Biochemical Engineering Journal 121 (2017) 13–16

Contents lists available at ScienceDirect

Biochemical Engineering Journal

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

Short communication

Up-concentration of sugars in pretreated-rice straw by an osmotic pressure-driven method

Masafumi Shibuya[a], Masahiro Yasukawa[a], Kengo Sasaki[b], Yasuhiro Tanaka[a], Tomoki Takahashi[a], Akihiko Kondo[b], Hideto Matsuyama[a,*]

[a] Center for Membrane and Film Technology, Department of Chemical Science and Engineering, Kobe University, 1-1 Rokkodaicho, Nada-ku, Kobe 657-8501, Japan
[b] Department of Innovation and Science Technology, Kobe University, 1-1 Rokkodaicho, Nada-ku, Kobe 657-8501, Japan

ARTICLE INFO

Article history:
Received 28 September 2016
Received in revised form 17 January 2017
Accepted 21 January 2017
Available online 25 January 2017

Keywords:
Forward osmosis
Ethanol fermentation
Sugar
Rice straw

ABSTRACT

Forward osmosis (FO), driven by high osmotic pressure, was used for the first time for bioethanol production from lignocellulosic biomass. A commercial membrane, TFC-ES (Hydration Technology Innovation), was used and 3.6 M triethylamine (TEA) was chosen as the draw solution because the concentration ratio against a model xylose solution was similar to that achieved with 2.5 M NaCl. The liquid fraction of hot-water-pretreated rice straw was concentrated by using the FO membrane. The initial sugar concentration of 199 mM increased to 825 and 1612 mM after 48 and 72 h of FO concentration, respectively, and these values were much higher than those obtained from nanofiltration. Simultaneous saccharification and fermentation of the liquid fraction after 48 h of FO concentration by xylose-fermenting recombinant *Saccharomyces cerevisiae* produced 17.7 g/L of ethanol after 24 h fermentation. Thus, the FO process has tremendous potential to up-concentrate sugars obtained from lignocellulosic biomass.

1. Introduction

Bioethanol production from lignocellulosic biomass, such as rice straw, has drawn attention [1]. Lignocellulosic biomass is mainly composed of cellulose, hemicellulose and lignin, which are organized in complex and three-dimensional structures. The hot-water pretreatment of rice straw produces a hemicellulose/lignin-rich liquid fraction and a cellulose/lignin-rich solid fraction, increasing the enzymatic accessibility to these fractions. Then cellulose and hemicellulose are saccharified enzymatically and the monomeric sugars obtained are fermented by using yeast. Finally, bio-ethanol is purified by distillation and dehydration. In commercial cellulosic ethanol production, the ethanol concentration after fermentation needs to be maximized, in order to decrease the energy consumption by post-stage purification processes. To achieve this, a culture broth containing a high concentration of sugars is needed for the ethanol fermentation step. However, sugars derived from hemicellulose are present in a low concentration in the liquid fraction after hot-water pretreatment of rice straw [2]. Membrane technologies are simple processes and can be easily scaled up and they are commonly used to obtain solutions containing high concentrations of sugars from pretreated lignocellulosic biomass [3]. Pressure-driven membrane processes, such as nanofiltration (NF), have often been used to concentrate sugars in the liquid fraction of pretreated lignocellulosic biomass [2,4]. However, concentrating sugars with these systems is difficult because of the technical limitations caused by applying pressure to these systems [2,4]. Recently, forward osmosis (FO) has been used as a membrane separation technology to recover fresh water [5,6]. In FO technology, water permeation is driven by an osmotic pressure difference. Water molecules are transferred from a low-osmotic pressure solution (feed solution: FS) to one with high osmotic pressure (draw solution: DS) without external pressure. If the draw solution can be regenerated easily, then energy costs can be lower than the pressure driven processes. For example, amine solutions can be recycled as DS by utilizing waste heat [7,8]. Therefore, the FO process has tremendous potential for decreasing the energy costs of water purification. Additionally, the FO process can yield higher final concentrations (after concentration) of the treated feed solution than the pressure-driven membrane processes if a high osmotic pressure solution is used as the DS [9]. However, to the best of our knowledge, the FO process has not been

