Separation and Purification Technology 132 (2014) 655–665

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

# Sugar concentration and detoxification of clarified biomass hydrolysate by nanofiltration

Mohammadmahdi Malmali [a], Jonathan J. Stickel [b], S. Ranil Wickramasinghe [a,*]

[a] Ralph E. Martin Department of Chemical Engineering, University of Arkansas, Fayetteville, AR 72701, USA
[b] National Renewable Energy Laboratory, National Bioenergy Center, Golden, CO 80401, USA

ARTICLE INFO

*Article history:*
Received 6 April 2014
Received in revised form 6 June 2014
Accepted 7 June 2014
Available online 18 June 2014

*Keywords:*
Filtration
Acetic acid
Biomass
Fouling
Permeability
Rejection

ABSTRACT

Development of efficient unit operations is critical in order to design economically viable processes for conversion of lignocellulosic biomass into chemicals and fuels. Here the use of nanofiltration membranes for concentration of sugars in a lignocellulosic biomass hydrolysate has been explored. In addition, simultaneous removal of compounds such as acetic acid, 5-(hydroxymethyl)furfural and furfural which are inhibitory to the microorganisms used in the subsequent fermentation step has also been investigated. Dead-end filtration experiments have been used to test a number of commercially available nanofiltration membranes under a range of operating conditions. Model feed streams as well as real hydrolysates have been tested. The results obtained here indicate that both concentration of sugars and removal of hydrolysis degradation products are feasible. However careful selection of the membrane and operating conditions are essential. The introduction of a nanofiltration step for concentration of sugars and removal of hydrolysis degradation products could enable the development of a continuous process for biomass hydrolysis.

## 1. Introduction

Today, production of 1st generation biofuels such as bioethanol from sugar cane and corn starch is well established [1]. Manufacturing processes that include the use of membrane-based unit operations have been described [2]. However increasing competition between food and energy production has led to significant efforts to convert lignocellulosic biomass into so called 2nd generation biofuels. Unlike 1st generation biofuels, production of 2nd generation biofuels is far more complex. Development of efficient separation and purification operations are essential for production of competitive 2nd generation drop-in biofuels. Membrane based separation processes are attractive as they could lead to significant process intensification and hence reduced operating costs [3].

Three main strategies exist for conversion of lignocellulosic biomass into liquid fuels and chemical intermediates: gasification, pyrolysis and hydrolysis [4]. Here we focus on hydrolysis of lignocellulosic biomass followed by fermentation. Dilute-acid pretreatment is a leading technology for hydrolysis [5]. Dilute sulfuric acid has been shown to effectively hydrolyze the hemicellulose component of the biomass to its monomeric sugars as well as enhance the enzymatic digestibility of cellulose [6]. Next, cellulose is enzymatically hydrolyzed to glucose. Prior to fermentation, the hydrolysate is conditioned or detoxified to remove byproducts and sugar degradation products (toxic compounds). These compounds inhibit subsequent bioconversion of the solubilized sugars [6]. In addition, the maximum glucose concentration is limited by product inhibition during enzymatic hydrolysis. However increasing the sugar concentration in the fermentation reactor is desirable in order to increase the fermentation product yield e.g. ethanol. In this work we focus on the development of a pressure driven membrane filtration step to remove toxic compounds as well as concentrate the soluble sugars prior to fermentation.

Abels et al. [1] recently reviewed membrane based separation processes for biorefinery applications. Several investigators have considered the use of ultrafiltration membranes for removal of glucose during enzymatic hydrolysis thus avoiding product inhibition [7–10]. Carstensen et al. [11] have reviewed membrane bioreactors for *in situ* product recovery. However, here the focus is concentration of sugars and removal of toxic compounds. Thus it is assumed that suspended solids have already been removed from the feed stream.

In more recent studies, a few investigators have considered the use of nanofiltration membranes. Nanofiltration, or low-pressure reverse osmosis, membranes were initially developed for softening of surface and ground waters [12]. These membranes typically exhibit over 99% rejection of multivalent ions but less than 70%

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[*] Corresponding author. Tel.: +1 479 575 8475; fax: +1 479 575 4940.
*E-mail address:* ranil.wickrmasinghe@uark.edu (S.R. Wickramasinghe).

http://dx.doi.org/10.1016/j.seppur.2014.06.014
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rejection of monovalent ions. In addition they exhibit over 90% rejection of dissolved organic compounds with molecular weights over 150–300. Weng et al. [13] investigated separation of acetic acid, a toxic compound produced during dilute acid hydrolysis of rice straw from xylose. They indicated a separation factor of acetic acid over xylose of 49. Higher separation factors were also obtained for acetic acid over glucose. Their work indicates that the actual separation factor depends on many variables such as pH and the presence of other species in the feed. Our recent work indicates the importance of pH on the flux, rejection and selectivity of nanofiltration membranes [14]. Qi et al. [15] have investigated separation of furfural (a xylose degradation product) from model feed streams containing glucose, xylose and furfural. Their result also indicated the importance of feed pH and the presence of other species on glucose and xylose rejection. In real hydrolysates it is likely that the presence of other dissolved species could have a significant effect on membrane performance.

Maiti et al. [16] conducted a far more detailed study where they investigated separation of a number of toxic compounds from rice straw hydrolysates by several commercially available nanofiltration membranes. Model and real hydrolysate feed streams were investigated. Their study indicated that removal of toxic compounds and concentration of monomeric sugars is possible using nanofiltration membranes. However nanofiltration membrane performance depends on size exclusion as well as surface interactions between the membrane and dissolved species, feed pH, ionic strength and the concentration of the various dissolved solutes. Consequently membrane performance is difficult to predict as it will depend on the interplay between all of these parameters.

