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An integrated biological hydrogen production process based on ethanol-type fermentation and bipolar membrane electrodialysis

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ABSTRACT

An integrated bio-hydrogen production system involving fermentative hydrogen production and product separation is proposed. In this process, microorganisms conduct ethanol-type fermentation and generate H_2 gas in anaerobic bioreactor, and acetate is removed from fermentation broth by using a two chamber bipolar membrane electrodialysis as separation unit. A comparative study of fermentative hydrogen production of *Ethanoligenens harbinese* B49 in the integrated system with traditional fermentation process was carried out. Compared to traditional process, accumulated H_2 elevated 23%, glucose utilization ratio increased by 135% and cell growth increased by 27% in the integrated system. The specific hydrogen production rate reached 2.2 mol H_2/mol glucose, indicating that separation of acetate from fermentation system has a great role in promoting hydrogen producing capacity. Bipolar membrane electrodialysis showed high acetate separation efficiency and low glucose loss rate. In the integrated system, pH could be used to direct electrodialysis operation, since it has an exponential correlation with acetate concentration in fermentation broth. These results provide a new method for achieving efficient and stable H_2 production with simultaneous glucose recovery and acetate inhibition release.

Introduction

Product inhibition is very general in hydrogen production by metabolic functions of anaerobic organisms. If the dissociated part of soluble metabolites (ie. ethanol, acetate, propionic acid and butyric acid) is present in the fermentative hydrogen production system at a high concentration, the ionic strength will increase, which may result in the cell lysis of hydrogen-producing bacteria. As a result, at a high concentration, these soluble metabolites can inhibit hydrogen-producing bacteria growth and then inhibit the fermentative hydrogen production accordingly [1–6].

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Ethanol-type fermentation is a fermentation type with high efficiency hydrogen generation and is characterized by the dominance of ethanol and acetate in the fermentation liquid products (>80%) [7–9]. Inhibitory effects of acetate and ethanol on biohydrogen production from glucose by *Ethanoligenens harbinese* B49 [10,11], a representative strain of ethanol type fermentation, were investigated in previous study. The $C_{I,50}$ values (for inhibitor concentration giving 50% inhibition) of ethanol and acetate on hydrogen production rate were estimated as 154 and 62 mmol/L, respectively. Therefore, acetate was identified as the primary inhibitory factor of hydrogen production with ethanol-type fermentation [6].

Bipolar membrane electrodialysis technology (BMED) which is emerged in recent years provides a possibility of product separation for fermentative hydrogen production. The bipolar membrane is a layered membrane constructed so that one surface is a cation exchange layer, while the opposite surface is an anion exchange layer [12]. Under the direct current electric field, the bipolar membrane implement the electro-dissociation of water, which split water into protons and hydroxyl ions at a very fast rate [13]. When it couples with other ion exchange membrane, acids and bases recovery from salt streams can be realized without salt introduction. Thus, BMED inherently possesses economical and environmental benefits. Efforts have been made to apply the bipolar membrane technology in the fields of pollution control [14,15], resource recovery [16] and chemical processing [17,18].

Thus, we developed an integrated system involving fermentative hydrogen production and product separation, which take bipolar membrane electrodialysis as separation unit coupling with an anaerobic bioreactor. A comparative study of fermentative hydrogen production of *E. harbinese* B49 in the integrated system with traditional fermentation process was carried out to exam the performance and compatibility of the integrated system.

Materials and methods

Microorganism and media

E. Harbinese B49 (AF481148 in EMBL) was used in fermentative hydrogen production experiments. Cells from stock cultures were transferred into sterilized growth medium and incubated at 35 ± 1 °C. When cells were in the logarithmic growth phase, 200 mL of the precultured broth was inoculated into bioreactors containing 1000 mL of medium anaerobically at 35 ± 1 °C for 130 rpm by magnetic stirre. The medium consisting of (in g/L): glucose 10, polypepton 4, beef extract 2, yeast 1, NaCl 4, $MgCl_2$ 0.1, $FeSO_4{\cdot}7H_2O$ 0.1, K_2HPO_4 1.5, L-cysteine 0.5. The medium also contained 1% trace element solution, 1% vitamin solution, and 0.2% resazurin. The cells were harvested at the end of the exponential phase, centrifugated and washed with a PBS (Phosphate Buffered Saline) buffer and used as inocula for the comparative experiments.

Bipolar membrane electrodialysis construction

Electrodes of two compartment electrodialysis were titanium ruthenium plate (100 × 100 × 2 mm). The space of the electrode and membrane was 0.5 cm, the membranes space was 3 cm, and single membrane area was 100 cm^2. Bipolar membranes and anion exchange membranes were both from NEOSEPTA®. The volume of the desalination and concentrate chambers were both 300 mL, and electrode liquid was 5% Na_2SO_4.

Bipolar membrane electrodialysis system was composed of bipolar membranes and anion exchange membrane. Its working principle was shown in Fig. 1. In the device, the part between the anion exchange layer of bipolar membrane and the anion exchange membrane was called dilute chamber. The part between anion exchange membrane and the cation exchange layer of bipolar membranes was called concentrating chamber. The fermentation broth (containing glucose sugar, ethanol, acetate, etc.) was pumped into the dilute chamber with a peristaltic pump. Under the driving force of an direct current electric field, ion Ac^- in dilute chamber passed through anion-exchange membrane into the concentrating chamber. Ion OH^- generated by anion exchange layers of bipolar membrane entered dilute chamber, neutralizing with the remaining H^+. Glucose, protein, amino acids, and ethanol and other non-electrolyte stayed in dilute chamber, achieving the purpose of acetate separation from fermentation broth of biohydrogen production at the same time recovery and reuse glucose. While in the concentrating chamber, ion Ac^- migrated from dilute chamber and H^+ resulted from water dissociation of bipolar membrane, gradually combined to regain acetate. Acetate was separated from the fermentation broth of bioreactor until it reaches a certain concentration, and it can be further recycled.

Comparative experiments

Batch tests were carried out for comparative study of traditional fermentation and integrated process containing fermentation and BPEM. The processes conducted hydrogen production in two same bioreactors. The experimental conditions were shown in Table 1.

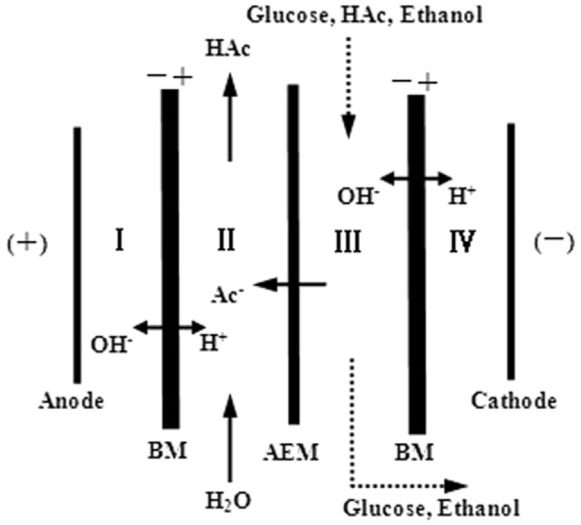

Fig. 1 – Schematic description of separation of sugar and HAc using two-cell electrodialysis with bipolar membrane.