L·m⁻²·h⁻¹ to 14.31L·m⁻²·h⁻¹ for the 5wt.% furfural mixture and from 0.201L·m⁻²·h⁻¹ to 8.601L·m⁻²·h⁻¹ for the 4wt.% furfural mixture with an increase in the transmembrane pressure. It was however seen that the transmembrane pressure had little influence on the flux at low concentrations of furfural in the feed. The decline in furfural flux at higher transmembrane pressures indicates that concentration polarization might be present at higher concentrations of furfural in the feed. The selectivity of the membrane towards acetic acid and furfural was calculated and is shown in Fig.11. This membrane also displayed a relatively high selectivity towards furfural at low concentrations of furfural in the feed.

The selectivity toward furfural was found to increase with a decrease in the furfural concentration in the feed. The high selectivities toward furfural indicated that separation of the furfural and acetic acid was indeed achieved with the nanofiltration membranes. The scanning electron microscopy images of the used membranes (see Fig.12) indicated damage to the membrane at high concentrations of furfural and that at low concentrations of furfural a thin gel layer formed on the surface of the membrane, this might be due to condensation of the furfural from the mixture, confirming the low permeate flux data obtained.

Fig.12 (A) NFS100-250 membrane active surface damage at 5% furfural concentration (B) NFX150-300 membrane active surface gel layer at 1% furfural concentration

Repeatability experiments were done using the NFX150-300 membrane at 2wt.% furfural and 5bar, as well as at 5wt.% furfural at 5bar and 10bar to determine the experimental error with regard to the selectivities. The experimental error for the 2wt.% furfural mixture at 5bar was found to be 9.35%, the experimental error at the 5wt.% furfural mixture at 5bar was found to be 3.88% and at 10bar 2.96%.

E. Membrane Stability with an Industrial Feed Solution

In order to determine the polymeric membrane stability an industrial PHL was used as feed to the NFX150-300 membrane. It was found that after a time period of 110 minutes the flux through the membrane was negligible and therefore, no numerical data could be obtained. A scanning electron microscopy image of the treated membrane (see Fig.13) indicated that octahedral crystals had formed on the membrane surface. The PHL was therefore analysed using an ICP-OES analyser to determine whether metals were present in the
mixture. The ICP-OES results indicated that high concentrations in (ppm) of sulphur and sodium were present in the mixture. Research about the different reactions that can occur between sulphur and sodium indicated that sodium sulphate (Na$_2$SO$_4$) has an octahedral molecular geometry and caused the formation of the crystals identical to the crystals formed on the membrane.

Fig.13 Octahedral crystal structure on the membrane surface

From a scanning electron microscopy analysis of the used membrane (see Fig.14), it was evident that a gel layer formed on the membrane surface which resulted in fouling of the membrane and explained why no flux could be obtained through the membrane.

Fig.14 (A) Gel type layer formed on membrane surface (B) Particles in mixture clogging membrane pores

IV. CONCLUSION

It was shown in this study that nanofiltration can be used to separate water from acetic acid and furfural from a ternary mixture of water, acetic acid and furfural. Transmembrane pressure and feed concentration had a significant influence on both the total flux and selectivity towards water (binary mixtures) and furfural (ternary mixtures). Although an industrial PHL mixture could not be separated successfully with the membranes used in this study, the pure model mixture experiments showed that separation is possible if the dissolved solids in the PHL can be removed prior to membrane separation.

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