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Development of combined nanofiltration and forward osmosis process for production of ethanol from pretreated rice straw

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HIGHLIGHTS

- NF-FO hybrid process to treat the liquid fraction from hot water-pretreated rice straw.
- NF-FO hybrid process generated a ethanol concentration of 25.6 g L^{-1}.
- NF-FO hybrid process has the potential for ethanol production from pretreated rice straw.

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ABSTRACT

A membrane process combining nanofiltraion (NF) and forward osmosis (FO) was developed for the sugar concentration with the aim of high bio-ethanol production from the liquid fraction of rice straw. The commercial NF membrane, ESNA3, was more adequate for removal of fermentation inhibitors (such as acetic acid) than the FO membrane, whereas the commercial FO membrane, TFC-ES, was more adequate for concentration of the sugars than the NF membrane. The liquid fraction was subjected to the following process: NF concentration with water addition ($NF_{(+H2O)}$) → enzymatic hydrolysis → FO concentration. This $NF_{(+H2O)}$-FO hybrid process generated a total sugar content of 107 g·L^{-1}. Xylose-assimilating *S. cerevisiae* produced 24 g·L^{-1} ethanol from the liquid fraction that was diluted 1.5-fold and then concentrated by the $NF_{(+H2O)}$-FO hybrid process. The $NF_{(+H2O)}$-FO hybrid process has the potential for optimized ethanol production from pretreated lignocellulosic biomass.

1. Introduction

Second-generation liquid biofuels (from non-food biomass) offer many advantages such as availability, sustainability, and non-competitiveness with the food chain; nevertheless, the production process is hampered by many technical and economic constraints (Paulova et al., 2015; Sims et al., 2010). Previously, to increase the enzyme accessibility to achieve improved biomass digestibility, several pretreatment methods have been developed (Alvira et al., 2010). Hydrothermal treatment with hot liquid-state water was utilized in this study, because this process is cost-saving as no catalyst is required and water has a low-corrosion potential (Alvira et al., 2010). During the hot water pretreatment process, two fractions are obtained: a solid, cellulose-enriched fraction and a liquid fraction rich in hemicellulose-derived sugars. However, a low ethanol concentration is produced from the liquid fraction because the solubilized hemicelluloses are present in lower concentration, and by-products (weak acids, furan derivatives, and phenolic compounds) that inhibit the enzymes and fermentation microorganisms in the subsequent steps are also obtained (Sasaki et al., 2014). To obtain high ethanol yields and productivity during fermentation, a high ethanol concentration in the distillation feed is necessary to reduce the energy demand (Paulova et al., 2015).

Membrane technology is a simple process with easy scale-up, and is one of the best solutions for increasing the sugar concentration and for removing fermentation inhibitors to optimize the subsequent biofuel production process (He et al., 2012). The pressure-driven process, nanofiltration (NF), has been widely used to concentrate and purify the sugars in the liquid fraction of

Abbreviations: DS, draw solution; FS, feed solution; FO, forward osmosis; NF, nanofiltration; TEA, triethylamine.

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pretreated lignocellulosic biomass (Sasaki et al., 2014; Qi et al., 2012; Weng et al., 2010). On the other hand, forward osmosis (FO) is an emerging membrane technology that is used in areas such as seawater desalination and wastewater recycling (Chekli et al., 2016; Valladares Linares et al., 2014; Zhao et al., 2012). In the FO process, water molecules are transferred from a low osmotic pressure solution to a high osmotic pressure solution. The driving force of FO is the osmotic pressure difference across the FO membrane. In our previous study (Shibuya et al., 2017), the FO process was, for the first time, applied to the production of bio-ethanol from pretreated lignocellulosic biomass, and a much higher concentration ratio (8 times) of the hemicellulose-derived sugar solution was obtained relative to that from NF. These results suggested that the NF and FO processes offered different advantages, and the combined process has the potential as a new technique for optimizing the subsequent production of bioethanol by *Saccharomyces cerevisiae*.

The aim of the present study is to apply the NF-FO hybrid process on the liquid fraction of hot water-pretreated rice straw for obtaining higher bioethanol production. The performances of only NF and FO processes are evaluated and compared with these of the NF-FO hybrid process. Xylose-assimilating *S. cerevisiae* is utilized for fermentation (Sakamoto et al., 2012) because the liquid fraction after enzymatic hydrolysis is rich in hemicellulose-derived xylose.

2. Materials and methods

2.1. Membrane

A commercial FO membrane (TFC-ES), of which salt rejection is 99.6%, was purchased from Hydration Technology Innovation (HTI). A commercial NF membrane (ESNA3), of which molecular weight cut off is 150 Da, was obtained from Nitto Denko Corporation. The TFC-ES and ESNA3 membranes are composite membranes with top skin layers of polyamide.

