Bioresource Technology 155 (2014) 229–234

Contents lists available at ScienceDirect

Bioresource Technology

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

Enhanced ethanol fermentation in a pervaporation membrane bioreactor with the convenient permeate vapor recovery

Senqing Fan [a], Zeyi Xiao [a,*], Yan Zhang [a], Xiaoyu Tang [b], Chunyan Chen [c], Weijia Li [a], Qing Deng [a], Peina Yao [a]

[a] School of Chemical Engineering, Sichuan University, 610065 Chengdu, China
[b] Biogas Institute of Ministry of Agriculture, 610041 Chengdu, China
[c] College of Chemistry and Chemical Engineering, Southwest Petroleum University, 610500 Chengdu, China

HIGHLIGHTS

- Continuous and complete coupling of ethanol fermentation and pervaporation.
- Second cell growth feature.
- Enhanced ethanol fermentation performance.
- Convenient permeate vapor recovery and refining without refrigeration unit.

ARTICLE INFO

Article history:
Received 5 November 2013
Received in revised form 25 December 2013
Accepted 27 December 2013
Available online 4 January 2014

Keywords:
Ethanol fermentation
Pervaporation membrane bioreactor
CCCF system
Permeate vapor recovery

ABSTRACT

A continuous and closed-circulating fermentation (CCCF) system with a pervaporation membrane bioreactor was built for ethanol fermentation without a refrigeration unit to condense the permeate vapor. Two runs of experiment with a feature of complete and continuous coupling of fermentation and pervaporation were carried out, lasting for 192 h and 264 h, respectively. The experimental measurement indicated that the enhanced fermentation could be achieved with additional advantages of convenient permeate recovery and energy saving of the process. During the second experiment, the average cell concentration, glucose consumption rate, ethanol productivity, ethanol yield and total ethanol amount produced reached 19.8 g L^{-1}, 6.06 g L^{-1} h^{-1}, 2.31 g L^{-1} h^{-1}, 0.38, and 609.8 g L^{-1}, respectively. During the continuous fermentation process, ethanol removal *in situ* promoted the cell second growth obviously, but the accumulation of the secondary metabolites in the broth became the main inhibitor against the cell growth and fermentation.

1. Introduction

With increasing gap between the energy requirement of the industrialized world and inability to replenish such needs from the limited sources of fossil fuels, an ever increasing level of greenhouse pollution from the consumption of fossil fuels in turn aggravated the perils of global warming and energy crisis (Balat and Balat, 2009). Biofuels, derived from renewable resources are realistic substitutes to fossil fuels.

Bioethanol, the main biofuel produced by fermentation of biomass, constituted a rapid and significant answer to these problems, by far the most widely used in the worldwide for the transportation sector (Amillastre et al., 2012). Ethanol could be combined and blended with petrol or burned in its pure form within modified spark-ignition engines (Nigam and Singh, 2011).

During the traditional ethanol batch fermentation process, the accumulation of ethanol in the broth inhibits the cell growth and fermentation, leading to low ethanol productivity, low ethanol concentration in the broth and great wastewater discharge. In the subsequent process, a lot of energy is consumed for product recovery from the broth (Nguyen et al., 2011). Separation technologies have been explored for ethanol removal *in situ* from the broth during fermentation to meet the requirement of reducing the cost of ethanol recovery. These approaches included gas stripping, extraction, adsorption, distillation and pervaporation (Vane, 2008). Gas stripping, the removal of ethanol from a fermentation broth by transferring ethanol into a stream was conceptually appealing owing to its simplicity, the ability to operate at fermen-

* Corresponding author. Address: Sichuan University, No. 24 South Section 1, Yihuan Road, 610065 Chengdu, China. Tel./fax: +86 028 85401057.
E-mail address: mgch@scu.edu.cn (Z. Xiao).

0960-8524/$ - see front matter © 2014 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.biortech.2013.12.114

tator temperatures not lethal to cell, and the option to use the carbon dioxide produced during the fermentation as the stripping gas (Domínguez et al., 2000; Taylor et al., 1995; Taylor et al., 1998; Taylor et al., 2000). In the extraction operation, the fermentation broth was placed in mass-transfer contact with an extractant liquid and compounds were transferred from the broth to the extractant (Bothun et al., 2003; Boudreau and Hill, 2006; Gyamerah and Glover, 1996; Larsson and Zacchi, 1996). In the case of adsorption, ethanol was preferentially transferred from the feed liquid or fermentation broth to a solid adsorbent material, and the absorbents should not be soluble in either water or ethanol in addition to a high selectivity. (Bowen and Vane, 2006; Cartón et al., 1998; Holtzapple and Brown, 1994; Oumi et al., 2002).

