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# Development and evaluation of a trickle bed bioreactor for enhanced mass transfer and methanol production from biogas

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ABSTRACT

Biological conversion of the biogas produced by landfills and anaerobic digestion systems (60–70% methane ($CH_4$), 30–40% carbon dioxide ($CO_2$)) to methanol using methanotrophs (aerobic $CH_4$-oxidizing bacteria) is an emerging approach to convert waste-derived biogas to liquid chemicals and fuels. The purpose of this work was to develop a trickle-bed reactor (TBR) to improve mass transfer of $CH_4$ and oxygen ($O_2$) to methanotroph growth media for enhanced $CH_4$ oxidation and methanol production. Mass transport of $O_2$ in a TBR packed with ceramic balls was nearly two-fold higher than an unpacked TBR. $CH_4$ oxidation in the TBR (0.4–0.6 mmol/h) was about four times higher than that in shake flasks that used similar inoculum and headspace:volume and biogas:air ratios. Using optimal operating parameters (biogas:air = 1:2.5, 12 mmol formate addition, 3.6 mmol phosphate), methanol productivity (0.9 g/L/d) from the non-sterile TBR was among the highest reported in the literature. Operation under non-sterile conditions caused differences in the microbial community composition between experiments, and the most predominant methanotrophs appeared to be members of the genus in which the inoculum is classified (*Methylocaldum* sp. 14B).



## 1. Introduction

Methane ($CH_4$) is a valuable energy source, but it is also a potent greenhouse gas that has ~25 times the 100-year global warming potential of carbon dioxide ($CO_2$) [1,2]. In fact, nearly 11% of all of the greenhouse gases produced in the United States each year are due to $CH_4$ emissions from human activities (>700 million metric tons of $CO_2$ equivalent) [2]. Two of the most important sources of those $CH_4$ emissions are landfills (20%) and manure management sites (8%) [1,2], where anaerobic microorganisms convert organic wastes to biogas (30–70% $CH_4$, 30–70% $CO_2$, 0–2000 ppm hydrogen sulfide ($H_2S$)) that is released directly to the atmosphere [1]. Promising opportunities to address this issue include the installation of biogas recovery systems at landfills and the diversion of organic wastes to engineered anaerobic digestion (AD) systems [3]. In both cases, biogas can be captured and used as a source of renewable fuel, such as compressed natural gas (CNG), or can be converted to liquid chemicals (i.e. methanol) via thermochemical methods [4]. However, many landfills produce biogas with flow rates (10–15 $m^3\ h^{-1}$) and $CH_4$ contents (<30%) that are too low to implement cost-effective gas recovery systems [5–7]. Additionally, the processes to clean, store, transport, upgrade, and thermochemically convert biogas have high costs and energy demands [4]. Furthermore, the low price (<$3 per million $ft^3$, industrial price) of natural gas (>90% $CH_4$) has made the use of biogas for renewable energy unattractive [8]. Therefore, mitigation of human-induced, waste-derived $CH_4$ emissions requires development of flexible, low-cost technologies that can directly convert biogas to easily transportable fuels and chemicals.

Biological upgrading of biogas with methanotrophs (aerobic $CH_4$ oxidizing bacteria) is an attractive approach to valorize waste-derived $CH_4$, because methanotrophs grow at moderate temperatures and ambient pressures, can use $CH_4$ at low concentrations (<20%), and can produce liquid chemicals such as methanol with high efficiency [9–11]. Methanotrophs convert $CH_4$ and $O_2$ to methanol using the methane monooxygenase (MMO) enzyme. Normally, methanol is further oxidized to formaldehyde via methanol dehydrogenase (MDH). Then, formaldehyde is either assimilated

