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Integrated acidogenic digestion and carboxylic acid separation by nanofiltration membranes for the lignocellulosic carboxylate platform

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ABSTRACT

The major goal of this work was to evaluate the ability of two commercially available nanofiltration membranes (NF) to efficiently separate a mixture of carboxylic acids while simultaneously retaining sugars in actual lignocellulosic biomass digestion liquor. The process achieved separation by high sugar rejection (> 90%) and low acid rejection (0–40%), with the exception of butyric acid (100% rejection). Lower pH led to a significantly lower acetic and lactic acid rejection. The recovery of acids was further enhanced by operating at low pressure. Salt addition did not have a strong influence on acid and sugar rejection. Integrating separation with digestion recovered 86% of the acid during a 21 day digestion run, reducing acid concentration in the digestate by nearly 90% relative to a control without acid removal. These results demonstrate proof of concept for use of NF based anaerobic membrane bioreactors to recover carboxylic acids produced from the lignocellulosic carboxylate platform.

1. Introduction

Lignocellulosic biofuel production has long been focused on two reactive intermediates: sugar and syngas. The sugar platform utilizes purified enzymes to hydrolyze biomass to five and six carbon sugars (C5 and C6, respectively), while the syngas platform converts biomass into syngas (CO, H_2 and CH_4) through gasification [1]. This research focuses on a third emerging platform of reactive intermediates with considerable potential, *carboxylic acids*. Acidogenic microorganisms can anaerobically convert lignocellulosic biomass feedstock into short- and medium- chain carboxylic acids, such as lactic, formic, acetic, propionic, butyric, valeric and hexanoic acids, which by themselves are valuable products. But as platform intermediates, carboxylic acids can also be processed into fuels and chemicals (i.e. alcohols, esters, and alkanes) via biochemical, thermochemical and electrochemical processes [2].

As commercial scale-up of the sugar platform continues to be challenged by the high costs to produce C5 and C6 intermediates [3], the simplicity of the carboxylate platform has received increasing attention [2,4]. As with consolidated bioprocessing [5] and anaerobic digestion [6], carboxylate platform costs are reduced and overall conversion efficiency can be increased by integrating enzyme production, hydrolysis, and fermentation into one single process [7]. The use of undefined mixed microbial consortia derived from rumen fluid [8], wastewater [2], or marine sediment [7] eliminates the need for sterilization and impact of contamination. Furthermore, the mixed culture can easily adapt to changing feedstocks and naturally co-ferment multiple substrates, which can be challenging for pure cultures [8]. In summary, acidogenic digestion is a simple, efficient and robust process and an alternative strategy for converting lignocellulosic feedstock to platform intermediates for biofuel and biochemical production.

Operating acidogenic digestion systems with high solids loading reduces process volume and energy usage and can yield high acid concentrations [7]. However, a high acid concentration has an inhibitory effect on microbial activity, thus reducing the overall acid yield and conversion rate [9]. Previous studies have shown direct evidence of concentration dependent microbial growth inhibition from acetic, propionic, butyric and hexanoic acid [10–12]. To improve system efficiency, several reactor configurations and/or separation strategies have been developed to reduce the concentration of one or more carboxylic acids during digestion. These include the MixAlco process [7], on-line acid extraction for pure culture fermentation using supported liquid membranes (SLMs) [13], and use of ion exchange resins for *in-situ* hexanoic acid removal [11]. However, challenges exist for implementing each of these processes, including stabilization of the complex MixAlco process, incompatibility during

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contact of biomass and solvents with SLMs, and complex preparation and regeneration processes for ion exchange resins.

In this study we investigated nanofiltration (NF) as an alternative strategy to separate and recover carboxylic acids. Pressure-driven membrane separations such as NF have the advantages of simplicity, high selectivity (in this case to distinguish carboxylic acids from sugars), high energy efficiency, and low chemical usage compared to conventional separation technologies [14]. NF membranes can reject small molecules such as multivalent ions and monosaccharides, while permeating monovalent ions. Several prior studies have used NF membranes to effectively separate acetic acid and other inhibitors from sugars in lignocellulosic hydrolyzates prior to fermentation [15–18]. Low rejections of acetic acid and furan were observed at pH 3 and average xylose and glucose rejection was higher than 94% [15,18]. Freger et al. [19] and Cho [14] also reported 60% lactic acid rejection and 5% butyric acid rejection by NF membranes using synthetic solutions as feed. Although these prior investigations targeted synthetic solutions and pre-digestion hydrolyzates, they suggested that NF membranes had the potential to separate carboxylic acids from sugar nutrients in acidogenic digestion liquor.

