State-of-the-Art Review

Membrane and Fluid Contactors for Safe and Efficient Methane Delivery in Methanotrophic Bioreactors

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Abstract: Methane (CH_4), a potent greenhouse gas, is globally available as both natural gas and biogas for residential, commercial, and industrial use. Though an excellent source of heat and power, CH_4 is often flared or released into the air due to the lack of economically attractive end use options. One promising option is its use as a low-cost feedstock for growth of CH_4-oxidizing microorganisms (methanotrophs) and production of single cell protein, methanol, bioplastics, and other bioproducts. However, such opportunities are impeded by the low aqueous solubility of CH_4 and concerns about explosion hazards. To enable oxidation of CH_4 at low levels, methane monooxygenase enzymes have evolved high affinities for CH_4, as reflected in low half-saturation coefficients ($K_s < 0.1$–6 mg/L). Specific rates of CH_4 consumption can therefore become maximum at low levels of dissolved CH_4. For such kinetics, high volumetric productivities can be achieved by increasing biomass concentrations. Historically, this has been achieved by pressurizing CH_4 feedstock. New methods include coupling high media recirculation rates with in-line mass transfer devices (static mixers, gas permeable membranes); recirculating fluid contactors, such as polymers or oils; and modifying fluid media with hydrophilic additives, such as electrolytes and alcohols. These new methods ensure that a flammable mixture is not created and provide many opportunities for innovation. **DOI: 10.1061/(ASCE)EE.1943-7870.0001703.**

Introduction

Humanity's dependency on petroleum-based products (i.e., fuels, plastics, etc.) has led to atmospheric accumulation of greenhouse gases (GHGs), such as carbon dioxide (CO_2) and methane (CH_4). Most GHG mitigation research to date has focused on CO_2 by reducing fossil fuel combustion, capturing and storing CO_2, or utilizing CO_2 for biological applications (Olivier and Muntean 2013). Biological utilization of CO_2 has emphasized production of fuels, solvents, and bioplastics (Crépin et al. 2016; Lu et al. 2014; Reinecke and Steinbüchel 2008). This review focuses on CH_4, the second most abundant GHG, with a 100 year global warming potential over 20 times that of CO_2, accounting for >25% of global warming (AlSayed et al. 2018a; Hanson and Hanson 1996; Myhre et al. 2013). Global CH_4 emissions are estimated at ~770 Tg CH_4/year, of which 63% (566 Tg CH_4/year) can be attributed to anthropogenic activity such as the production and transport of petroleum products, agriculture, and the decay of organic waste from landfills (Kirschke et al. 2013; Strong et al. 2015; USEPA 2016). Traditionally, CH_4 is used as a fuel—primarily for generating electricity, but also for cooking, heating, or as a compressed fuel for use in vehicles (Stone et al. 2017). Conventional processes for CH_4 use require gas-to-liquid (GTL) conversion technologies that involve complex unit processes and high capital costs (Haynes and Gonzalez 2014). Biological routes for CH_4 conversion are attractive because they use a low-cost substrate, make use of self-replicating catalysts, and can function at near ambient temperatures (Conrado and Gonzalez 2014; Fei et al. 2014). Aerobic methane-oxidizing microorganisms (methanotrophs) use CH_4 as their sole carbon and energy source. Type II methanotrophs and some Type I methanotrophs can use CH_4 to produce intracellular granules of polyhydroxyalkanoate (PHA), natural polyesters that are fully biodegradable alternatives to fossil-fuel based plastics (Brandon and Criddle 2019; Hanson and Hanson 1996; Myung et al. 2014; Pieja et al. 2011). Methanotrophs can also use CO_2 as a supplementary carbon source (Acha et al. 2002). As a biotechnology feedstock, CH_4 is an attractive but flawed substrate. It is attractive due to its low-cost, widespread availability, nontoxicity, and high selectivity, enabling reproducible bioproduct quality (Myung et al. 2015; Yazdian et al. 2010); it is flawed due to its inherent risk of explosion, inefficient and highly exothermic metabolism, and low solubility in water.

