Journal of Membrane Science 487 (2015) 40–50

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Assessing nanofiltration and reverse osmosis for the detoxification of lignocellulosic hydrolysates

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ARTICLE INFO

Article history:
Received 23 December 2014
Received in revised form
24 March 2015
Accepted 28 March 2015
Available online 6 April 2015

Keywords:
Nanofiltration
Reverse osmosis
Detoxification
Inhibitor
Lignocellulosic hydrolysate

ABSTRACT

During hydrolysis of lignocellulosic materials for ethanol production, compounds toxic for fermentation are formed. Ten nanofiltration (NF) and reverse osmosis (RO) membranes with low molecular weight cut-off (150–400 g mol^{-1}) were screened on a flat-sheet plant for their ability to separate C5 and C6 sugars from acetic acid, furfural, 5-hydroxymethyl furfural and vanillin in a model solution. RO led to the highest sugars rejection (> 97%) but inhibitors transmission was low. NF membranes, especially NF270, NF- and NF245 (Dow) and DK (GE Osmonics) were found suitable for detoxification with glucose rejection > 94% and inhibitors transmission > 80%. At high Volume Reduction Ratio, *VRR*, transmission of inhibitors was still enhanced (> 96% at *VRR*=8 and 10 bars). In these conditions, NF270 gave the highest permeate flux (20 L h^{-1} m^{-2}) followed by DK, NF- and NF245. However, DK and NF- could be preferred because of lower sugar loss.

1. Introduction

Lignocellulosic biomass is currently being considered as a new renewable source of energy for the production of second generation bioethanol. Carbohydrate content can be converted into fermentable sugars directly by acid hydrolysis or indirectly by a two-stage process involving pretreatment and enzymatic hydrolysis. Although dilute-acid hydrolysis is a fast and cheap method for obtaining sugars from lignocellulosic materials, it leads to the formation of toxic compounds for fermentation such as furan derivatives (furfural and 5-hydroxymethyl furfural (HMF)), aliphatic acids (mainly acetic, formic and levulinic acids) and phenolic compounds. Such inhibitory substances adversely affect the productivity and the yield of ethanol fermentation [1]. In order to enhance the effectiveness of fermentation, sugars concentration should be increased and inhibitors should be removed. Various detoxification methods have been reviewed ([2–4]). The most extensively studied are based on physical and chemical principles, such as evaporation, overliming, solvent extraction, adsorption and ion-exchange. Biological methods also recently appeared based on the bioconversion of inhibitors into less toxic compounds. So far, however, none of these treatments proved its ability to remove all families of inhibitors and each of them has its own drawbacks: high processing costs (evaporation), high chemicals consumption and production of wastes (overliming, ion-exchange, adsorption), hazardous solvent handling (liquid/liquid extraction), significant sugar loss or degradation (overliming), and low efficiency (biological methods). Moreover, with the exception of evaporation, they do not allow simultaneous detoxification and concentration of sugars.

Pressure-driven membrane technology has already shown advantages in various fields of biorefinery as compared to other separation and purification techniques, including lower energy consumption, sustainable processing and flexibility. However, regarding the detoxification of lignocellulosic hydrolysates for the production of second-generation ethanol or other bioconversions, pressure-driven membranes have been considered only recently and the first review addressing their potential in this particular field is that of Abels et al. [5]. Actually, major inhibitors have lower molecular weight (MW) than sugars (formic acid: 46; acetic acid: 60; levulinic acid: 116; furfural: 96, HMF: 126 g mol^{-1} compared to 150 and 180 for C5 and C6 sugars, respectively). Thanks to size exclusion effects, membranes with small molecular weight cut-off (MWCO of around 150 g mol^{-1}) can be expected to let inhibitors as acids, furfural and HMF pass through while retaining sugars in the retentate. Moreover, at the low pH of the

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http://dx.doi.org/10.1016/j.memsci.2015.03.072
0376-7388/

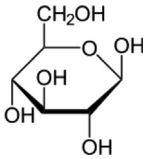
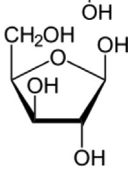
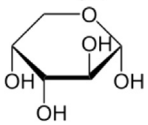
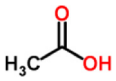
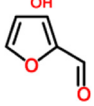
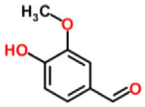
hydrolysates (pH ≈ 3), acids are mostly in their undissociated form (only 1.7% of acetic acid is dissociated) and membrane charge density is low; electrostatic repulsion is therefore minimized. Transmission of phenolic inhibitors is more questionable because they have higher MW than the smallest monosaccharide (for example vanillin: 152, vanillic acid: 168, syringaldehyde: 182, ferulic acid: 194, syringylpropane: 196 g mol^{-1}). However, most of them have a marked hydrophobic character as shown by octanol–water partition coefficients K_{OW} higher than >1.5 [6]. Hydrophobic compounds may show lower rejection than could be predicted from size-exclusion mechanisms ([7,8]); this would be related to enhanced adsorption on the surface which facilitates transport through the membrane ([9,10]).

