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Short Communication

Removal of inhibitors from lignocellulosic hydrolyzates by vacuum membrane distillation

Jingwen Chen [a], Yaqin Zhang [b], Yafei Wang [b], Xiaosheng Ji [b], Lin Zhang [b,c,*], Xigeng Mi [c], He Huang [a,*]

[a] College of Biotechnology and Pharmaceutical Engineering, Nanjing University of Technology, Nanjing 210009, China
[b] Department of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China
[c] State Key Laboratory of Motor Vehicle Biofuel Technology, Nanyang 473000, China

HIGHLIGHTS

- VMD was effectively used to remove inhibitors from lignocellulosic hydrolyzates.
- The difference between the removal efficiencies of inhibitors was verified by VLE.
- Fermentability of lignocellulosic hydrolyzates was improved after detoxification.

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ABSTRACT

In this study, vacuum membrane distillation (VMD) was used to remove two prototypical fermentation inhibitors (acetic acid and furfural) from lignocellulose hydrolyzates. The effect of operating parameters, such as feed temperature and feed velocity, on the removal efficiencies of inhibitors was investigated. Under optimal conditions, more than 98% of furfural could be removed by VMD. However, the removal efficiency of acetic acid was considerably lower. After furfural and acetic acid were selectively removed from hydrolyzates by VMD, ethanol production efficiency increased by 17.8% compared to original hydrolyzates.

1. Introduction

During the bioconversion process of lignocellulose to bioethanol, pretreatment (Kim et al., 2011; Yan et al., 2009) is required to hydrolyze lignocellulose into the corresponding sugars in order to be utilized by microorganisms. However, during the hydrolysis process many derivatives, such as aliphatic acids, furans and phenolic compounds, are formed. Such byproducts can significantly inhibit fermentation and decrease the ethanol productivity (Mussatto and Roberto, 2004; Ximenes et al., 2010), and the amounts of these inhibitors and their toxicity depend on type of pretreatment and fermentation microorganism. For instance, Kim et al. (2011) determined that the soluble phenolic compounds were released during liquid hot water pretreatment as the major inhibitory component to β-glucosidase. In this study, acetic acid and furfural, two of the prototypical inhibitors, were selected to study in detail due to the highest content of acetic acid in the diluted acid pretreated hydrolyzates (Yan et al., 2009) and strong toxicity of furfural to *Saccharomyces cerevisiae* (Palmqvist et al., 1999).

Several methods were employed to remove acetic acid and furfural from hydrolyzates, including biological treatment, neutralization, solvent extraction, evaporation, activated charcoal and ion exchange resin adsorption (Palmqvist and Hahn-Hägerdal, 2000). Drawbacks of these methods, however, are the high energy input, or complicated and long process, or extensive loss of sugars, or generation of additional waste products. Recently, membrane separations, such as reverse osmosis (RO) and nanofiltration (NF), used as new methods for hydrolyzates detoxification have begun to receive more attention due to their simplicity and energy-efficient compared to conventional processes.

Vacuum membrane distillation (VMD) is an increasingly popular and cost-effective membrane separation technology. The principle of VMD separation is based on liquid–vapor phase equilibrium that controls the process selectivity, enabling removal of volatile

* Corresponding authors at: Department of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China. Tel.: +86 571 8795121.
E-mail addresses: linzhang@zju.edu.cn (L. Zhang), biotech@njut.edu.cn (H. Huang).

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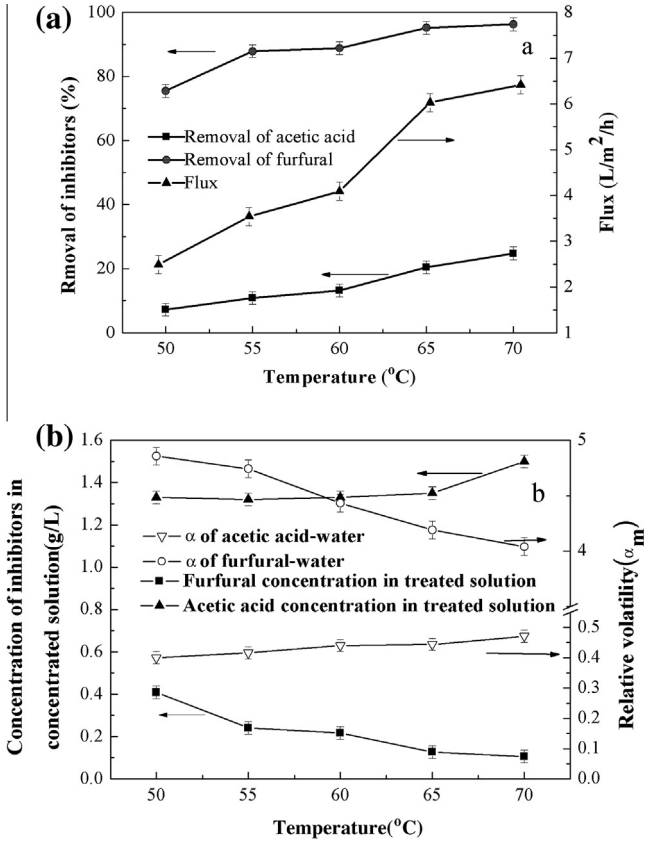

