Bioresource Technology 263 (2018) 375–384

Contents lists available at ScienceDirect

Bioresource Technology

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

Bubble coalescence suppression driven carbon monoxide (CO)-water mass transfer increase by electrolyte addition in a hollow fiber membrane bioreactor (HFMBR) for microbial CO conversion to ethanol

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ARTICLE INFO

Keywords:
Gas–liquid mass transfer
Bubble coalescence
Syngas fermentation
Carbon monoxide
Bioethanol

ABSTRACT

This study investigated the effects of electrolytes ($CaCl_2$, K_2HPO_4, $MgSO_4$, NaCl, and NH_4Cl) on CO mass transfer and ethanol production in a HFMBR. The hollow fiber membranes (HFM) were found to generate tiny gas bubbles; the bubble coalescence was significantly suppressed in electrolyte solution. The volumetric gas-liquid mass transfer coefficients (k_La) increased up to 414% compared to the control. Saturated CO (C^*) decreased as electrolyte concentrations increased. Overall, the maximum mass transfer rate (R_{max}) in electrolyte solution ranged from 106% to 339% of the value obtained in water. The electrolyte toxicity on cell growth was tested using *Clostridium autoethanogenum*. Most electrolytes, except for $MgSO_4$, inhibited cell growth. The HFMBR operation using a medium containing 1% $MgSO_4$ achieved 119% ethanol production compared to that without electrolytes. Finally, a kinetic simulation using the parameters got from the 1% $MgSO_4$ medium predicted a higher ethanol production compared to the control.

1. Introduction

Global warming and the frequencies of natural disasters have dramatically increased as a result of excessive fossil fuel use associated with technological advances since the industrial revolution (Crowley, 2000). A variety of renewable and sustainable energy resources are currently being developed in an effort to reduce global warming (Balachandra et al., 2010). Synthesis gas (syngas) could potentially replace a substantial portion of the conventional fossil fuel-based energy demands (Kennes et al., 2016; Munasinghe and Khanal, 2010a; Verma et al., 2016). Syngas typically contains carbon monoxide (CO), hydrogen (H_2), carbon dioxide (CO_2), and a variety of impurities (Phillips et al., 1993). Syngas is not only available as a waste gas discharged from industrial processes associated with thermal power plants, iron works, and crude oil refinery processes, but it is also synthetically produced through the gasification of coal and biomass (Leibold et al., 2008; Phillips et al., 1993). Syngas can be converted into platform chemicals for industrial uses and energy fuels, such as C2 and C4 chemicals, including ethanol, and butanol (Munasinghe and Khanal, 2010a). The global syngas consumption market was estimated to be 115,000 MWth in 2015 and is expected to grow to 256,000 MWth by 2024 with a 9.4% compound annual growth rate (CAGR) (Transparency Market Research Analysis, 2013). The Fischer–Tropsch (FT) process has been used to convert CO and H_2 in syngas into hydrocarbon fuels (Dry, 2002; Li and Fan, 2008); however, this method suffers from several drawbacks. Most FT processes require high energy inputs to maintain the pressure and temperature needed to achieve metal-catalyzed CO and H_2 conversion (Dry, 2002; Yasin et al., 2015). This process typically emits large amounts of environmental pollutants (Munasinghe and Khanal, 2010a; Verma et al., 2016).

The conversion of syngas to carbon compounds using a microbial reaction is called “syngas fermentation” and notable for its relatively low energy requirements compared to the physicochemical routes (Munasinghe and Khanal, 2010a; Phillips et al., 1993). Carboxydotrophic microorganisms can produce organic acids and alcohols from syngas (Henstra et al., 2007); however, several issues should be addressed before the technology can be scaled up and commercialized. The alcohol production rate is limited under typically operated gas conversion systems by the gas-liquid mass transfer limitations (Bredwell et al., 1999; Garcia-Ochoa and Gomez, 2009). Syngas-