Abbreviations: DS, draw solution; FO, forward osmosis; FS, feed solution; NF, nanofiltration; SPS, switchable polarity solvent; TEA, triethylamine; TEA-CO_2, triethylamine-carbon dioxide; TMA-CO_2, trimethylamine-carbon dioxide; YPD, yeast extract-polypeptone-glucose; YPX, yeast extract-polypeptone-xylose.

* Corresponding author.
E-mail address: matuyama@kobe-u.ac.jp (H. Matsuyama).

http://dx.doi.org/10.1016/j.bej.2017.01.012
1369-703X/

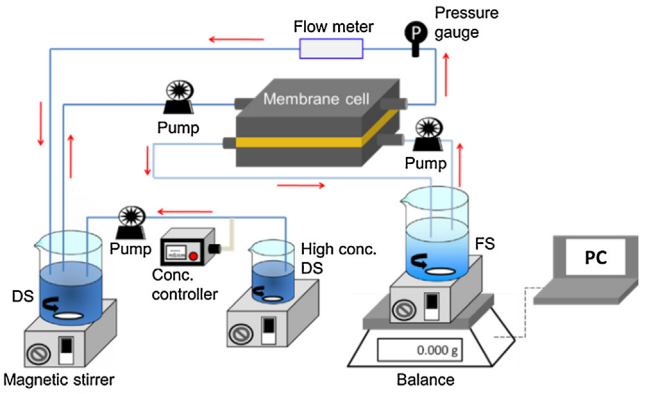

Fig. 1. Schematic illustration of the FO performance evaluation system to up-concentrate sugars in the solution.

applied to increase the sugar concentration of the liquid fraction obtained from pretreated lignocellulosic biomass.

In this study, the up-concentration of sugars in the liquid fraction of hot water-pretreated rice straw was investigated using the FO process. A permeation test was performed using a flat sheet membrane cell to evaluate the performance of the commercial FO membrane. First, three types of DSs were examined to permeate water using a model sugar solution containing mainly xylose. After determining the suitable DS for this process, we used the actual liquid fraction of hot water-pretreated rice straw as the FS. Finally, we evaluated ethanol fermentation from the up-concentrated sugar solution using a xylose-assimilating stain of *Saccharomyces cerevisiae* [2].

2. Material and methods

2.1. Feed solution

Rice straw pretreated with liquid hot water [10], at pressures below 10 MPa and at high temperatures (130–300 °C), was provided by Mitsubishi Heavy Industries, Ltd. (Tokyo, Japan). The liquid fraction (pH 4.1) was separated from the solid fraction by a mesh filter and used. It contained mainly hemicellulosic sugars. Additionally, a model sugar solution was prepared from 20 g/L xylose (Wako Pure Chemical Industries, Ltd.) and 0.45 g/L acetic acid (Wako Pure Chemical Industries, Ltd.). The pH of the model sugar solution was 5.2.

2.2. Draw solution

A switchable polarity solvent (SPS) was used as the draw solute in this study. A SPS switches from being water miscible in the presence of CO_2 to being water-immiscible in the absence of CO_2 [7]. A high osmotic pressure can be generated when the SPS solute is in its polar form. Triethylamine-carbon dioxide (TEA-CO_2) and trimethylamine-carbon dioxide (TMA-CO_2) were utilized as SPS solutes and evaluated in FO experiments. These amine-type solutions (TEA-CO_2 and TMA-CO_2) were used as DSs after bubbling CO_2 though them for 48 h. The performances of these amine-type solutions were compared with that of a sodium chloride (NaCl) solution.

