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Efficient production of acetone–butanol–ethanol (ABE) from cassava by a fermentation–pervaporation coupled process

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HIGHLIGHTS

- Continuous ABE production from cassava was studied by a fermentation–PV coupled process.
- The coupled process offered higher solvent yield and productivity.
- A concentrated permeate containing 201.8 g/L ABE with 122.4 g/L butanol was obtained.
- The membrane performance was stable during continuous ABE production from cassava.

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ABSTRACT

Production of acetone–butanol–ethanol (ABE) from cassava was investigated with a fermentation–pervaporation (PV) coupled process. ABE products were *in situ* removed from fermentation broth to alleviate the toxicity of solvent to the *Clostridium acetobutylicum* DP217. Compared to the batch fermentation without PV, glucose consumption rate and solvent productivity increased by 15% and 21%, respectively, in batch fermentation–PV coupled process, while in continuous fermentation–PV coupled process running for 304 h, the substrate consumption rate, solvent productivity and yield increased by 58%, 81% and 15%, reaching 2.02 g/L h, 0.76 g/L h and 0.38 g/g, respectively. Silicalite-1 filled polydimethylsiloxane (PDMS)/polyacrylonitrile (PAN) membrane modules ensured media recycle without significant fouling, steadily generating a highly concentrated ABE solution containing 201.8 g/L ABE with 122.4 g/L butanol. After phase separation, a final product containing 574.3 g/L ABE with 501.1 g/L butanol was obtained. Therefore, the fermentation–PV coupled process has the potential to decrease the cost in ABE production.

1. Introduction

Butanol is an important industrial chemical with many applications in the plastic, food and flavor industries (Green, 2011). In addition, butanol is also considered as a promising liquid fuel because of its high energy content, low vapor pressure, less corrosiveness, and ability to be mixed with gasoline and diesel oil in high proportions (Blanch, 2012; Lee et al., 2008). Recently, concerns of unstable crude oil supplies and prices in the world market have generated renewed interests in producing butanol from abundant renewable biomass (Dürre, 2011; Jang et al., 2012).

ABE fermentation is a promising process to produce renewable butanol, in which the solventogenic *Clostridia* converts carbohydrates into acetone, butanol and ethanol at a ratio of 3:6:1 (w/w) (Ezeji and Blaschek, 2008; Green, 2011; Jones and Woods, 1986). However, one of the major obstacles to limit the economic viability of ABE fermentation is the low resulting butanol concentration caused by product inhibition. It was reported that the total solvent (acetone, butanol, and ethanol) concentration rarely exceeded 20 g/L in the batch ABE fermentation (Jones and Woods, 1986; Qureshi et al., 2013). This means that only a dilute sugar solution can be used by the organism, which leads to the low productivity, large process volumes and disposal of large waste streams (Ezeji et al., 2010; Friedl et al., 1991; García et al., 2011). Therefore, *in situ* product recovery technologies were developed to solve the problem, including gas-stripping (Lu et al., 2012; Xue et al., 2012), pervaporation (PV) (Huang and Meagher, 2001; Liu et al., 2011; Saravanan et al., 2010), liquid–liquid extraction (Dhamole et al., 2012; Yen and Wang, 2012), vacuum (Mariano et al., 2012, 2011), and adsorption (Ezeji et al., 2010). Among those techniques, PV is considered to be the most promising one due to its energy

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Nomenclature

A	pervaporation membrane area (m^2)	R_p	solvent productivity (g/L h)
$C_{g,0}$	glucose concentration in the reactor at time 0 (g/L)	V_0	volume of fermentation medium at time 0 (L)
$C_{g,e}$	glucose concentration in the reactor at the end of the fermentation (g/L)	V_e	liquid volume in the reactor at the end of fermentation (L)
$C_{g,in}$	glucose concentration in the feeding medium (g/L)	V_{in}	volume of feeding medium (L)
$C_{S,e}$	concentration of solvent in the reactor at the end of the fermentation (g/L)	V_n	volume of the nth permeate solution recovered from the cold trap (n = 1,2,3,...,n) (L)
$C_{S,n}$	concentration of solvent in nth permeate solution (n = 1,2,3,...,n) (g/L)	W	weight of the permeate solution collected in time h_r (g)
h	fermentation time (h)	X	weight fraction of butanol/solvent in reactor (–)
h_r	time period during which permeate W was collected (h)	Y	weight fraction of butanol/solvent in permeate (–)
J	total flux (g/m^2 h)	$Y_{P/S}$	solvent yield (g/g)
R_g	glucose consumption rate (g/L h)	α	butanol or solvent separation factor (–)