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https://doi.org/10.1016/j.biortech.2018.05.012
Received 8 March 2018; Received in revised form 30 April 2018; Accepted 2 May 2018
Available online 04 May 2018
0960-8524/

utilizing microorganisms take up and metabolize the dissolved gas molecules. The gas delivery to the cell occurs through multiple steps including the gas-liquid mass transfer which acts as a rate determining step (RDS) due to the limited gas delivery area determined by the bubble size (Doran, 1995; Jeong et al., 2016; Yasin et al., 2015). This multiple steps delivery of gaseous substrate is avoided by the direct contact of liquid film with microbial cells (Shen et al., 2017). The direct uptake of gaseous substrate is possibly due to short distance between gas bubbles and microorganisms, and increased surface area of tiny bubbles in the aqueous phase (Al-mashhadani et al., 2016).

Several approaches have sought to increase the gas–liquid transfer (Munasinghe and Khanal, 2010b; Orgill et al., 2013; Riggs and Heindel, 2006; Shen et al., 2014a, 2017; Yasin et al., 2014). Conventional approaches rely on mechanical agitation to improve gas-liquid mass transfer using a high operating energy. Up to 50% of the operational energy costs is devoted to aeration in wastewater treatment plants (Henderson, 2002). A linear increase in gas-liquid mass transfer is possible by increasing the agitation speed in continuous stirred tank reactors (CSTRs), at the expense of cubic increase in power input (Yasin et al., 2015). Substantial amount of energy (1–10 kW/m^3) is required to transfer sparingly soluble gases (CO, and H_2) into suspended culture fermentation broths by employing STRs (Schulte et al., 2016). This energy can be saved by using membrane-based bioreactors that facilitate a high gas delivery rate by generating relatively fine bubbles without agitation or liquid circulation (Munasinghe and Khanal, 2012; Shen et al., 2014b; Yasin et al., 2014).

Even with an enhanced overall gas–liquid mass transfer efficiency, gas bubble coalescence is usually observed at the site where bubbles are generated (Garrett, 2004; Tsang et al., 2004; Zhu et al., 2009). Once tiny bubbles are generated on the membrane surface, the gas bubbles quickly coalesce within the bulk liquid. Chemical additives, such as nanoparticles (Lee et al., 2016b; Zhu et al., 2010, 2008), salts (Craig et al., 1993; Kim et al., 2016a; Schumpe, 1993; Zhu et al., 2009), or surfactants (Sardeing et al., 2006) have been tested to determine whether additives can suppress bubble coalescence and increase the gas-to-liquid interfacial area. Salts readily ionize into cations and anions in a liquid phase (i.e., the culture medium), and the ions were shown to form dense electrical double layers around the gas bubbles, leading to strong repulsion among the gas bubbles (Craig et al., 1993; Garrett, 2004; Tsang et al., 2004). The addition of electrolytes to water in a stirred microreactor significantly improved the mass transfer. The reactor system produced a k_La for CO that was 520% of the control reactor by reducing bubble coalescence (Zhu et al., 2009). The introduction of electrolytes to enhance the methane–water mass transfer reduced the methane solubility in water due to a salting out effect (Kim et al., 2016b); however, the k_La was boosted to 720% (Kim et al., 2016a).

An integrated approach that combines the use of additives (e.g., electrolytes) and an effective gas diffusing system (such as an HFM) may increase the gas–liquid mass transfer efficiency and enhance the ethanol productivity of syngas fermentation. Interestingly, the use of electrolytes in syngas fermentation has not yet been reported. Additionally, use of modeling and simulation to predict the performance of microbial syngas utilizing systems is rarely found in literature (Chen et al., 2018; Jang et al., 2017). The kinetic simulations to predict the k_La of CO in a batch cultivation system was performed (Jang et al., 2017). However, to the best of our knowledge, no effort has been directed to predict the time course performance of cell recycled syngas fermenting system which can achieve high chemical productivity. Hence, prediction of microbial CO uptake, reduction in C^*, and product formation (acetic acid and ethanol) in HFMBR system with cell recycled system using kinetic simulations would be a value addition for the researchers, and policy makers working on using ethanol as an alternative fuel.