Scale-up of methanotrophic processes can potentially occur at wastewater treatment plants, where anaerobic digestion is a cheap source of biogas CH_4; CH_4 can also be used at such locations as a source of reducing power for denitrification (Alrashed et al. 2018; Clapp et al. 1999; Kampman et al. 2014; Lai et al. 2016a, b; Luo et al. 2017, 2018, 2015; Modin et al. 2007, 2008; Stein and Klotz 2011; Sun et al. 2013). Biorefineries could also support scale-up technologies that convert CH_4 into diverse products and coproducts, including biofuels, bioplastics, and single cell protein (Chistoserdova 2018; Haynes and Gonzalez 2014; Strong et al. 2016). Bioconversion of CH_4 is an attractive alternative to

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conventional GTL technologies, but the limited bioavailability of CH_4 in aqueous media is a major limitation (Stone et al. 2017; Strong et al. 2015). To date, cost-effective production of value-added products has been limited by the comparatively low growth rates of methanotrophs, the need for mitigation of gas explosion risks, and high energy inputs for mixing of gaseous substrates (Pieja et al. 2017; Stone et al. 2017).

Conventional methanotrophic bioreactors have typically relied on bubbled stirred column reactors with gas-sparged media and venting of effluent gas (Stone et al. 2017). These reactors can operate at elevated pressures (Wendlandt et al. 1993, 2001). Improved designs are needed that enable enhanced rates of gas transfer to the aqueous phase at atmospheric pressure. To achieve high productivity, high rates of volumetric mass transfer ($k_L a$) are needed, where k_L is the mass transfer coefficient (LT^{-1}) and a is the specific surface area (L^2/L^3) (Criddle et al. 1991). For biomass productivity on a scale of grams per liter per hour, $k_L a$ values on the order of 700–1,000 h^{-1} are recommended (Haynes and Gonzalez 2014). Critical to the design of such systems are the delivery mechanisms for CH_4 and O_2 and gas mixing ratios. Because mixtures of CH_4 and O_2 can be explosive, strict attention must be paid to flammability limits, with lower explosive limit (LEL) for CH_4 in air of 5% and an upper explosive limit (UEL) of 15% (Modin et al. 2008). Operation above the UEL is usually avoided because leakage of air into the system can decrease the percentage of CH_4, dropping it into the explosive range.

This state-of-the-art review provides an overview of aerobic methanotrophic bacteria kinetics and the coupled mass transfer rates needed to promote biological conversion of CH_4 at reasonable productivities. The focus is membrane and fluid contactor technologies that increase $k_L a$ and the effective aqueous solubility of CH_4 to achieve efficient mass transfer.

Methanotroph Fundamentals

Methanotrophs are ubiquitous in soil and freshwater sediments, marine waters, rice fields, and wastewater treatment bioreactors. They also thrive in extreme environments, ranging from acidic hot springs to Antarctic lakes (AlSayed et al. 2018b; Jiang et al. 2011). Engineered systems have focused on their use for biodegradation of toxic chemicals, production of methanol and organic acids, production single cell protein, and synthesis of biodegradable plastics (El Abbadi and Criddle 2019; Fei et al. 2014; Hanson and Hanson 1996). Researchers have also evaluated many bioreactor configurations for methanotrophs, including bubble stirred tank reactors, expanded-bed reactors, fluidized-bed reactors, and rotating cylinder biofilms (Jiang et al. 2011).

Diversity and Kinetics of Growth

As shown in Fig. 1, consumption of CH_4 is initiated by methane monooxygenase (MMO). This activity incurs a significant energy cost for activation of methane requiring 2 mol of reducing equivalents and one mole of oxygen for each mole of methane oxidized to methanol. MMO may be present as a cytoplasmic soluble MMO (sMMO) or as membrane-bound particulate MMO (pMMO). Soluble MMO is characterized by presence of Fe in the active site and lack of substrate specificity, enabling co-oxidation of many alkanes, alkenes, alycyclics, and aromatics (AlSayed et al. 2018a). pMMO is likewise fairly nonspecific but is characterized by Cu in the active site and some forms have a very high affinity for CH_4 (Baani and Liesack 2008). Expression of sMMO or pMMO is controlled by copper concentration. Low levels of copper (<1 μmol/g dry weight) favor expression of sMMO (Glass and Orphan 2012). The 2-electron oxidation of methanol to formaldehyde is mediated by diverse methanol dehydrogenase (MDH) enzymes—the XoxF and MxaF quinoproteins—that contain pyrroquinoline quinone and either calcium or a lanthanide at the active site. Lanthanides can significantly increase the rate of methanol oxidation (Keltjens et al. 2014), and lanthanide-containing MDH-XoxF can oxidize methanol to formaldehyde (2-electron oxidation) and to formate (4-electron oxidation).