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into biomass or eventually oxidized to $CO_2$ and $H_2O$ by other enzymes to generate energy for metabolic reactions [12]. Thus, MDH inhibitors and external electron donors such as formate are needed to support methanol production by methanotrophs [11]. Electrochemical catalysis and photocatalysis of $CO_2$, direct hydrogenation of $CO_2$, and selective oxidation of biomass are promising approaches to produce renewable and low-cost formate [13,14]. There are also several studies that have used pure cultures of methanotrophs to convert clean $CH_4$ (>99% $CH_4$) to methanol. However, few have used reactor design (i.e. membrane bioreactor, continuous stirred tank reactor (CSTR)) to address the important issue that biological upgrading of $CH_4$ can be limited by the low solubility and mass transport of substrate gases ($CH_4$, $O_2$) in methanotroph growth medium [15–17].

Trickle bed reactors (TBRs) are an intriguing design for methanotroph cultivation, because they have limited power requirements, low capital costs compared to membrane bioreactors, and favorable mass transfer properties compared to CSTRs [18–20]. TBRs are cylindrical reactors packed with an inert material that has a high specific surface area [21]. Nutrient medium is circulated through the TBR to provide a thin liquid layer on the packing surface, and gases are pumped either co-current (with) or counter-current (against) to the liquid [18]. The thin liquid film has a low resistance to mass transport, allowing gases to be rapidly transferred to the biocatalyst [18]. In biological TBRs, both immobilized cells on the packing surface and suspended cells in the liquid medium have been shown to contribute in gas conversion [7,18,22,23]. TBRs have been designed for anaerobic fermentation of syngas (CO, $H_2$) to ethanol [18]. Additionally, the continuous methanotrophic biotrickling filter is an example of a TBR used for oxidation of dilute $CH_4$ streams (0–2%) to $CO_2$ [7,22]. However, there are no published reports on the use of TBRs for biological conversion of biogas to methanol. Therefore, the objective of this study was to develop a TBR for $CH_4$ conversion and methanol production from biogas. The TBR was inoculated with a mixed culture containing methanotrophs classified in the genus *Methylocaldum*, and was operated non-sterilely throughout the study. Several operating conditions were varied to test the performance and robustness of the TBR. Subsequently, the microbial community in the TBR at different operating phases was investigated.

## 2. Materials and methods

### 2.1. TBR set-up

The trickle bed reactor (TBR) was made of rigid clear polyvinyl chloride (PVC) (H = 686 mm, ID = 51 mm) with a rounded bottom and an airtight rubber cap (Fig. 1). The TBR was randomly packed with 4.81 ± 0.39 mm KRYPTOKNIGHT™ 'M' Inert Ceramic Balls (Koch Knight LLC, East Canton, OH, USA) onto a wire mesh disc (20 × 20 mesh, D = 51 mm, McMaster Carr, Aurora, OH, USA) fitted approximately 76 mm above the reactor bottom. According to supplier documentation, the apparent free space, water absorption, apparent porosity, packing density, and specific gravity of the ceramic balls were reported at 40%, 1.0%, 2.0%, 1362 kg/m$^3$ (85 lb/ft$^3$), and 2.3 g/cm$^3$ (144 lb/ft$^3$), respectively [24]. The total packed bed height was 508 mm, which provided a 0.21 L headspace at the top (H = 102 mm) and an approximately 0.16 L liquid holding reservoir at the bottom (H = 76 mm). Gas and liquid were circulated in flexible PVC tubing (5.2 mm ID) using peristaltic pumps (Master-Flex L/S Easy Load II, Cole-Parmer, Chicago, USA). The liquid inlet was at the top of the reactor, and liquid was distributed through a 5.2 mm plastic orifice centered over the packed bed. The liquid outlet was at the bottom, where liquid was pumped back upward to the liquid inlet. Gas was pumped counter-current to liquid flow

