



Concentration of lignocellulosic hydrolyzates by solar membrane distillation

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HIGHLIGHTS

- ▶ Membrane distillation based on solar energy was used to concentrate lignocellulosic hydrolyzates.
- ▶ The loss of glucose was negligible in the process.
- ▶ The concentration of bioethanol in the broth was increased by 2.64 times.

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ABSTRACT

A small solar energy collector was run to heat lignocellulosic hydrolyzates through an exchanger, and the heated hydrolyzate was concentrated by vacuum membrane distillation (VMD). Under optimal conditions of velocity of 1.0 m/s and 65 °C, glucose rejection was 99.5% and the flux was 8.46 L m⁻² h⁻¹. Fermentation of the concentrated hydrolyzate produced 2.64 times the amount of ethanol as fermentation using the original hydrolyzate. The results of this work indicated the possibility to decrease the thermal energy consumption of lignocellulosic ethanol through using VMD.

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1. Introduction

One of the biggest challenges in commercializing lignocellulosic ethanol technology is that low ethanol concentrations after fermentation caused by low sugar concentrations in hydrolyzates, results in high energy consumption for subsequent purification processes (Dehkhoda et al., 2009; Weng et al., 2010). In order to improve the yield of ethanol fermentation, the hydrolyzates should be concentrated before ethanol fermentation. Methods such as heating, vacuum evaporation (Dehkhoda et al., 2009; Yadav et al., 2011) and membrane separation (Qi et al., 2012) have been used to concentrate the hydrolyzates; however, vacuum evaporation and ordinary distillation methods are energy-intensive processes and require high-grade energy sources. Since the ultimate goal of bioethanol production is net energy output, new technologies need to be developed to decrease energy input during lignocellulosic ethanol production.

Vacuum membrane distillation (VMD) is an attractive and cost-competitive membrane separation technology (El-Bourawi et al., 2006; Lawson and Lloyd, 1997). Compared with conventional separation processes, VMD has higher rejection for non-volatile com-

ponents and can be carried out at low temperature. Thus, it can utilize low-level heat or alternative energy sources such as waste hot steam and water, geothermal, and solar energy. As solar energy is the most abundant green energy with low operating and maintenance costs, solar energy has been explored as heat source for membrane distillation (solar membrane distillation) (Mericcq et al., 2011). The feasibility of a hollow-fiber-based VMD system to produce potable water using a solar energy collector as heat source has already been demonstrated and the largest permeate flux obtained was 32.19 L m⁻² h⁻¹ with an 8 m² solar energy collector (Wang et al., 2009).

In the present study, VMD was used to concentrate lignocellulosic hydrolyzates using solar energy as a low-level heat source. Flow rate, feed temperature and sugar concentration were optimized with model solutions. The fermentation of concentrated hydrolyzates was carried out to evaluate the feasibility of VMD in the production of lignocellulosic ethanol.

2. Methods

2.1. Chemicals and experimental setup

The enzyme used in this study was from Nonozymes (NS22074cellulase complex), *Saccharomyces cerevisiae* was from

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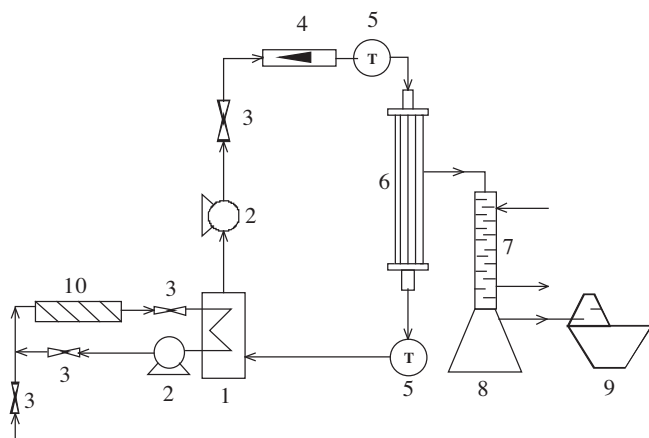


Fig. 1. Schematic diagram of the vacuum membrane distillation apparatus. 1 feed tank; 2 pumps; 3 flow regulating valves; 4 flow meter; 5 thermometers; 6 hollow fiber membrane module; 7 condenser; 8 permeate tank; 9 vacuum pump; 10 solar thermal collector.

Hubei Angel Co. Ltd., China. The module solution contained 5 g L⁻¹ glucose in deionized water.

The experimental apparatus of the solar-heated VMD process is shown in Fig. 1. The system had three major components, a hollow fiber module, a flat-plate solar energy collector and a permeation condenser. The module was fitted with PVDF membranes and the membrane average pore diameter and porosity were 0.18 μm and 85%, respectively. The area of the flat-plate solar energy collector was 8 m².

