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Enhanced mass transfer rate of methane via hollow fiber membrane modules for *Methylosinus trichosporium* OB3b fermentation

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ABSTRACT

Polyvinylidine fluoride (PVDF) hollow fiber membranes were employed to enhance mass transfer rate of methane in water for the fermentation of *Methylosinus trichosporium* OB3b. Compared to common alumina bubbler, hollow fiber membrane modules (HFMMs) afforded smaller methane bubble size and larger methane–water volumetric mass transfer coefficient (k_La) as high as 150.1 h^{-1}. Furthermore, cell growth rate and maximum optical density of *M. trichosporium* OB3b were increased by 67.3 and 77.4%, respectively, by adapting forty HFMMs, compared to those of alumina bubbler.

Introduction

Methane gas, major component of natural gas, has been used widely as one of the high energy resources on the planet [1]. The development of shale gas, natural gas trapped within shale formation, has accelerated the use of methane in industry [1,2]. Among various processes utilizing methane as a major resource, biological conversion of methane into secondary product such as alcohol by microorganism or enzyme has potential to be developed as cost-effective, energy-efficient, and eco-friendly industrial process [3,4].

In order to enrich the productivity of biological conversion of methane and apply this process to industrial scale, control of cultivation environment for microorganisms is one of the important parameters [3]. For instance, temperature, pH, mixing, substrate concentration, and solubility of methane in media are important factors to consider for maximizing the productivity of the process [5]. However, low solubility of methane in water (22.7 ppm at SATP) is big barrier hindering efficient conversion of methane by microorganism [3,4]. One possible solution to overcome the low solubility of methane in water is rapid dissolution of methane in water [6,7]. The volumetric mass transfer coefficient of methane indicates the dissolution rate of methane in gas diffusing system [6,7]. By enhancing gas–liquid volumetric mass transfer coefficient (k_La), the parameter indicating the rate of gas dissolution into liquid medium, high conversion rate of methane can be achieved [8], resulting in increased cell concentration [9].

The k_La consists of 'k_L' (gas–liquid mass transfer coefficient) and 'a' (interfacial area between gas bubbles and liquid medium) [10,11]. Hence, enhancement of k_La can be achieved by increasing 'k_L' and/or 'a' [10]. Various factors including diffusivity of gases, viscosity and density of liquid medium, and gas–liquid affinity have been known to affect k_L values [10]. For instance, addition of (nano)particles in the media have been demonstrated to enhance k_L values by facilitating the transport of gas molecules into the bulk liquid [12,13]. However, additives with potential toxicity in the fermentation media could lead to cell damage, possibly interrupting the cultivation of microorganism [14].

Gas–liquid interfacial area ('a') could relatively easily be increased by decreasing the bubble size [11]. Certain additives such as electrolytes have been known to inhibit bubble coalescence, leading to smaller bubble size and enhanced gas–liquid interfacial area [15]. However, high salt concentration could hinder growth of microorganisms [14,16]. Although increasing impeller speed could easily induce smaller bubble

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size by breaking bubbles, this increases the consumption of power for operating impeller in a reactor and could induce high shear stress, leading to cell damage [6,14,17]. In this regard, use of spargers (e.g. bubbler, membrane modules) which can generate bubbles with small size by pressure difference could be an energy-efficient and bio-friendly way to enhance gas–liquid interfacial area [14,18]. Hollow fiber membrane modules (HFMMs) with small pore size can easily be adapted in sparger to generate small bubbles, leading to high k_La values, as demonstrated for carbon monoxide in water [18].

Among different kinds of methanotrophs employed in the literatures, including *Methylosinus trichosporium* OB3b and *Methylococcus capsulatus* (Bath), methanotrophic methane-to-methanol conversion on the biotechnological scale has been investigated primarily using *M. trichosporium* OB3b [16]. Hence, we employed *M. trichosporium* OB3b to investigate the effect of HFMMs on the efficiency of methane conversion.

Experimental

Fabrication of HFMMs

The microporous PVDF fibers (0.1 μm pore size, 1.2 mm OD, 0.7 mm ID; ECONITY, Korea), cut in length of 19.5 cm and sealed with epoxy and hardener mixture, were used for the fabrication of HFMMs, as described in previous study [18]. In order to investigate the effect of total external surface area of hollow fiber membranes, different number (10, 20, and 40) of fibers was used to fabricate modules. In comparison, alumina bubbler (pore size: 16–40 μm) was used.