Pervaporation is one of the most promising approaches for the recovery of alcohols from fermentation broths. It was simple, nontoxic to fermenting microorganisms, and potentially less energy consuming than distillation (Lee et al., 2012). The feed or fermentation broth was forced flowing on one side of the membrane, and a gaseous phase permeate would be released. Two options, a vacuum or sweep gas less common were exerted at the other side of the membrane to supply a driven force between the membrane upstream and downstream sides. The influence of fermentation by-products on the purification of ethanol from water using pervaporation, demonstrated that sugar and salts increased the membrane performance but 2,3-butanediol decreased the ethanol flux and selectivity, and glycerol exhibited no effect (Chovau et al., 2011). Before pervaporation coupling with fermentation of corn fiber hydrolysate, the anion exchange neutralized hydrolysate contained substantially lower levels of the inhibiting compounds compared to the lime neutralized hydrolysate (O'Brien et al., 2004). In the research of ethanol pervaporation from lignocellulosic fermentation broth, the effects of different feedstock used and pretreatment method applied, on the membrane properties could not be distinguished due to presence of several unknown components in the broth (Gaykawad et al., 2013). During the fuel ethanol production process, the permeate vapor at the downstream of the hydrophobic pervaporation membranes could be refined to an azetropic point, then the remaining water in the azetropic composition could be further removed by pervaporation with hydrophilic membranes (Cardona and Sanchez, 2007). In our previous work, the coupling of ethanol fermentation with pervaporation was intermittent due to the limitations of conditions and operation, and the ethanol fermentation characteristics in the CCCF system could not be discovered clearly since the process in the intermittent condition was unsteady (Chen et al., 2012). The aim of this work was to explore the ethanol fermentation characteristics in the CCCF system by continuous coupling pervaporation with fermentation, and the recovery performance of the permeate vapor without the refrigeration unit.

2. Methods

2.1. Membranes and module

The composite polydimethylsiloxane (PDMS) membrane was self-prepared. It was nonporous and hydrophobic with good stability and nice tolerance to the organic solvent. The operating temperature of the PDMS material was in the range of 20 °C and 90 °C (Vane, 2005). The preparation procedure of the membrane had been fully described in the previous work (Li et al., 2004). The membrane module, illustrated in Fig. 1, was of a plate-frame structure, and two pieces of membrane with the effective membrane area 0.16 m^2 filled in the module. The perforated support consisted of a rectangular frame and two perforated plates, and the space enveloped by the frame and plate was for collecting the permeate vapor from membranes. A piece of membrane and a seal gasket were pressed between a cover and the plate. The space enveloped by the cover and the membrane surface could provide the flow channel for the broth. The solid arrow indicated the inlet and outlet for feed fluid and the dashed arrow was for outlet of the permeate vapor.

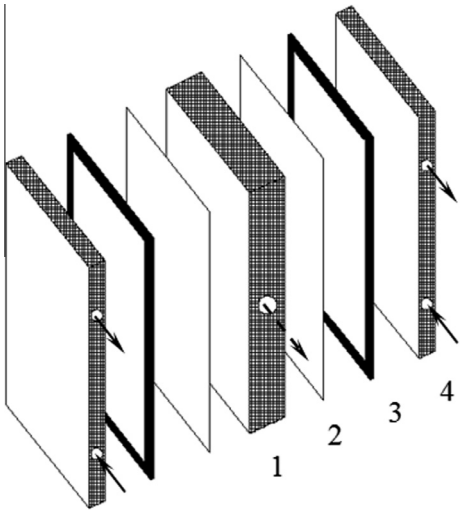

Fig. 1. Membrane module in the CCCF system. (1) Perforated support; (2) membrane; (3) seal gasket; (4) cover.

2.2. Microorganism and medium

The thermostable alcohol-active dry yeast (ADY), *Saccharomyces cerevisiae*, purchased from Angel Yeast Corporation (Hubei, China) was employed in the CCCF system. Prior to inoculation, 9 g of the yeast was rehydrated for 20 min in 250 ml glucose (15 g L^{-1}) solution at 38 °C followed the revival operation for 1.5 h at the temperature of 34 °C.

The synthetic medium (in 1 L) used in the CCCF system contained: glucose 100 g, yeast extract 8 g, $(NH_4)_2SO_4$ 5 g, KH_2PO_4 1.5 g, $MgSO_4{\cdot}7H_2O$ 0.55 g, $CaCl_2$ 0.15 g. All the materials in the medium were purchased from Kelong Chemical Reagent Corporation (Chengdu, China) and sterilized in an autoclave at 121 °C for 20 min.

2.3. CCCF procedure

The schematic diagram of the CCCF system for was shown in Fig. 2. The continuous and closed-circulating fermentation process was conducted after inoculation of 6 L of fermentation medium with the rehydrated seed. During the first 4 h after inoculation, the filtered air was sparged into the broth by a compressor for the aerobic fermentation, and then aeration was stopped for the anaerobic fermentation during the remaining period. When the ethanol concentration in the broth reached about 70 g L^{-1} after 24 h, membrane pervaporation was started and the broth was circulated through the membrane module and fermentor at a flow rate of 100 L h^{-1} by the circulating pump. During the fermentation process, the broth was kept at 35 ± 1 °C by the thermostat. The pH was adjusted 4.0 ± 0.5 with the ammonia water of 25 wt.%. Glucose and water were added to maintain the glucose concentration in the range of 20 g L^{-1} and 50 g L^{-1} and broth volume of 6 L. At the downstream of the membranes, some of the vapor was cooled into the liquid by the condenser with a spiral coil pipe and the running water as coolant. At the bottom of the condenser was the catch pot A for collecting the condensate. The remaining vapor released from