In this arrangement, the feed solutions were heated by heat transfer with solar hot water to the range of 50–70 °C, and then pumped into the shell side at velocities of 0.6–1.1 m/s. The trans-membrane permeate was removed by a vacuum pump and collected in the permeate bottle after cooling.

2.2. Enzymatic hydrolysis and fermentation

After pretreatment and enzymatic hydrolysis (Yan et al., 2009), the hydrolyzates (provided by Nanjing University of Technology) were concentrated by solar membrane distillation to increase the concentration of glucose in the liquid. In order to evaluate the concentration effect of VMD, the origin, twice and three-times concentrated hydrolyzates were fermented with dry *S. cerevisiae*. The hydrolyzates were supplemented with additional nutrients to provide a base medium compositions of (L): 0.2 g MgSO₄, 2 g KH₂PO₄, 2 g (NH₄)₂SO₄, 0.2 g CaCl₂ and 2 g yeast extract, then 10 g dry yeast/L liquid was added and the fermentation flasks were incubated at 35 °C.

2.3. Analytical methods

The concentration of glucose and ethanol were quantified by the DNS method and GC (GC-950, ParapakQ, Haixin Corp. Shanghai, China), respectively.

Flux and rejection were used to describe the performance of the VMD process (Weng et al., 2010).

3. Results and discussion

3.1. Effect of operation conditions

Fig. 2 shows membrane flux and rejection of glucose as a function of feed velocity, feed temperature and glucose concentration. The rejection of glucose was almost constant under the

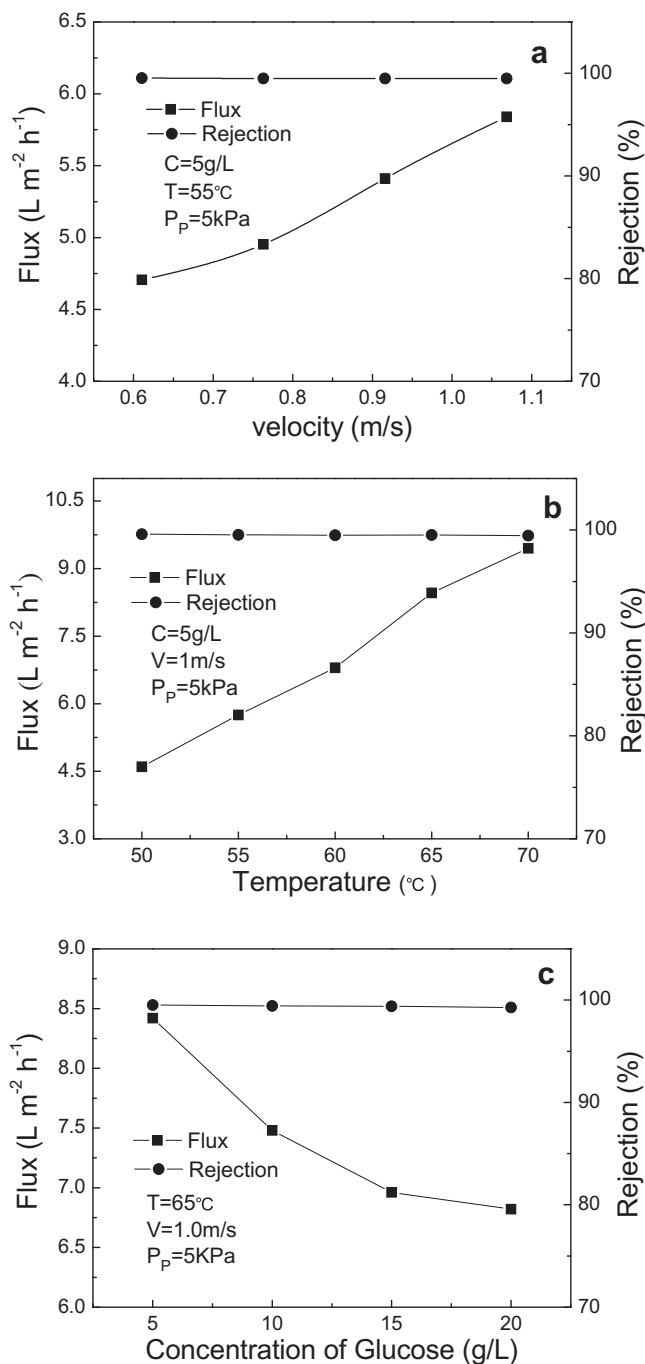


Fig. 2. Effect of operation parameters on vacuum membrane distillation flux and rejection rate. (a) Feed velocity; (b) Feed temperature; (c) Solute concentration.