Over 100 different aerobic methanotrophs have been identified, thanks largely to the work of Whittenbury et al. (1970). The growing number of genera are classified into four phyla that are primarily differentiated by their carbon assimilation pathways and CO_2 requirements (Fig. 1): (1) gamma proteobacteria [Type I and Type X,

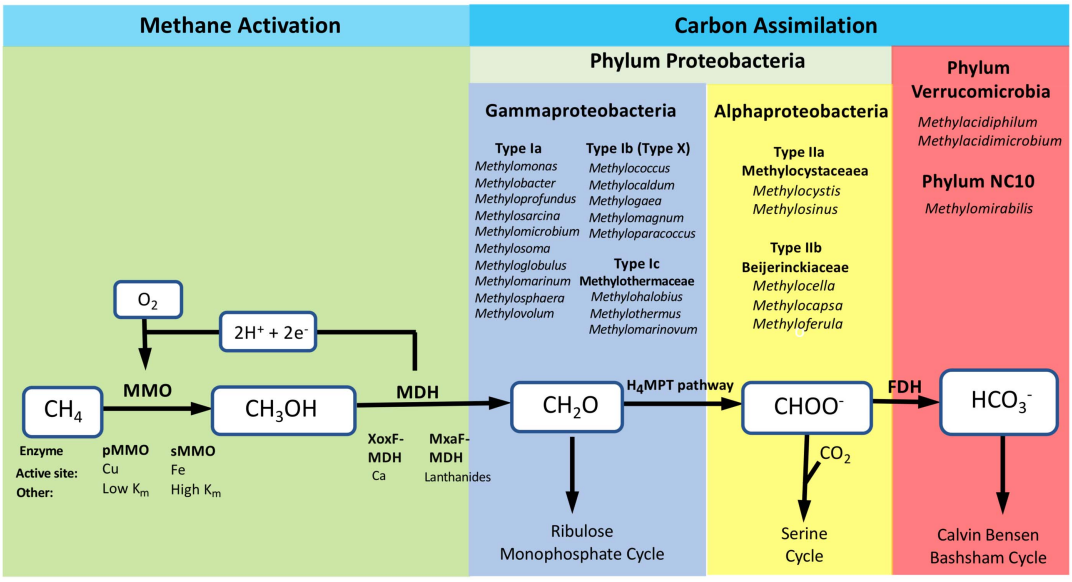

Fig. 1. Methanotroph clades, enzymes, and carbon assimilation pathways. MMO = methane monooxygenase; MDH = methanol dehydrogenase; H4MPT = tetrahydromethanopterin pathway; and FDH = formate dehydrogenase.

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(Bowman 2006)] that assimilate carbon at the level of formaldehyde and primarily use the ribulose monophosphate (RuMP) cycle for carbon assimilation; (2) alpha proteobacteria (Type II) that assimilate carbon as formate and CO_2 via the serine cycle (Crowther et al. 2008); and (3) verrucomicrobia methanotrophs feature a compartmentalized cell plan while NC10 phylum methanotrophs are capable oxygen generation from nitric oxide; both verrucomicrobia and NC10 methanotrophs use the Calvin-Bensen-Bassham cycle pathway for CO_2 assimilation (AlSayed et al. 2018a; Jiang et al. 2011).

Table 1 lists a number of applications of aerobic methanotrophs, reported half-saturation coefficients (K_s [$M_s L^{-3}$]) and when available, other kinetic parameters such as observed maximum specific growth rate (μ [h^{-1}]), cell yield (Y_x [$M_x M_s^{-1}$]), and the maximum specific rate of CH_4 utilization ($\hat{q}$ [$M_s M_x^{-1} T^{-1}$]), where M_s = mass of substrate, M_x = biomass, and T = time. In general, Type I methanotrophs have higher growth rates than Type II, verrucomicrobia, and NC10 methanotrophs. This can be attributed to the efficiency of Type I methanotrophs in assimilating carbon (RuMP pathway) compared to the other methanotrophs.