This study aims to enhance the CO mass transfer, and ethanol productivity of syngas fermentation by introducing electrolytes to an HFMBR system. A variety of salts were screened for their utility in the anaerobic medium preparation. $CaCl_2$, K_2HPO_4, $MgSO_4$, NaCl, and NH_4Cl were selected as the final test electrolytes. *C. autoethanogenum* was selected as a model strain to test the inhibitory effects of the electrolytes on cell growth. Syngas fermentation was conducted to confirm the practicality of the electrolytes under real fermentation conditions. Kinetic simulations were performed to predict the steady-state mass transfer and ethanol production.

2. Material and methods

2.1. Microbial strain and culture conditions

C. autoethanogenum DSM10061 was used throughout the study. The lyophilized culture was activated in an anaerobic tube containing reinforced clostridial medium (RCM, 10 mL) without agar. An aliquot of the RCM culture was transferred into 2-(*N*-morpholino) ethanesulfonic acid-buffered basal medium (MBBM, 60 mL) in a serum vial pressurized at 1 atm P_{CO} (Shinil Gas Co., Korea), and the culture was grown at 37 °C. The MBBM (1 L) contained: yeast extract, 2 g; NaCl, 0.9 g; $MgSO_4{\cdot}2H_2O$, 0.2 g; $CaCl_2$ anhydrous, 0.15 g; NH_4Cl, 1 g; cysteine·HCl, 0.5 g; resazurin solution (0.1%, 0.1 mL), and the pH was adjusted to 6.05. After autoclaving the medium, a vitamin stock solution (500×, 0.2%, Balch's vitamin), 1 M K_2HPO_4 (1%), and 1 M MES (1%) were separately injected into the vial. Cell growth was monitored at 600 nm (OD_{600}) using a UV–VIS spectrophotometer (V-730, Jasco, Japan). One unit of OD_{600} corresponded to 0.317 g dry cell/L (Bruno-Barcena et al., 2013). In order to minimize the measurement error of OD_{600} by micro bubbles, samples were given the sufficient time for natural de-bubbling.

2.2. Cell viability in the electrolyte solutions

Cell growth was monitored in a 26.5 mL pressure tube containing 10 mL MBBM and the electrolytes. Electrolytes frequently used for microbial media preparation, such as $CaCl_2$, K_2HPO_4, $MgSO_4$, NaCl, and NH_4Cl, were tested. Cell viability tests of *C. autoethanogenum* were conducted using glucose to exclude the growth-limiting effects by different gas-liquid transfer in each electrolyte solution. The cell concentration was measured using a spectrophotometer at 600 nm (SPECTRONIC 20D$^+$, Thermo Scientific, USA).

2.3. Analytical methods

Solutions containing dissolved CO were stored in Hungate roll tubes and then heated on a hot plate at 98 °C over 20 min to desorb dissolved CO. A 0.1 mL of the head space gas was analyzed using gas chromatography equipped with a thermal conductivity detector (GC-TCD, ACME6100, Young Lin instrument Co., Anyang, Korea). A packed column (60/80 Carboxen 1000, SUPELCO) was used to separate the gases. The GC-TCD oven program and setting conditions are described elsewhere (Yasin et al., 2014).

Liquid metabolites were analyzed using gas chromatography and a flame ionized detector (GC-FID, ACME6100, Young Lin instrument Co., Anyang, Korea). A capillary column (DA AquaWax, Alltech) was used to separate the liquid products. The GC-FID oven program and setting conditions are described elsewhere (Yasin et al., 2014). The supernatant of the liquid sample (0.22 mL) was acidified using phosphoric acid (0.03 mL, 1 M). Hexanoic acid was used as an internal standard.

2.4. CO-water mass transfer coefficient and rate measurements

The stand-alone HFMBR illustrated in Fig. 1 was used to measure the CO–water mass transfer. A polyvinylidene fluoride (PVDF) hollow fiber was obtained from Econity (Yongin, Korea), and a module was fabricated as described previously (Yasin et al., 2014), except that the edge of each membrane fiber was separately closed. The module was