conditions examined, with values higher than 99.5% and higher than those achieved with nanofiltration (Sjoman et al., 2007). As VMD is a mass transfer and heat transfer coupling process, feed velocity and temperature had a significant effect on VMD flux. For example, the flux increased by 24% from 4.7 L m⁻² h⁻¹ at 0.6 m/s to 5.8 L m⁻² h⁻¹ at 1.1 m/s (Fig. 2a). The effect of increased feed velocity is an increase in the heat transfer coefficient and reduction in temperature and concentration polarization effects. Fig. 2b depicts a linear increase in the MD flux from 4.6 to 9.5 L m⁻² h⁻¹ as the temperature was raised from 50 °C to 70 °C. This outcome was due to the exponential increase in vapor pressure of the feed solution with temperature, which increased the trans-membrane vapor pressure. The effect

of feed concentration on flux is shown in Fig. 2c. As the concentration of glucose increased from 5 to 20 g L⁻¹, the flux decreased from 8.42 to 6.82 L m⁻² h⁻¹. This result was attributed to the concentration polarization and reduction in partial vapor pressure of the water. Considering flux and solar energy support, the optimal condition of the velocity of 1.0 m/s and 65 °C were used in the following experiments.

3.2. Concentration of the hydrolyzates

After enzymatic hydrolysis, the hydrolyzates contained 35.96 g L⁻¹ glucose, which is too low for efficient ethanol fermentation. Fig. 3 shows the concentration of glucose and flux over operation time by VMD under optimal conditions. The rate of concentration increased over time, but the increasing rate was small in the later stage due to flux reduction. It took 150, 210, and 270 min to obtain glucose solutions of 67.33, 96.37, 136.07 g L⁻¹, respectively. The flux during this process decreased by 40% from 5.55 L m⁻² h⁻¹ at the beginning to 3.30 L m⁻² h⁻¹ in the end. This result was mainly attributed to membrane fouling and the decrease in water vapor pressure as the solute concentration increased. The water vapor pressure declined not only due to the decrease in water concentration but also from the glucose effect. The vapor pressures can be significantly altered by adding sugars to the solution as the hydroxyl groups in sugars interact with water through hydrogen bonding (Chovau et al., 2011). Aroujalian et al. (2006) found that in a 38 wt.% ethanol/water solution at 20 °C, the vapor pressure of water decreased by 18% in the presence of 0.072 mol L⁻¹ sucrose. In the present study, the glucose concentration changed from 0.20 mol L⁻¹ at beginning to 0.76 mol L⁻¹ in the end, thus the decrease in flux was small. The rejection of glucose declined slightly because the membrane became less hydrophobic and some defective pores were wetted due to the complex components in the hydrolyzates and concentration polarization, but the value remained higher than 98% during the entire concentrated process.

The energy requirements for this process are mainly for heating the hydrolyzates and vacuum application at the permeate side. For heating, solar energy was adopted as it has low operating costs. For vacuum pump operations, it costs 0.52 kW kg⁻¹ h⁻¹ to maintain a pressure at 50 mbar, in agreement with findings by Criscuoli et al. (2008), who studied the energy consumption of VMD with pure water. These authors obtained an energy requirement of 1.1 kW kg⁻¹ h⁻¹, including heating and vacuum application. The insignificant sugar loss and low energy input indicated that VMD was a potentially useful process in concentration of hydrolyzates.

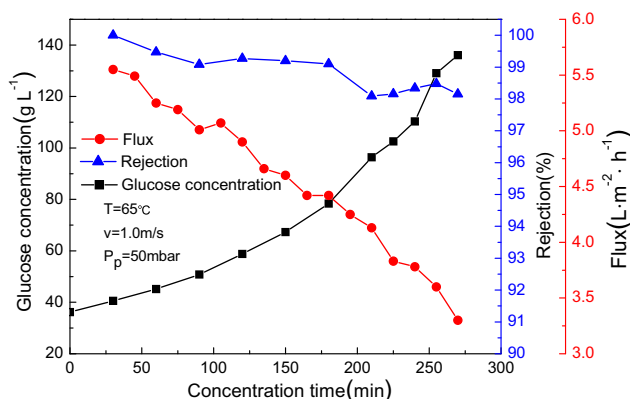


Fig. 3. Glucose concentration, flux and rejection as a function of operation time.