Methanotroph Stoichiometry, Kinetics, and Exothermic Metabolism

Aerobic methanotroph stoichiometry is constrained by oxygen. A lower bound of 1 mole of O_2 per mole of CH_4 (oxidized to CH_3OH) is set by the oxygen demand of methane monooxygenase; an upper bound of 2 mol of O_2 per mole of CH_4 oxidized is set by the oxygen requirement for complete oxidation of CH_4 to CO_2 and H_2O. Typical molar ratios typically range from 1.4 to 1.8. In this review, we assume that CH_4 is mass transfer- and growth-limiting, and that dissolved oxygen is supplied in excess of the minimum molar ratio required by the biological stoichiometry. Of course, in cases where biomass density is too high, oxygen may also be limiting, regardless of high oxygen input and oxygen must be supplied at a rate greater than or equal to the stoichiometric requirement. An additional constraint on aerobic methanotrophic growth is the highly exothermic nature of the reaction (El Abbadi and Criddle 2019). This is amply illustrated by comparing the heat of combustion of 1 mol of methane (Strong et al. 2015) [Eq. (1)] with the heat released by methanotrophic oxidation of 1 mol of methane and production of biomass ($C_5H_7O_2N$) (El Abbadi and Criddle 2019)

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)} + 891\ \text{kJ} \quad (1)$$

$$CH_{4(g)} + 1.48O_{2(g)} + 0.10NH_3 \rightarrow 0.10C_5H_7O_2N + 0.48CO_{2(g)} + 1.79H_2O_{(l)} + 643\ \text{kJ} \quad (2)$$

Comparing Eqs. (1) and (2) reveals a surprising fact: biological oxidation of methane releases 72% of the heat released by the abiotic combustion of CH_4. This heat must be accounted for in bioreactor design, especially at high cell densities, where it can increase temperature and decrease the solubility of dissolved CH_4 and dissolved O_2. To date, most methanotroph research has been conducted at low cell densities and at low growth rates, with doubling times in the range of 4–20 h (Table 1). Under such conditions, heat release per unit volume is also less. However, at large scale and high cell densities volumetric rates become increasingly limited by CH_4 mass transfer, and heat cannot be ignored.

Membrane Contactors

Membrane contactors are units in which gas is directed into the interior (lumen) of hollow fibers or into pockets between sealed membrane sheets then through the pores of the membranes and into the surrounding aqueous phase. Both flat sheet modules or bundles of membrane fibers (Jiang et al. 2011; Modin et al. 2007; Stone et al. 2017) can enable high mass transfer rates while reducing or eliminating risk of combustible mixtures of CH_4 and O_2. At present, membrane contactors have received relatively little attention in the literature for CH_4 delivery. While Stone et al. (2017) recently published a minireview on methanotrophic bioprocess engineering, emphasizing reactor types and fluid contactors, membrane contactors received comparatively little attention.

Mechanism

Fig. 2 illustrates the mechanism of operation of membrane contactors. Gradients of CH_4 and O_2 are illustrated, with a biofilm attached to the membrane.

Applications Overview

Table 2 summarizes the current body of literature for membrane contactors that deliver CH_4 via dense membrane contactors (e.g., silicone) and porous membrane contactors [e.g., polyvinylidene fluoride (PVDF), polyethylene (PE), composite hollow fiber (CHF)]. Porous membrane materials generally provide high mass transfer rates but need to be operated at low pressures (e.g., $< \sim 200$ kPa) to avoid bubbling and loss of biofilm. Dense membranes are composed of silicone (i.e., PDMS) and polyurethane and are generally free of clogging and can be operated at elevated pressures to overcome mass transfer limitations. Major applications include remediation of halogenated aliphatics (Hanson and Hanson 1996), production of methanol (Strong et al. 2015), and denitrification (Kampman et al. 2014; Modin et al. 2008; Sun et al. 2013).

Degradation of Toxic Chemicals

Clapp et al. (1999) evaluated methanotroph-mediated degradation of trichlorethylene (TCE). CH_4 and O_2 were delivered through the lumen of silicone fibers, and TCE-contaminated water was fed through the membrane module where methanotrophic biomass accumulated. The module achieved 100% CH_4 and O_2 utilization efficiencies, while sustaining TCE removal efficiencies of 80% to 90%. The results stimulated development of porous and dense modules for delivery of CH_4 and O_2. Building on the work of Clapp et al. (1999), several groups have evaluated membrane contactors for methanotrophic degradation of other toxic substances, including bromate, perchlorate, chromate, and selenite (Table 2). Delivery of CH_4 was accomplished through the lumen of porous membranes, and the bulk fluid was completely mixed via recirculation. The O_2 was not delivered using membrane fibers but was instead produced in situ by dismutase activity or introduced via the bulk liquid—eliminating risk of combustion. In each case, methanotrophic enrichments removed toxic chemicals efficiently with removal efficiencies of 95%–100%.