efficiency, low cost, as well as no harmful effects on the microorganisms (Izák et al., 2008; Leland, 2005). PV separation of butanol from model solutions and fermentation broths has shown its positive effect on ABE fermentation (Leland, 2005; Qureshi et al., 1999). Moreover, the feasibility of PV in continuous butanol fermentation was investigated and it was found that the fermentation efficiency was highly dependent on the pervaporation materials. For example, polypropylene hollow fiber showed a total flux of only 7.1 g/m^2 h when coupled to solvent production (Friedl et al., 1991). This low flux reduced its viability in industrial applications. The most commonly used pervaporation membrane material is polydimethylsiloxane (PDMS) (Li et al., 2011; Liu et al., 2011). Hecke et al. (2013) investigated the ABE production by integrating commercial PDMS composite membranes with ABE fermentation. However, the separation factor of butanol for the membrane was only 13.7–15.7, which was difficult to remove effectively butanol from the fermentation broth, so butanol inhibition on ABE-producing microorganism still remained (Hecke et al., 2013). Since butanol is toxic to the ABE producing microorganism and the product inhibition would occur when its concentration was up to 5 g/L, it would be preferred to kept butanol concentration as low as possible during ABE fermentation (Qureshi and Ezeji, 2008). Therefore, PV membranes with higher solvent flux and higher separation factor are in urgent need for more efficient and more economical butanol production by a fermentation–pervaporation coupled process.

The economics of butanol fermentation has been given considerable attention and the high cost of carbon sources has been identified as a major factor affecting the economic viability of the large-scale ABE fermentation. Previous reports show that substrate cost accounted for up to 79% of the solvent production costing a conventional ABE fermentation (Green, 2011; Pfromm et al., 2010). Cassava as a carbon source in butanol production has attracted much attention during the past three decades because it is a high-yield, non-grain crop, and can grow in dry and poor soils, avoiding land competition with other major food crops (Jansson et al., 2009). It can be expected that butanol production cost could be decreased when the cheap carbon source cassava is used. Moreover, a continuous ABE production accomplished by a fermentation–PV coupled process would further decrease the cost if the solvent toxicity to the microorganism could be alleviated by *in situ* removal of butanol from fermentation broth and consequently the productivity could be increased. To the best of our knowledge, there is no report on continuous butanol production from cassava by a fermentation–PV coupled process.

Our previous work showed that silicalite-1 filled polydimethylsiloxane (PDMS)/polyacrylonitrile (PAN) composite membranes had an excellent stability in terms of separation factor and flux in separating ABE fermentation broth and was proved to be effective in a continuous butanol production from glucose (Li et al., 2014). The objective of the present work is to further investigate the feasibility of efficient production of butanol from cassava by means of a continuous fermentation coupled with the composite PV membrane, with focus on the effect of PV separation on ABE fermentation such as ABE concentration, productivity and yield, etc. Moreover, the performance of the silicalite-1 filled PDMS/PAN composite PV membrane was also evaluated. The outcome of this work could be helpful to develop a fermentation–PV coupled process for efficient butanol production with cassava as carbon source.

2. Methods

2.1. Microorganism and fermentation medium

A stock culture of *Clostridium acetobutylicum* DP217 was maintained as a spore suspension in corn medium at 4 °C. 10 mL of the spore suspension was heat-shocked at 100 °C for 1.5 min, and grew anaerobically in 70 g/L corn medium at 37 °C for 24 h. Vegetative cells grew anaerobically for 24 h at 37 °C before they were transferred into a bioreactor.

2.2. Enzymatic hydrolysis of starch

Two enzymes (Jinmaoyuan Biological Chemical Industry Co., Ltd., Jiangsu, China), α-amylase with an activity of 3,500,000 U/mL, and glucoamylase with an activity of 2,800,000 U/mL were used for cassava flour hydrolysis as described below: 550 g of cassava flour was suspended in distilled water in a flask with a working volume of 700 mL. The liquefaction was carried out by adding of α-amylase to the mash at pH 6.0 and incubating at 90 °C for 0.5 h, then boiling at 100 °C for 2.5 h. Saccharification was carried out by adding glucoamylase at pH 5.5 and maintaining at 60 °C for 1 h. Thus, 68.3% of the polysaccharides in the mash were converted to fermentable sugars. After adding 4.34 g corn steep powder and 20 mg ferrous sulfate, the pH was adjusted to 6.90, the concentrated liquid cassava mash was sterilized at 121 °C for 120 min, then could be further used as feeding medium (Wan et al., 2011).

2.3. Pervaporation membrane and module

The ultra-thin film silicalite-1 filled PDMS/PAN composite membrane was made in our laboratory. The membrane module with an effective membrane area of 0.0072 m^2 was connected with two