Development of a nanofiltration step to detoxify the hydrolysate and concentrate the monomeric sugars could be economically beneficial. Optimizing the sugar concentration prior to fermentation will lead to a more efficient fermentation process. In addition, in order to mitigate product inhibition during enzymatic hydrolysis, a continuous hydrolysis process is desirable as it will lead to higher glucose production rates though the glucose concentration in the product stream will be lower than in batch processing. Hence a sugar concentration step will be needed before fermentation. Selection of an appropriate membrane and operating conditions will be essential in order to determine the feasibility of such a step. The purpose of this work was to develop a method to screen a number of membranes under a range of conditions. All experiments have been conducted in dead-end filtration mode. In industrial practice, nanofiltration is conducted in tangential flow filtration mode. However dead-end filtration experiments provide much more control over operating conditions and are well suited for comparing the performance of different membrane and feed conditions [17]. Five commercially available nanofiltration and low pressure reverse osmosis membranes were tested. The effect of feed pH and pressure, total glucose and xylose (monomeric sugar) concentration as well as the total concentration of acetic acid, 5-(hydroxymethyl)furfural (HMF) and furfural (toxic compounds) were determined for model feed streams. In addition, the filtration of real hydrolysates through selected membranes was performed. Design of experiments software was used to guide the selection of experimental conditions. Finally, membrane surfaces were characterized by X-ray photoelectron spectroscopy (XPS), contact angle and zeta potential measurements.

## 2. Experimental

### 2.1. Material and methods

Unless otherwise noted, all chemical were ACS reagent grade. D-glucose and D-xylose were purchased from Sigma Aldrich (St. Louis, MO). 5-(hydroxymethyl)furfural (HMF) 99% and 2-furaldehyde (furfural) 99% were purchased from Thermo Fisher Scientific (Waltham, NJ). Sodium azide 5% w/v, acetic acid and sulfuric acid were purchased from Seastar Chemicals Inc. (Sidney, BC, Canada). Sodium hydroxide was purchased from J.T. Baker (Philipsburg, NJ). Deionized water (conductivity <10 $\mu$S cm$^{-1}$ and resistance >18.5 M$\Omega$) was obtained from a Labconco (Kansas City, MO) water purification system (Water Pro RO and Water Pro PS Polishing Stations).

Three commercially available Alpha Laval (Wood Dale, IL) membranes (RO90, RO98 and RO99) and two Dow Filmtec (Edina, MN) membranes (NF90 and NF270) were tested. The Alpha Laval membranes are marketed as low pressure (brackish water) reverse osmosis membranes while the Dow Filmtec membranes are marketed as nanofiltration membranes. Table 1 gives further information on the 5 membranes tested here. As can be seen the Alpha Laval membranes are generally tighter (lower NMWCO). All experiments were conducted using a stirred cell HP4750, Strelitech Corporation (Kent, WA). The cell is designed to operate at a maximum feed pressure of 69 bar using 49 mm membrane discs with 14.6 cm$^2$ active membrane area.

A virgin membrane was used for each experiment. Prior to testing with model and real hydrolysate, the DI water flux of the membrane was determined. All membranes were soaked in DI water for 24 h. The membrane was then placed in the filtration cell and precompacted at a pressure of 40 bar and a temperature of 42 °C for 60 min. DI water fluxes were then measured at 20, 30 and 40 bar over a period of 1 h and the values compared to the manufacturer's values. If the flux was outside the specified range, the membrane was discarded. Next, 160 mL of model or real hydrolysate was loaded into the nanofiltration cell. In all the experiments the contents of the feed reservoir were stirred. Permeate samples (1.5 mL) were collected at regular intervals for HPLC analysis.

### 2.2. Statistical design of experiments

Design Expert 8.0.7.1 (Stat-Ease, Minneapolis, MN) was used to determine a set of experimental conditions. Table 2 lists the

**Table 1**
Membranes tested together with manufactures specifications.

| Membrane | NF270 [18] | NF90 [19] | RO90 [20] | RO98 [21] | RO99 [22] |
|---|---|---|---|---|---|
| Manufacturer | Dow Filmtec, Edina, MN | Dow Filmtec, Edina, MN | Alpha Laval, Lund, Sweden | Alpha Laval, Lund, Sweden | Alpha Laval, Lund, Sweden |
| Structure | Thin film composite polyamide, polysulfone and polyester support | Thin film composite polyamide, polysulfone and polyester support | Thin film composite polyamide, polyester support | Thin film composite polyamide, polypropylene support | Thin film composite polyamide, polyester support |
| Molecular weight cut off and rejection | 250–300 Da 50% NaCl<br>>98% $MgSO_4$ | 200 Da 90–96% NaCl<br>>98% $MgSO_4$ | >90% NaCl | >97% NaCl | >98% NaCl |
| Charge at pH 7.0 | Negative | Negative | Negative | Negative | Negative |
| Operating range | 5–45 °C<br>3–10 pH<br>Up to 41 bar | 5–45 °C<br>3–10 pH<br>Up to 41 bar | 5–50 °C<br>3–10 pH<br>Up to 55 bar | 5–60 °C<br>2–11 pH<br>Up to 55 bar | 5–50 °C<br>3–10 pH<br>Up to 55 bar |