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Review

A mini review on bioreactor configurations and gas transfer enhancements for biochemical methane conversion

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ABSTRACT

Methane is an essential component of the global carbon cycle and one of the most powerful greenhouse gases (GHGs), yet it is also a rich source of carbon and energy. Methanotrophs that use methane as their sole carbon and energy source have drawn renewed interest due to their capability of converting methane under ambient conditions in an environmentally benign fashion. In this work, we provide a mini review on recent progress in process development, particularly on bioreactor design and gas transfer enhancements for biological methane conversion. Bioreactor configurations reported in recent research papers and patents are tabulated, together with their key characteristics, performances, pros and cons. Bioreactor configurations for gas feed with high concentration of methane (*e.g.*, natural gas) and that with low methane concentrations (*e.g.*, anthropogenic emission) are reviewed. For gas transfer promoting agents, recent results on using vectors, polymers, nanoparticles, electrolytes, and non-ionic surfactants to enhance mass transfer of methane are reviewed and summarized with a table. Process safety and future research directions are also briefly discussed.

Contents

1. Introduction

Methane is a rich source of carbon and energy and is the most abundant organic gas in the atmosphere. At the same time, methane is a powerful greenhouse gas (GHG) with a global warming potential over 20 times that of CO_2. There are two main sources of

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methane: non-renewable natural gas and renewable biogas. For natural gas, which contains 80%–95% CH_4, there is more than 6800 trillion cubic feet of proven reserves globally and the production of natural gas is expected to continue increasing based on the U.S. Energy Information Administration (EIA) projection [WR1]. On the other hand, biogas, which contains 50%–70% CH_4 and 30%–40% CO_2, can be produced within a short period of time from anaerobic digestion of organic matter. The potential of biogas production is enormous, and a 2014 U.S. government report estimated that 654 billion cubic feet of biogas per year can be produced in the country [1].

Methane is mainly used for heating, cooking and electricity generation. In its compressed form (*e.g.*, compressed or liquefied natural gas), methane can be used also as a transportation fuel. However, such usage is constrained owing to methane's inherently low volumetric energy density and the lack of infrastructure required for its broader adoption. An alternative means to use methane as a transportation fuel involves thermochemical gas-to-liquid (GTL) conversion technologies and subsequent conversion *via* the Fischer-Tropsch (FT) process. However, the technical complexity of the GTL-FT process results in exceptionally large-scale facilities (>$20 billion per facility) that cannot be economically scaled down [2], and therefore are not suitable for smaller, distributed biogas sites and natural gas wells [3].

In contrast to thermochemical processes, nature has its own way of converting methane through methanotrophs, which are largely aerobic bacteria that consume methane as their sole carbon and energy source. With the use of the particulate and/or soluble form of methane monooxygenase (MMO), methanotrophs can catalyze the oxidation of methane to methanol under ambient conditions in an environmentally benign fashion [4–6]. Driven by the need for renewable energy, plus recent increases in unconventional natural gas production in the United States, as well as the record breaking development of biogas plants in Europe in recent years [WR2], there is a renewed interest in biological methane conversion. As a result, methanotrophs are starting to gain a foothold in bioindustries with great progress seen in aquaculture and for energy production [7]. However, their industrial applications and developments are limited compared to the conversion of biomass to ethanol through industrial microorganisms [8]. To fully industrialize biological conversion of methane, several technical hurdles have to be overcome which are discussed in [9]. Among the identified technical hurdles, a major one is bioprocess development. This includes biocatalyst development, such as strain selection and modification, and process development, such as bioreactor design, and optimization of operation conditions. Several excellent reviews have been published in the last few years to capture recent advances [7,10–22]. Together, these recent reviews provide comprehensive coverage of various biological conversion routes of methane to potential products [16,22], especially on methanol and biodiesel [10,12,17] and associated challenges and opportunities [7,10,12,16,17]. All of these recent reviews focus on the biochemistry background and biological considerations; while only three of them lightly touched on process considerations [7,12,20].

