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Gas-liquid mass transfer coefficient of methane in bubble column reactor

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Abstract−Biological conversion of methane gas has been attracting considerable recent interest. However, methanotropic bioreactor is limited by low solubility of methane gas in aqueous solution. Although a large mass transfer coefficient of methane in water could possibly overcome this limitation, no dissolved methane probe in aqueous environment is commercially available. We have developed a reactor enabling the measurement of aqueous phase methane concentration and mass transfer coefficient (k_La). The feasibility of the new reactor was demonstrated by measuring k_La values as a function of spinning rate of impeller and flow rate of methane gas. Especially, at spinning rate of 300 rpm and flow rate of 3.0 L/min, a large k_La value of 102.9 h^{-1} was obtained.

Keywords: Methane, Mass Transfer Coefficient, Bubble Column Reactor, Shale Gas

INTRODUCTION

Although crude oil has been the main resource for energy demand in the past century, the expected depletion of crude oil reserves and environmental issues such as global warming triggered the search for alternative energy resources [1,2]. Recently, shale gas - natural gas formed within shale formations - is rapidly becoming an increasingly important source of energy [3-5].

Methane, a primary component of shale gas, is generally used as a source of fuel. However, it is very expensive to transport methane as gas to remote locations. Furthermore, methane is blamed for the increase of global warming due to its high global warming potential compared to other greenhouse gases [1]. To this end, biological conversion of methane to some useful chemicals at ambient condition has been of great interest [5-7]. Since microorganisms or enzymes are used for the biological conversion of methane, appropriate conditions for bioreactors such as pH, temperature, and concentration of salt in the media are required [8-10]. Among many experimental limitations, mass transfer limitations due to low solubility (~22 mg/L at 20 °C and 1 atm) of methane in water are a big hurdle for obtaining high methane conversion rate [11,12]. Although high pressure and low temperature could increase the solubility of methane in water, it could also increase the cost of reactor operation and be detrimental for living microorganisms [13,14].

To understand and control the process kinetics in methanotrophic bioreactors, we need to know the concentration of methane gas in water. Although mass transfer kinetics of other gases such as carbon monoxide and carbon dioxide have been reported for various reactor systems in the literature [15-18], a methane probe in water is not commercially available [19]. Furthermore, the mass transfer coefficient (k_La) of methane in water has hardly been reported. For example, Yu et al. estimated aqueous phase methane concentration based on the relation between methane and oxygen in water, but reported a very small k_La value of 16.3 h^{-1} [19]. To this end, we have developed a bubble column reactor for the determination of aqueous phase methane concentration and mass transfer coefficient. To test the feasibility of newly developed reactor, the spinning rate of impeller and flow rate of methane gas were varied, and increased mass transfer coefficient was measured at high spinning rate of impeller and at high flow rate. Especially, at spinning rate of 300 rpm and flow rate of 3.0 L/min, a large k_La value of 102.9 h^{-1} was obtained.

EXPERIMENTAL

1. Reactor Setup

The reactor setup developed in this study (Figs. 1 and S1) is based on a bubble column reactor to satisfy measuring k_La values within a short time period. An impeller was used to maintain the solution homogeneity during the measurement of methane concentration [19]. Two septum points were used for taking solution samples with disposable syringes. The reactor temperature was maintained at 30 °C by the water circulator (WiseCircu, Wisd Laboratory Instruments Co.) surrounding the reactor [16]. Methane gas was pumped into the reactor from the bottom, while being vented to the top, in order not to remain in the reactor. Check valve was used to prevent water from flowing backward (to the bottom) and flow rate of methane gas was controlled by mass flow controller (TSC-D220, MFC Korea Co.).

2. Mass Transfer Coefficient (k_La) Measurement

The liquid samples containing the dissolved methane gas were

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‡This article is dedicated to Prof. Hwayong Kim on the occasion of his retirement from Seoul National Univerisity.

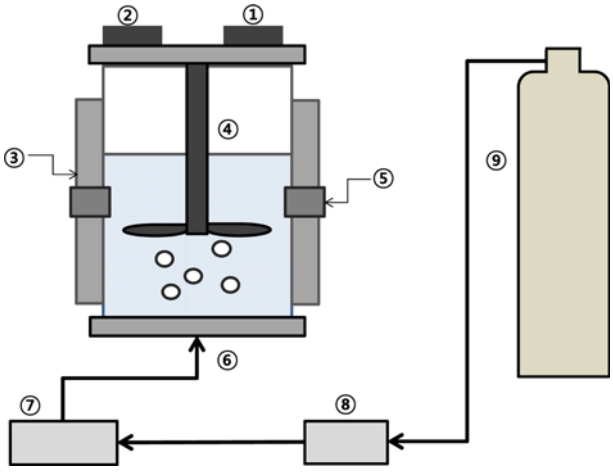

Fig. 1. Schematic diagram of a bubble column reactor employed in this study (dimensions not to scale).