2.3. FO performance test

The TFC-ES membrane was purchased from Hydration Technology Innovation (HTI) and the membrane performance was evaluated with the apparatus that is schematically illustrated in Fig. 1. The DS side flow was supplied by a low-pressure pump (AQUATEC CDP-8841), while the FS side flow was supplied by a low-pressure pump (Nitto Kohki Co. Ltd, BHP-474G). To make the DS and FS solutions uniform, the contents of the DS and FS tanks were continuously stirred with a magnetic stirrer. The inlet DS concentration was kept constant by using a concentration control unit during the experiment. To investigate the type and concentration of the DS, the active layer of the FO membrane was oriented toward the FS (AL-FS mode) and the support layer was oriented toward the DS. The DS inlet flow rate was 0.75 L/min and the FS inlet flow rate was 0.4 L/min. The water flux (J_w) was calculated by measuring the reduction in the FS volume using a real-time data logging system connected to a personal computer. After the experiments, the concentrations of sugars (glucose, xylose, and fructose) and fermentation inhibitors (acetate, formate, furfural, and 5-HMF) in the solutions were determined using previously reported methods [2,11].

2.4. Ethanol fermentation

S. cerevisiae strain MN8140X/TF-TF was used for ethanol fermentation [12]. It harbors a PIUX1 × 2XK plasmid (URA3, intracellular co-expression of xylose reductase and xylitol dehydrogenase from *Pichia stipitis* and xylulokinase from *S. cerevisiae* genes). It was aerobically precultivated for 24 h at 30 °C and 150 rpm in 5 mL of yeast extract-polypeptone-glucose (YPD) medium (10 g/L yeast extract, 20 g/L polypeptone, 20 g/L glucose), and then cultivated for 72 h in 500 mL of yeast extract-polypeptone-xylose (YPX) medium (10 g/L yeast extract, 20 g/L polypeptone, 20 g/L xylose) at 30 °C and 150 rpm. The cells were collected by centrifugation at 3000 × *g* at 4 °C for 10 min and washed twice with distilled water. The pH of the liquid fraction of the hot-water-pretreated rice straw after concentration was adjusted to 5.5 using 10 M NaOH or 5 M HCl. *S. cerevisiae* was inoculated into solutions containing yeast extract (final concentration: 10 g/L), peptone (final concentration: 20 g/L), 8 g/L hemicellulase (G-Amano, Amano Enzyme, Japan), and 800 mL/L hemicellulosic solution concentrated by the FO membrane. The initial concentration of *S. cerevisiae* was 50 g/L of wet cells, corresponding to 10 g/L of dry cells. Ethanol fermentation was performed under oxygen-limited conditions at 35 °C, with mild agitation, in 50-mL bottles equipped with an outlet for CO_2. Sampling was conducted at 0, 3, 6, 9, 24, and 48 h.

3. Results and discussion

3.1. Effect of DS for the model sugar solution

Three types of DSs (TEA, TMA, and NaCl) were compared in order to choose a suitable DS for the sugar concentration process. Many researchers have used inorganic salts as DSs because of their high osmotic pressure [13]. However, these inorganic salts are difficult to regenerate and recover. Thus, we investigated the effect of two SPSs, TEA and TMA, as DSs on the sugar concentration. The variation of J_w and FS concentration ratio as a function of elapsed time using the three types of DS solutes is shown in Fig. 2. J_w decreases with elapsed time due to increase in the osmotic pressure on the FS side and decrease in the driving force for water transport. As expected, J_w was highest when NaCl was used as the DS because of its high diffusivity. In contrast, J_w was lowest when TMA was used as the DS. In this case, J_w was restricted due to leakage of TMA which decreased the osmotic pressure difference between the DS and FS. Here, the reverse salt fluxes (J_s) of TMA and TEA were 100 and 2.5 mmolMH, respectively. Xylose concentrations and pH after concentration of the FS for 48 h are listed in Table 1. The final xylose concentrations are approximately 172 and 191 g/L when using 3.6 M TEA and 2.5 M NaCl as the DS, respectively. These concentrations are about eight times higher than the initial concentration. When the amine