The potential of nanofiltration (NF) for this particular application was first demonstrated by Weng et al. [11] with GE Osmonics Desal 5 DK membrane on a xylose–acetic acid mixture and further confirmed on rice straw hydrolyzate [12]. The presence of sugars seems to decrease acetic acid rejection to even negative values. With Desal 5 DK and Alfa-Laval-NF membranes, Zhou et al. [13] observed rejections from 85–89% for xylose to 96–98% for glucose and confirmed negative values for acetic acid rejection. Encouraging observations were reported by Qi et al. [14] for furfural removal by Dow NF90 and NF270 from a glucose–xylose mixture but the experimental set-up (a dead-end filtration cell with 4.5 cm^2 filtration area and magnetic stirring) was far from cross-flow conditions. They are few published results relating to phenolic compounds. Maiti et al. [15] tested flat polyamide membranes with MWCO between 100 and 400 g mol^{-1} and a spiral-wound PES membrane with a 150 g mol^{-1} MWCO on a synthetic mixture of mono- and di-saccharides and several inhibitors including vanillic and ferulic acids: high transmission of phenolics was observed.

With reverse osmosis (RO), quite complete sugar recovery may be expected but perhaps at the expense of detoxification efficiency. Not much work can be found. One of them is with a model solution of acetic acid, xylose and glucose and Alfa-Laval RO98pHt and RO99 membranes [13]. Rejection close to 100% was found for sugars at 30 bars but detoxification was limited with rejection of about 45% for acetic acid. This is consistent with the results of Sagne et al. ([16,17]) on detoxification of beet distillery condensates containing similar inhibitory compounds: acetic acid and furfural rejections were found less than 50% with Hydranautics CPA2 membrane at similar pressure. Higher transmissions could be achieved at lower pressure, with the drawback of lower permeate flux.

The aim of this work was to screen a large panel of NF and RO membranes on a flat-sheet laboratory plant for their ability to separate inhibitors from sugars. This was done on a complex model solution simulating the average composition of a dilute acid hydrolysate containing three sugars: glucose, xylose and arabinose and inhibitors of various chemical families: acetic acid as major inhibitor of the carboxylic acids family, furfural and HMF as furan derivatives and vanillin as phenolic compound. For each membrane, effect of transmembrane pressure and concentration on permeate flux and solute rejection was studied. Membranes and operational conditions providing the highest sugar rejection together with the highest inhibitor transmission were selected for future pilot-scale studies and fermentation evaluation.

Table 1
Characteristics of the solutes used in model hydrolysate (sugars are represented under their dominant form in water).

	Structure	MW (g mol^{-1})	pK_a	Stokes diameter (nm)	log K_{OW}
Glucose		180	12.28 [12]	0.726 [12]	−3.24 [19]
Xylose		150	12.15 [12]	0.638 [12]	−1.98 [8]
Arabinose		150	–	0.635 [12]	–
Acetic acid		60	4.75	0.412 [12]	−0.17 [6]
HMF		126	>12 [15]	0.463 [12]	−0.37 [6]
Furfural		96	>12 [15]	0.438 [12]	0.41 [6]
Vanillin		152	8.2 [20]	–	1.21 [6]

2. Materials and methods

2.1. Model solution

Model solution was chosen based on a literature survey of hydrolysates compositions ([18]). It contained xylose (15 g L^{-1}), glucose (10 g L^{-1}), arabinose (5 g L^{-1}), acetic acid (5 g L^{-1}), 5-hydroxymethylfurfural (1 g L^{-1}), furfural (0.5 g L^{-1}) and vanillin (0.05 g L^{-1}). Chemicals were purchased from Sigma-Alldrich (St Quentin Fallavier, France) and Interchim (Montluçon, France). pH of model solution was 3, close to the pH of real hydrolysates. Solutes characteristics are given in Table 1.

2.2. Membrane selection

Ten commercially available RO and NF membranes (Table 2) were selected from literature results including own research on condensates detoxification [25] and data from suppliers. For NF membranes, MWCO was in the range of 150–400 g mol^{-1} as given by manufacturers. MWCO is indicative because determination methods may vary from one manufacturer to the other. All membranes were thin-film composite membranes with a polyamide active layer. Fully aromatic polyamide is used for NF90 and RO membranes and mixed aromatic/aliphatic polyamide (polypiperazine amide) for NF. Membranes may also undergo specific and proprietary treatments, such as blending with unreactive polymers to change hydrophobicity and density of the top layer or surface grafting. Maximal operating conditions are 45–50 °C and 41 bar (except NF245: 54.8 bar) and 2–3 to 10–11 for pH.

Virgin membranes were first dipped in KOH solution (0.4 g L^{-1}) to remove storage chemicals and then flushed in desionized water for at least 24 h until tested in the pilot. After each filtration experiment, the membranes were cleaned with KOH (0.4 g l^{-1}) under low pressure and high flow rate and rinsed many times with desionized water in order to recover the initial