Production of Methanol

Use of membrane contactors for methanotrophic value-added products has largely focused on production of methanol and short chain fatty acids (SCFAs) (Fei et al. 2014; Strong et al. 2015, 2016). Duan et al. (2011) investigated use of dense silicone membranes for production of methanol using pure cultures of *Methylosinus trichosporium* OB3b. Bubble-free delivery of CH_4 and O_2 was achieved, and explosion risk was eliminated by delivering CH_4 and O_2 through separate fibers. The efficiency of methane conversion was 60%, and methanol accumulated to 1.12 g/L. This value was 4.5-fold higher than previously reported values. Subsequently, Pen et al. (2014) developed a membrane contactor using porous

Table 1. Kinetics of aerobic methanotrophic bacteria

Phylum	Enrichment	Application	Observed maximum specific growth rate, μ (h^{-1})	Yield (g CDW/g CH_4)	K_s (mg CH_4/L)	$\hat{q}$ (g CH_4/g CDW-h)	Operational parameters	Reference
γ-proteobacteria	*Methylococcus, Methylobacter, Methaylocaldum, MethylomicrobiumMethy-lomonas, Methylosarcina, Methylosphaera*	Methane oxidation	0.358	0.6	1.04	0.6	CH_4:O_2 = 1:1 pH: 7 ± 0.3 T: 25–28°C Mixing: 165 rpm	AlSayed et al. (2018b)
	Methylomicrobium album	—	0.05	0.28	0.29	0.18[a]	NR	Cáceres et al. (2017)
γ-proteobacteria/ α-proteobacteria	*Methylosarcina, MethylomicrobiumMethylosoma MethylobacterMethylocystis*	Kinetics and population structure	NR	NR	0.2	$4.8 \times 10^{-4} \pm 8.1 \times 10^{-5}$	T: 25°C Mixing: 250 rpm	López et al. (2014)
	Mixed, genera not specified	Methane oxidation	0.8	NR	6	NR	T: 25°C	Ménard et al. (2014)
α-proteobacteria	*M. trichosporium* OB3b	Chlorinated ethene degradation	0.06	0.55[a]	0.02	0.11	T: 20°C Mixing: 150 rpm	Anderson and McCarty (1996)
	M. trichosporium OB3b	Chlorinated ethene degradation	0.07[a]	0.43	6.85	0.16	CH_4:O_2 = 1:2.3 T: 21°C	Chang and Criddle (1997)
	M. trichosporium OB3b	Methane oxidation	0.07	0.9	NR	0.08[a]	CH_4:Air = 1:4 pH: 6.5 T: 30°C Mixing: 150 rpm	Rodrigues et al. (2009)
	Methylocystis sp. strain MOX 1	Methane oxidation	0.018	NR	0.45	NR	T: 30°C Mixing: 120 rpm	Van Bodegom et al. (2001)
	Methylosinus sporium	Methane oxidation	0.093	0.7	0.11	0.13	pH: 7 T: 25°C Mixing: 150 rpm	Ordaz et al. (2014)
	Methylocystis sp.	Methane oxidation	0.05	0.28	0.43	0.18[a]	NR	Cáceres et al. (2017)
	Methylocystis sp. GB 25	Biomass productivity	0.34	0.8	NR	0.43[a]	P: ≤ 0.5 MPa pH: 5.7 T: 38°C	Wendlandt et al. (1993)

[a]Values were marked calculated using the following relationship, $\mu = Y\hat{q}$.