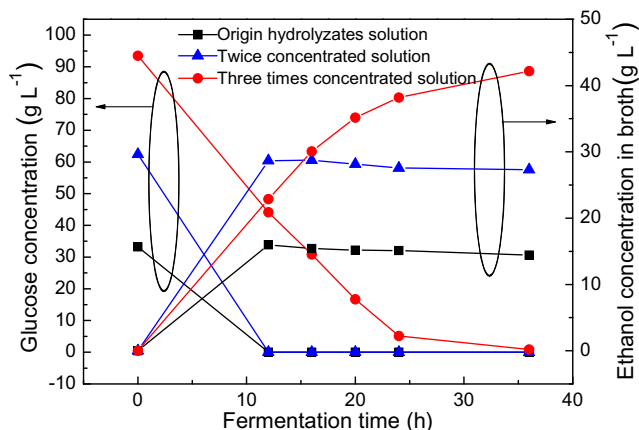


Fig. 4. Glucose and ethanol concentrations in fermentation medium over time.

3.3. Fermentation

The consumption of glucose and the production of ethanol with fermentation time are illustrated in Fig. 4. The highest ethanol production was achieved with the three-times concentrated hydrolyzate as 42.18 g L⁻¹ after 36 h, which is 2.64 and 1.47 times as much as that of the origin and twice concentrated hydrolyzates, respectively. For all hydrolyzates, the ethanol yields were more than 89.1% and the maximum ethanol yield for three-times concentrated hydrolyzate was 93.8% at 16 h.

4. Conclusions

The results showed that the VMD process based on solar energy can effectively concentrate sugars in hydrolyzates obtained from steam explosion hydrolysis of corn stover. The rejection of glucose was higher than 98% and the concentration of ethanol in broth of concentrated hydrolyzates was 2.64 times as much as that of the original solution. With a lower level heat source, the VMD process is a competitive concentration method in lignocellulosic ethanol production.

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References

- Aroujalian, A., Belkacemi, K., Davids, S.J., Turcotte, G., Pouliot, Y., 2006. Effect of residual sugars in fermentation broth on pervaporation flux and selectivity for ethanol. *Desalination* 193 (1–3), 103–108.
- Chovau, S., Gaykawad, S., Straathof, A.J., Van der Bruggen, B., 2011. Influence of fermentation by-products on the purification of ethanol from water using pervaporation. *Bioresource Technology* 102 (2), 1669–1674.
- Criscuoli, A., Carnevale, M.C., Drioli, E., 2008. Evaluation of energy requirements in membrane distillation. *Chemical Engineering and Processing* 47 (7), 1098–1105.
- Dehkoda, A., Brandberg, Tomas., Taherzadeh, Mohammad.J., 2009. Comparison of vacuum and high pressure evaporated wood hydrolysate for ethanol production by repeated Fed batch using flocculating *Saccharomyces cerevisiae*. *Bioresources* 4 (1), 309–320.
- El-Bourawi, M.S., Ding, Z., Ma, R., Khayet, M., 2006. A framework for better understanding membrane distillation separation process. *Journal of Membrane Science* 285 (1–2), 4–29.
- Lawson, K.W., Lloyd, D.R., 1997. Membrane distillation. *Journal of Membrane Science* 124 (1), 1–25.
- Mericq, J.P., Laborie, S., Cabassud, C., 2011. Evaluation of systems coupling vacuum membrane distillation and solar energy for seawater desalination. *Chemical Engineering Journal* 166 (2), 596–606.

- Qi, B., Luo, J., Chen, G., Chen, X., Wan, Y., 2012. Application of ultrafiltration and nanofiltration for recycling cellulase and concentrating glucose from enzymatic hydrolyzate of steam exploded wheat straw. *Bioresource Technology* 104, 466–472.
- Sjoman, E., Manttari, M., Nystrom, M., Koivikko, H., Heikkila, H., 2007. Separation of xylose from glucose by nanofiltration from concentrated monosaccharide solutions. *Journal of Membrane Science* 292 (1–2), 106–115.
- Wang, X.Y., Zhang, L., Yang, H.J., Chen, H.L., 2009. Feasibility research of potable water production via solar-heated hollow fiber membrane distillation system. *Desalination* 247 (1–3), 403–411.
- Weng, Y.H., Wei, H.J., Tsai, T.Y., Lin, T.H., Wei, T.Y., Guo, G.L., Huang, C.P., 2010. Separation of furans and carboxylic acids from sugars in dilute acid rice straw hydrolyzates by nanofiltration. *Bioresource Technology* 101 (13), 4889–4894.
- Yadav, K.S., Naseeruddin, S., Prashanthi, G.S., Sateesh, L., Rao, L.V., 2011. Bioethanol fermentation of concentrated rice straw hydrolyzate using co-culture of *Saccharomyces cerevisiae* and *Pichia stipitis*. *Bioresource Technology* 102 (11), 6473–6478.
- Yan, L., Zhang, H., Chen, J., Lin, Z., Jin, Q., Jia, H., Huang, H., 2009. Dilute sulfuric acid cycle spray flow-through pretreatment of corn stover for enhancement of sugar recovery. *Bioresource Technology* 100 (5), 1803–1808.