Reactor setup

For the determination of the methane–water k_La, various flow rates (40 cc/min, 1, 2, and 3 L/min) were employed. For relatively large flow rates (1, 2, and 3 L/min), glass reactor with two septum points surrounded by water jacket was used, as reported in previous study [19]. Temperature of the reactor was maintained at 30 °C by the water jacket. To exclude the influence of impeller on k_La values, impeller was not used in this study. Methane gas was injected through HFMMs or alumina bubbler. For low flow rate of 40 cc/min, ball flow meter was used to maintain constant flow rate and joint flask was used instead of glass reactor for the measurement of methane concentration. Note that relatively small flow rates were employed in this study for the application of HFMMs since robustness of the membranes could be compromised at high flow rates in large industrial scale.

Determination of gas–liquid k_La

The methane–water k_La was determined by using gassing-out method, as described in previous studies [13,19,20]. The concentration of methane in aqueous solution (C_L) was determined based on average value of triplicate measurements by gas chromatography (ACME 6100, Young Lin Instruments Co., Korea). The overall volumetric mass transfer rate ($R = M/h$) for a liquid during the gas transfer process in a solution can be described as:

$$R = \frac{dC_L}{dt} = k_La(C^* - C_L) \quad (1)$$

where k_La is the gas–liquid volumetric mass transfer coefficient (h^{-1}) and C^* is saturated concentration of methane in liquid [6]. Taking logarithm after integration of Eq. (1) gives,

$$\ln\left(1 - \frac{C_L}{C^*}\right) = -(k_La)t \quad (2)$$

The k_La is obtained by calculating the slope of the line, where t is the time.

$$C_L = C^*(1 - e^{-(k_La)t}) \quad (3)$$

Eq. (3) was used to determine the C^* based on methane concentration change over time (vide infra).

Cultivation of M. trichosporium *OB3b and analysis of cell concentration*

The 4 mL seeding of *M. trichosporium* OB3b (KCTC 12760) was cultured in a joint flask containing 400 mL of culture medium with composition as in Table 1 [16,21]. Hot plate was used to maintain the temperature of the cultivation media at 30 °C and stirring at 200 rpm ensured homogeneous media. Methane (99.99%, MS Incheon gas, Korea) was injected through alumina bubbler or HFMMs at a flow rate of 40 cc/min. Note that only low flow rate was employed for the cultivation of *M. trichosporium* OB3b since high methane flow rate could induce turbulent flows in liquid medium, possibly interrupting the growth of the microorganism [14]. The pH of culture solution was maintained at pH 6.8 using phosphate buffer during cultivation. A cell density meter (WPA CO8000, Biochrom Ltd., UK) was used to determine the optical density (OD) of the media at a wavelength of 600 nm every 24 h until OD value was saturated.

Results and discussion

Determination of methane–water k_La

Methane concentration in water was measured until saturation concentration is reached. Fig. 1a and b shows methane concentration as a function of time using alumina bubbler and 40 HFMMs, respectively. Saturated methane concentration of 21.7 ppm was obtained for both cases, as reported in previous studies [13,15,19]. However, different behavior of methane saturation was observed. For instance, methane concentration was saturated at about 100 s for 40 HFMMs after injection of methane, while ~200 s was needed for the saturation of methane in case of alumina bubbler. Membrane modules with different number (10 and 20) of fibers showed similar behavior to that of 40 HFMMs, where dissolved methane in water started to saturate at about 100 s (Fig. S1).

Gas–liquid k_La values were determined using the Eq. (2), as described in "Experimental" section. Table 2 shows the k_La values obtained using alumina bubbler and HFMMs at various flow rates. As shown, HFMMs afforded higher k_La values compared to alumina bubbler. For instance, 10, 20, and 40 HFMMs afforded k_La values of 98.3, 115.9, and 150.1 h^{-1}, respectively, while alumina bubbler showed much smaller k_La value of 41.4 h^{-1}, at a flow rate of 3 L/min. Furthermore, higher k_La values were measured at higher

Table 1
The composition of media stock for the cultivation of *M. trichosporium* OB3b.

Element	Composition (mL/L)
$MgSO_4{\cdot}7H_2O$ Stock	1
KNO_3 Stock	1
$CaCl_2{\cdot}2H_2O$ Stock	1
3.8% (w/v) solution Fe-EDTA	0.01
0.1% (w/v) $NaMo{\cdot}4H_2O$	0.05
Trace element solution	0.01
Phosphate Stock	1
Vitamin Stock	0.1
Copper Stock	1
DI water	94.83