Fig. 1. Effect of temperature on total flux, removal of inhibitors (a) and treated concentrations of inhibitors and the relative volatility in VMD (b).

components. Several reports on removal of volatile components (such as alcohol, ketone and aroma compounds) from aqueous solutions using VMD have been described in the literature. For example, Wu et al. (2006) applied VMD using a polyvinylidene fluoride (PVDF) hollow fiber membrane to remove volatile 1,1,1-trichloroethane (TCA) from water, achieving a removal efficiency as high as 97%. Gryta and Barancewicz, (2011) reported VMD efficiently removed fermentation volatile product ethanol during the fermentation process, and the fermentation rate was significantly increased. As such, removal of volatile components using VMD is a very promising technique that deserves further investigation.

In the current study, VMD was applied to remove two byproducts, namely, furfural and acetic acid from dilute acid pretreatment of lignocellulosic biomass. Fermentation of detoxified lignocellulosic hydrolyzates was carried out to evaluate the effects of removing inhibitors by VMD.

2. Methods

2.1. Chemicals and experimental setup

Analytical grade glucose, furfural and acetic acid were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Analytically pure methanol for HPLC was supplied by Aladdin Chemistry Co., Ltd. (China). The standard solution was prepared by dissolving a pre-calculated amount of glucose, furfural and acetic acid.

The experimental apparatus of the solar-heated VMD, including a hollow fiber module, a flat-plate solar energy collector and a permeation condenser, was described in detail in our previous work (Zhang et al., 2012).

2.2. Pretreatment, detoxification and fermentation

Corn stover obtained from Inner Mongolia, PR China, was milled to attain a particle size between 200 and 400 μm and used. 35 g biomass was hydrolyzed with 2% (w/v) H_2SO_4 at 95 °C for 90 min at a solid to liquid ratio of 1:15. The solid and liquid phases were separated by filtration and the hydrolyzates (the liquid phase) were chemically characterized (Yan et al., 2009).

After dilute acid pretreatment, the hydrolyzates were detoxified by VMD to remove furfural and acetic acid. As VMD treatment was a glucose concentration and inhibitors detoxification coupling process, the treated hydrolyzates were diluted to initial sugar concentration to get rid of the fermentation difference due to the concentration of glucose.

Fermentation experiments were conducted using detoxified-diluted hydrolyzates, original hydrolyzates were used as controls. All fermentation experiments were carried out using dry *S. cerevisae* purchased from Hubei Angel Co. Ltd. (China), the cells were incubated for 20 min at 40 °C in the culture medium containing 20 g/L glucose and a cell suspension was prepared in sterile water. Each 250 mL Erlenmeyer flask containing 100 mL of either original or detoxified-diluted hydrolyzates having 40 g/L sugars and supplemented with: 2 g/L $(NH_4)_2SO_4$, 2 g/L KH_2PO_4, 0.2 g/L $MgSO_4$, 0.2 g/L $CaCl_2$ and 2 g/L dry yeast extract, pH 5.5 was inoculated with 0.5 mL of inoculum and incubated at 35 °C in screw-cap centrifuge tubes at 80 rpm

2.3. Analytical methods

2.3.1. Chemical analysis

The concentration of furfural and acetic acid were quantified using an HPLC system (Shimadazu Corp., Kyoto, Japan) (Qi et al., 2011). Ethanol was determined by gas chromatography (GC) with an elite-wax column at 120 °C, flame ionization detector (FID) at 210 °C and injector at 180 °C, and the carrier gas was nitrogen (Chandel et al., 2007).

2.3.2. Performance of VMD

Flux and removal efficiency were used to describe the performance of the VMD process (El-Bourawi et al., 2007). Moreover, the relative volatility (α_m) of acetic acid–water or furfural–water system in VMD process can be calculated according to the following formula:

$$\alpha_m = \frac{C_p}{(C_{f1} + C_{f2})/2} \times 100\% \quad (1)$$

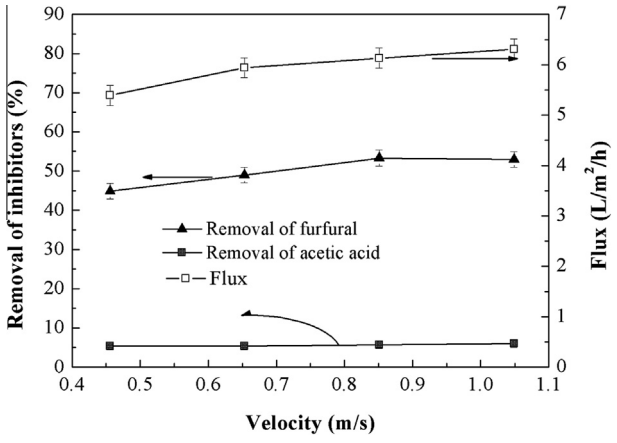

Fig. 2. Effect of velocity on total flux and removal of inhibitors.