2.2. FO concentration process

Concentration using FO was conducted over the course of 72 h with a water permeation apparatus, as previously described (Shibuya et al., 2017). The liquid fraction of rice straw pretreated with hot, liquid-state water (Alvira et al., 2010) under a pressure below 10 MPa at high temperature (160–240 °C) was provided by Mitsubishi Heavy Industries, Ltd. (Tokyo, Japan). The liquid fraction (pH: 4.1) containing mainly hemicellulosic sugars was separated from the solid fraction by passing through a mesh filter. Before FO concentration, the oligomeric sugars in the liquid fraction were hydrolyzed with 10 g·L^{-1} hemicelluase (G-Amano, Amano Enzyme, Japan) by shaking at 75 rpm at 37 °C for 48 h. The lignin precipitate produced during enzymatic hydrolysis was removed by centrifugation at 1000*g* at 4 °C for 10 min (Sasaki et al., 2015) and the supernatant was supplied as the feed solution (FS) for FO concentration; 3.6 M triethylamine (TEA) (Tokyo chemical, Japan) was chosen as the draw solution (DS).

The DS side stream was supplied by a low-pressure pump (AQUATEC CDP-8841), while the FS side stream was supplied by a low-pressure pump (Nitto Kohki Co., Ltd., BHP-474G). To maintain a uniform DS and FS concentration, the contents of the DS and FS tanks were continuously stirred with a magnetic stirrer. The DS and FS inlet flow rates were 0.75 and 0.40 L·min^{-1}, respectively. The effective membrane area was 43 cm^2. 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.

2.3. NF concentration

The liquid fraction of rice straw pretreated with hot water was directly applied as the FS for NF concentration. The NF concentration process was conducted with a water permeation apparatus, as previously described (Sasaki et al., 2014), using a membrane cell (C40-B; Nitto Denko Corporation) at room temperature. The membrane cell was placed on a magnetic stirrer and the feed solution was stirred at 800 rpm by an embedded magnetic spin blade in the membrane cell (effective membrane area: 32 cm^2). An applied pressure of 3.0 MPa was exerted by using nitrogen gas and a pressure control valve. Two types of NF concentration methods were used as follows: (1) NF concentration for 24 h (termed 1-cycle), and (2) NF concentration for 24 h → [5-fold dilution with water → NF concentration for 24 h] × 2 (termed 3-cycle). After NF concentration, the concentrate was enzymatically hydrolyzed as described above.

2.4. $NF_{(+H2O)}$-FO hybrid process

The liquid fraction of rice straw pretreated with hot water was concentrated by using the $NF_{(+H2O)}$-FO hybrid system (Fig. 5). Firstly, NF with water addition was conducted for 90 h by using an ESNA3 NF membrane and a MEMBRANE MASTER C70-F RO test cell (Nitto Denko Corporation). A pressure of 2.0 MPa was applied by using nitrogen gas and a pressure control valve. Distilled water was supplied to the membrane cell. The supplied volume of distilled water was controlled to be equal to the permeate volume to maintain constant volume inside the membrane cell. The $NF_{(+H2O)}$ concentrate was enzymatically hydrolyzed and centrifuged to remove precipitated lignin as described above. Finally, the supernatant was concentrated over the course of 72 h by using the FO membrane, as described above.

2.5. Ethanol fermentation

S. cerevisiae strain MN8140X/TF-TF harboring a PIUX1X2XK plasmid (URA3, intracellular co-expression of xylose reductase and xylitol dehydrogenase from *Pichia stipitis* (*P. stipitis*) and xylulokinase from *S. cerevisiae* genes) was used for ethanol fermentation (Sanda et al., 2011). The diploid xylose-fermenting strain MN8140X/TF-TF also co-expresses the transaldolase and formate

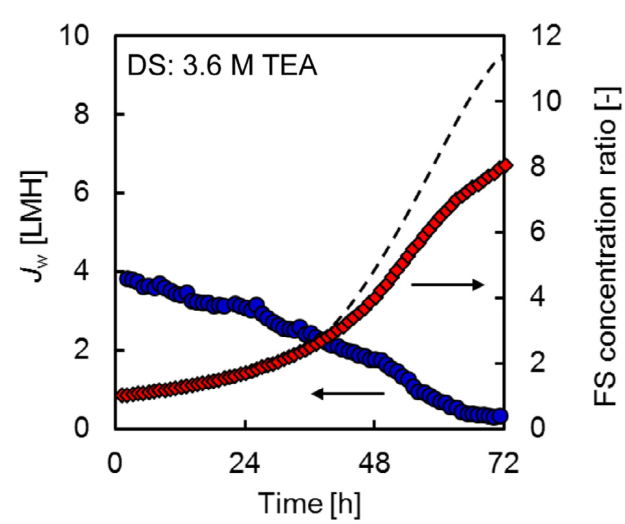

Fig. 1. Water flux, *Jw*, and sugar concentration ratio. The liquid fraction of rice straw pretreated with hot water after enzymatic hydrolysis was used as the feed solution (FS) for the commercial forward osmosis (FO) membrane, TFC-ES. Dotted line shows ideal FS concentration ratio.