In this work, we aim to provide a brief but comprehensive review on two aspects of bioprocess development, *i.e.,* bioreactor design and gas transfer enhancement, as they are critical enablers of commercializing methane bioconversion into various products. By doing so, we hope to promote the research in the process development for methane bioconversion, and to help accelerate the process of translating the recent progress in biocatalyst discovery and development (such as methanotroph mutant design) into real applications that can convert natural gas and biogas into value added products. This paper is organized as follows: first, we briefly discuss the challenges and solutions in measuring mass transfer rate of methane from the gas phase to the liquid; then, we provide a comprehensive review on different bioreactor configurations that have been used for methane conversion; next, we examine different approaches to enhance mass transfer of methane, and finally summarize the review with conclusion and discussion. It should be noted that this review focuses on lab scale set up as that is what most research was published on.

2. Mass transfer of methane and transfer rate measurement

A common challenge associated with gas phase fermentation is the low mass transfer rates of gaseous substrates into the liquid culture medium. Detailed reviews on gas (predominantly oxygen) to liquid mass transfer can be found in [23–31]. The mass transfer rate is usually characterized by the volumetric mass transfer coefficient, k_La, of the substrate. In this work, k_La is used as one of the major metrics to evaluate the performance of different bioreactor configurations and mass transfer enhancement approaches. However, it is worth noting that k_La is not a direct measure of a process performance. In addition, it is highly sensitive to cell density and broth properties. As a result, it can vary significantly during the course of any experimental run [32]. Therefore, more direct metrics, such as biomass productivity and methane consumption or removal rate, are also used wherever they are available.

Several methods to measure k_La have been reported and reviewed [33–35]. Among them, a few commonly applied approaches (such as dynamic method and its variations) require the measurement of dissolved gas concentration. For methanotrophs this would require the measurement of both dissolved oxygen and dissolved methane. Dissolved oxygen probes have long been used and are commercially available; however, very few probes for measuring dissolved methane are available. In fact, much of the dissolved methane sensor technology has been developed for geochemical studies and can be prohibitively expensive [36].

To address this challenge, a couple of in-house developed methane probes have been reported [37,38], which usually consists of a permeable membrane and a fast response methane sensor [38]. Another approach to measure dissolved methane is to strip the dissolved gas in the liquid into the gas phase, and then convert this gas phase concentration under equilibrium back to liquid phase concentration using Henry's Law. The gas phase methane concentration can be measured through methane detectors or standard analytical techniques such as gas chromatography [39].

Besides these approaches, the k_La of methane can also be estimated through the k_La of oxygen. For the applications of methane bioconversion, since the gas phase consists of mixed methane and oxygen, both gases share the same specific interfacial area and their volumetric mass transfer coefficients are only differentiated by their corresponding mass transfer coefficient k_L. Both the penetration theory and the surface renewal theory of mass transfer suggest a linear relationship between the gas component's mass transfer coefficient, k_L, and the square root of its diffusion coefficient, D [40]. For methane and oxygen, their diffusion coefficients are 1.49×10^{-5} cm^2/s and 2.1×10^{-5} cm^2/s [40], respectively, which suggests that $k_La_{CH_4} = 0.842k_La_{O_2}$. This relationship is similar to what Yu et al. [41] have reported: $k_La_{CH_4} = 0.855k_La_{O_2}$, which is used in this work. Because dissolved oxygen probes are widely available, using the measured k_La of oxygen to estimate the k_La of methane seems to be one of the easiest ways to quantify the mass transfer rate of methane from gas to liquid for methane bioconversion applications.

In the following sections of this review paper, k_La of methane and/or oxygen is used as one of the major criteria to compare different reactor configurations for mass transfer performance. Although all cited work in this paper focuses on methane utilization, not all sources reported the k_La of methane, mostly due to the lack of dis-