① Venting
② Purging
③ Water jacket
④ Impeller
⑤ Septum
⑥ Gas injection valve
⑦ Check valve
⑧ Mass flow controller
⑨ Methane gas cylinder

taken from the reactor every 20 s by disposable syringes via septum points. The liquid samples were immediately transferred into vials with screw caps, and were heated at 90 °C for 1 h in the heating block (DMB-2, Misung Instrument Co.). During heating, methane dissolved in water was considered to be evaporated completely since methane concentration in water at 90 °C is very low (~1 ppm) [12, 20]. Then, 0.1 mL of gas from the head space was taken by gas-tight syringe (Precision sampling syringe A-2, Valco Instruments Co.) from the vials, and was measured by gas chromatography (ACME 6100, Young Lin Instruments Co.) with flame ionization detector [19]. For the measurement of standard sample, 0.1 mL of 99% methane gas (MS Gas Co.) was used. Each data was an average value of triplicate measurements and standard deviations were mostly within 10%. The volumetric mass transfer coefficient of methane from gas to aqueous phase was determined by the static gassing-out method [21-25] The estimation of k_La of a reactor by gassing-out techniques depends upon monitoring the increase in dissolved methane concentration of a solution during aeration and agitation. The overall volumetric mass transfer rate (R=M/h) for a liquid during the gas transfer process can be described by:

$$R=dC_L/dt=k_La\,(C^*-C_L) \quad (1)$$

where k_La is the mass transfer coefficient (h^{-1}) based on liquid-phase resistance to the mass transfer, C^* is the saturated concentration of methane in water, and C_L is the dissolved gas concentration in the liquid. The mass transfer rate decreases during the period of aeration as C_L approaches C^* due to the decline in the driving force (C^*-C_L). Taking the logarithm after integration of Eq. (1) gives,

$$\ln(1-C_L/C^*)=-(k_La)\,t \quad (2)$$

Since Eq. (2) is a linear form, k_La could easily be obtained by calculating the slope of the line, where t is the time (sec) [16].

To determine C_L based on GC data, a series of calculation steps are required (See Supporting Information for details). First, the GC peak area of 0.1 mL sample (gas) is calculated, as compared to that of standard methane gas, and moles of methane in the headspace of vial are determined, assuming ideal gas behavior. In this experiment, since 0.4 mL of solution sample is transferred to 4 mL vial, the volume of the headspace of vial is 3.6 mL. Hence, moles of methane in solution samples were multiplied by 36 (3.6 mL/0.1 mL). Then, aqueous methane concentration (in ppm) in each sample was determined by multiplying by atomic weight of methane.

RESULTS AND DISCUSSION

The dissolved methane concentration (C_L) in water was determined from triplicate measurements by gas chromatography (Fig. 2(a)). As shown, C_L increased up to ~120 s and saturated. The resultant data were fitted using a hyperbolic curve to obtain the saturated concentration of methane (C^*). Fig. 2(b) shows the calibrated values of C_L and C^* from measurements which are used to find k_La using Eq. (2). Slope of the linear fitting function was obtained with fixing intercept of x-axis as zero.

The k_La values depend on the design and operating conditions of the reactor and are affected by the variable such as the geometry of the vessel and stirrer and the operating conditions [20,21]. To test the feasibility of newly developed bioreactor for the measurement of mass transfer coefficient, two important variables which