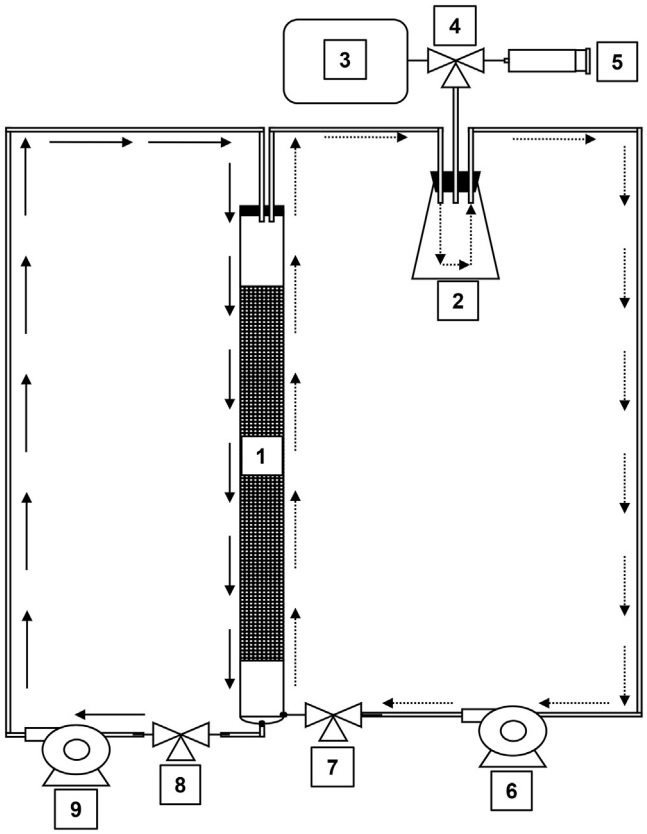


**Fig. 1.** TBR set up for biogas conversion to methanol: solid lines show direction of liquid flow and dashed lines show direction of gas flow. 1) TBR; 2) Gas feeding and sampling flask; 3) Gas bag; 4) Gas sampling and feeding port; 5) Syringe for vacuum creation; 6) Gas circulation pump; 7) Three-way valve for gas circulation shut off; 8) Three-way valve for liquid sampling and medium replacement; 9) Liquid circulation pump.

through an inlet at the bottom of the TBR. The gas outlet line at the top of the reactor was connected to a 560 mL Erlenmeyer flask with an inlet, an outlet, and gas sampling and feeding ports. Several three-way valves for liquid and gas sampling were fitted to circulation lines. The TBR volume (1.24 L) was determined by taking the sum of the volumes of distilled and deionized (DI) water needed to fill the packed bed reactor (0.62 L), circulation tubing (0.06 L), and Erlenmeyer flask (0.56 L) [25]. The headspace volume ($V_H$) was calculated by subtracting the volume of liquid added to the reactor ($V_L$) from the TBR volume. The TBR was placed in a walk-in incubator (36 ± 1 °C) throughout the study.

### 2.2. Gas feeding procedure

The TBR was supplied with either purified $CH_4$ (99% purity, Praxair, Danbury, CT, USA) or biogas sampled from a commercial anaerobic digester that was fed food waste (quasar energy group, Wooster, OH, USA). The biogas was sampled from the digester at several different times. Thus, the average composition of the biogas samples was 67.7 ± 2.8% $CH_4$, 29.9 ± 4.1% $CO_2$, 3.2 ± 3.0% $N_2$, and 1.2 ± 1.0% $O_2$ according to gas chromatography (GC) analysis. Also, the $H_2S$ content in the biogas varied from <50 ppm (lowest detection limit) to 400 ppm (Dräger Short Term Detector Tubes, Fisher Scientific, Hampton, NH, USA).

Prior to gas feeding, the TBR was purged of residual gases by continuously pumping ambient air through the system for 10–15 min. Then, headspace gas was removed from the reactor with a plastic syringe (Fig. 1) (item 5) to reduce the pressure in the TBR headspace. A Tedlar gas bag filled with purified $CH_4$ or biogas (Fig. 1) (item 3)