Prior NF membrane research related to lignocellulosic biofuels has mainly focused on two applications: (1) removal of inhibitors and concentration of sugars in pretreated biomass hydrolyzate, and (2) separation of acetic acid from the aqueous fraction of pyrolysis [20]. Few studies have reported separating multiple carboxylic acids (C1–C6) product simultaneously, and most of those utilized synthetic model solutions to conduct separation experiments [14,15,18]. We hypothesize that the wide variety of complex and undefined molecules created during the digestion of lignocellulosic biomass could interfere with the transport behavior of acids and sugars through membranes. Thus, testing on actual digestion liquor is of high importance in moving this field forward.

In this study we provide the first evidence of the feasibility of employing NF membranes to effectively separate mixed carboxylic acids while retaining sugar substrates from actual willow wood digestion liquor. Specifically, the effects of pH, feed pressure and ionic strength on solute rejection were investigated. We then integrated NF with the batch digestion process and evaluated the system with respect to acid concentration and yield. The results reported here provide proof of concept for an anaerobic membrane bioreactor system that advances the development of a robust and scalable process for the lignocellulosic carboxylate platform.

2. Materials and methods

2.1. Preparation of acidogenic digestion liquor

Whole willow (*Salix* spp.) stems were harvested from the East Lycoming School District located in Hughesville (Pennsylvania, USA). Willow chips were ground and hot water pretreated before digestion. Inoculum was extracted from silage, rumen fluid and compost and then mixed with water and pretreated willow biomass to initiate digestion. The inoculum was added to the willow at a volatile solids ratio of 1 g inoculum to 10 g willow, with a total solids loading rate of 75 g dry biomass/L. The digestion was conducted in 1 L Schott bottles (800 ml liquid volume) at 30 °C without pH control. Additional detailed information is provided in supplementary data section. Prior to NF experiments, the liquor was collected by centrifugation and then filtered through 1.5, 0.45 and 0.2 μm filters sequentially.

2.2. Membrane characteristics

Two commercially available NF membranes, Desal DK and Desal DL, were purchased from GE-Osmonics for use in this study. These membranes were selected based on an extensive literature review indicating they had previously been successful in separating of acids from sugars in other bioprocess systems. While these two membranes do not represent the full range of possible NF materials, the goal in this initial study was to demonstrate proof-of-concept. Table 1 summarizes the major characteristics of the two membranes. Both membranes are three-layer thin film composites (TFC) with polyamide as the top active layer and polysulfone as the support layer. The membranes were supplied in a dry form and were soaked overnight to remove chemical residues before sample testing. Surface charge of the NF membrane has a significant influence on solute transport, so the zeta potential under various pH values was measured using the streaming potential method by a SurPASS® (Anton Paar GmbH, Graz, Austria) electrokinetic analyzer. The detailed method was described previously by Xie et al. [21].

2.3. Cross-flow system set up

As presented in Fig. 1, the lab scale cross flow filtration system consisted of a feed tank, pump, membrane cell, pressure gauge, control valve and a heat exchanger system. A SEPA® CF II membrane cell system purchased from Sterlitech (Kent, WA) was used to host the membrane unit with an active filtration area of 138 cm^2. A feed spacer was placed on the membrane to create turbulence in the feed flow. The transmembrane pressure was monitored and auto-controlled by a custom designed LabVIEW program displaying real-time pressure data. Flux data was obtained by recording the permeate weight every minute using a digital balance. Filtration tests were conducted in full recycle mode, with both retentate and permeate recycled back into the feed tank. The feed tank was mixed using an overhead mixer so that the feed concentration and temperature remained constant throughout the filtration experiments. All the experiments were conducted at 25 ± 0.5 °C and the cross flow velocity was not controlled.

A new membrane was used for each set of experiments. Before sample filtration, the membrane was pre-compacted with DI water at 16 bar until the membrane flux reached a stable level and then

Table 1
Characteristics of the NF membranes used in this research (Data was obtained from the manufacture except water permeability constant values were measured in this study).

Name	Desal DL (DL)	Desal DK (DK)
Manufacturer	GE Osmonics	GE Osmonics
Configuration	Flat sheet	Flat sheet
Filtration area (cm^2)	138	138
Molecular Weight Cutoff (MWCO, Dalton)	150–300	150–300
Water permeability coefficient ($Lm^{-2}\,h^{-1}\,bar^{-1}$)	6.2	4.5
Salt rejection (%, solute)	96, $MgSO_4$	98, $MgSO_4$
Maximum pressure (bar)	41	41
pH range	3–9	3–9