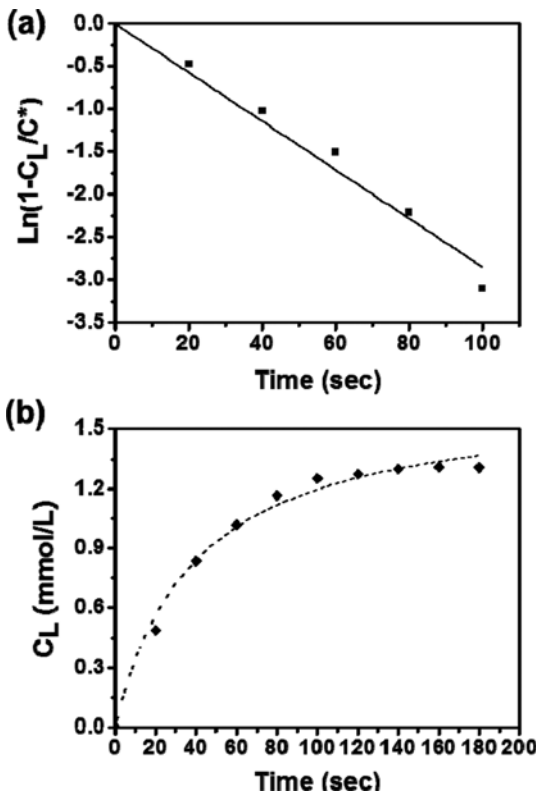

Fig. 2. (a) Measurement of dissolved methane concentration in water at a flow rate of 3 L/min and 300 rpm. The curve is fitted using hyperbolic function to get the saturated methane concentration (C^*). (b) Calibration data used to find k_La using Eq. (2).

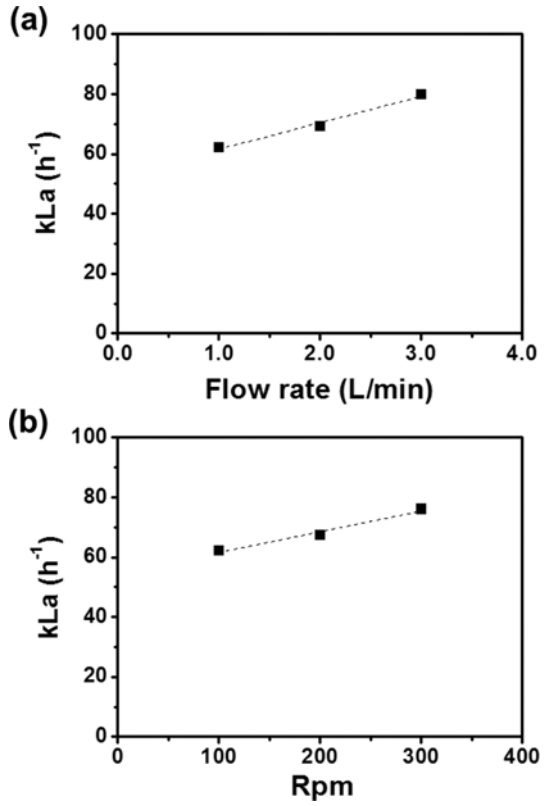

Fig. 3. Measurement of k_La values as a function of (a) methane gas flow rate (1.0, 2.0, and 3.0 L/min) with impeller spinning rate of 100 rpm (b) impeller spinning rate (100, 200, and 300 rpm) with methane gas flow rate of 1 L/min. Each data point was obtained from the triplicate measurement of C_L and C^*. Straight lines are guides to the eye.

are known to affect the mass transfer - impeller spinning speed and gas flow rate 0 were varied [22-25].

Fig. 3(a) shows the k_La values as a function of methane gas flow rate (1.0, 2.0, and 3.0 L/min). The calculated k_La values were 62.2, 69.1 and 79.8 h^{-1}, respectively. The larger k_La value was obtained at higher flow rate due to high driving force of mass transfer (more gas bubbles occupy the reactor at higher flow rate) caused by high flow rate [21]. Similarly, k_La values as a function of impeller spinning rate were also determined; k_La values of 62.2, 67.3, and 76.0 h^{-1} were obtained at 100, 200, and 300 rpm, respectively. The impeller mixes and dissolves the gaseous methane into the aqueous phase, and maximizes the interfacial area between the gaseous and aqueous phases [21,23]. Hence, large k_La values are obtained when high impeller speed is used (Fig. 3(b)). Especially, a large k_La value of 102.9 h^{-1} was obtained at impeller spin rate of 300 rpm and flow rate of 3 L/min, almost six times larger than that of previous report for methane in aqueous solution [19]. Note that k_La value of 72.0 h^{-1} was measured for carbon monoxide in aqueous solution, employing a similar reactor to that in this study [16].

CONCLUSION

A novel bioreactor was developed for the determination of mass transfer coefficient of methane in water. The k_La values were successfully determined based on the measurement of dissolved concentration of methane gas in water. The newly developed reactor was evaluated by varying process variables affecting mass transfer of methane in aqueous environment. The measured k_La values increased as a function of impeller spinning rate and gas flow rate. Especially, a large k_La value of 102.9 h^{-1} was obtained. Further studies on the determination of k_La values with different process variables and the application of our system in biological processes are underway.

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