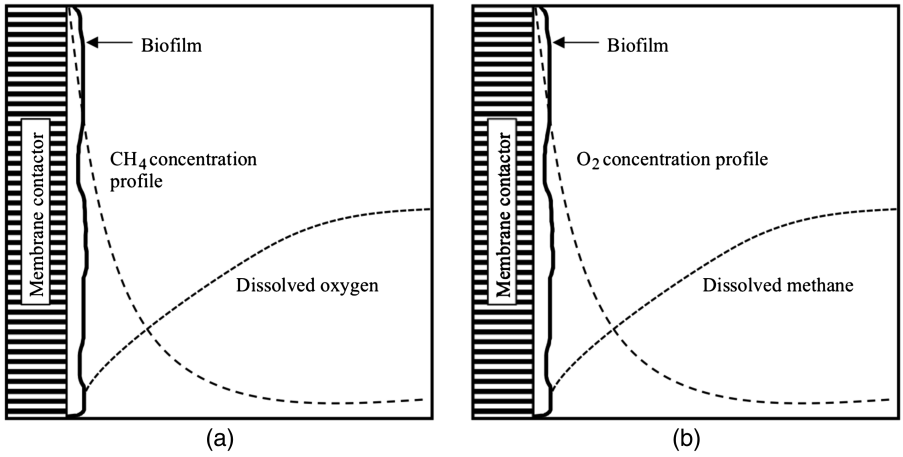

Fig. 2. Membrane contactors, showing (a) CH_4 diffusion profile; and (b) O_2 diffusion profile.

polyethersulfone (PES) membranes that enabled bubble-free operation. The complete configuration consisted of a bioreactor and two separate membrane modules where either CH_4 or air was introduced. Bulk fluid was recirculated outside the membrane modules allowing complete mixing and continuous feeding of gaseous substrates. The modules enhanced mass transfer by increasing gas surface area and achieved bubbleless aeration with gas delivery rates similar to those of gas-sparged reactors. In both studies, accumulation of methanol was induced by addition of a high concentration of phosphate buffer, a known inhibitor of methanol dehydrogenase (MDH).

Denitrification

Modin et al. (2008) were the first to consider use of silicone membrane contactors for nitrogen removal with methanotrophs. A membrane aerated bioreactor (MABR) configuration was able to achieve removal rates similar to those of suspended growth batch reactors, but the authors noted that CH_4 and O_2 gases mixed inside the lumen of the silicone tubing, indicating a need for further research. Other possible improvements were noted, including increase of the specific surface area using smaller diameter silicone tubing or hollow fibers.

Membrane Contactors and Mass Transfer

Table 3 compares membrane contactors with several reactor types (bubble stirred column, forced loop, string film) in terms of reported k_La values for sparingly soluble gases other than CH_4. These values were used to estimate k_La values for CH_4 by multiplying k_La by the ratios of the square roots of the respective diffusivities ($\mathcal{D}$)

$$k_L a_{\mathrm{CH}_{4,est.}} = \sqrt{\frac{\mathcal{D}_{\mathrm{CH}_4}}{\mathcal{D}_i}} * k_L a_i \tag{3}$$

where k_La and the diffusion coefficient in the denominator change for each gas i. Temperature variations in D are adjusted using the Stokes–Einstein equation (Cussler 2009)

$$\mathcal{D}_i = \frac{k_B T}{6\pi\sigma r} \tag{4}$$

where k_B = Boltzmann's constant (1.38×10^{-16} gcm^2 s^{-2} K^{-1}); T = temperature (K); σ = solvent (water) viscosity (0.01 gcm^{-1} s^{-1}); and r = gas molecule radius (Å). Relevant gas diffusion and molecular properties are listed in Table 4.

Membrane contactors have been developed for wastewater treatment applications, separation of gas streams from aqueous streams, and air delivery for aerobic processes (Martin and Nerenberg 2012; Montoya 2010; Reij et al. 1998; Syron and Casey 2008). Use of membranes for gas delivery is increasingly popular because such systems offer high surface area to volume ratios without intensive mixing. The mass transfer characteristics of such systems depend on inlet gas pressures, recirculation flow rates, membrane surface areas and packing density, and membrane module configuration (Shen et al. 2014). Membrane composition can also affect mass transfer. Advantages and disadvantages of membrane contactors and other reactor configurations are summarized in Tables 5 and 6.

Forced loop reactors (e.g., horizontal tubular, vertical tubular, U-loop) are also enabling new and promising design configurations that enhance mass transfer. Recirculation loops provide multiple entry points for injection of gases along with in-line static mixing elements. High mass transfer rates are achieved by radially mixing the liquid phase at optimized volumetric liquid flow rates and superficial gas velocities. Norferm A/S developed a forced loop reactor utilizing recirculation loops with horizontal and vertical sections and static mixers to enhance mass transfer. The reactor was developed for commercial scale production of single cell protein (SCP) with operations beginning in 2003 and ending 3 years later—due likely to high cost of feedstock (natural gas) and low productivities achieved. It is unclear why their system was unable to achieve the high productivities desired. Al Taweel et al. (2012) developed a theoretical mathematical model to describe the effect of mixing on growth rates and mass transfer in a loop bioreactor. The model predicted high k_La values for O_2 (~9,000 h^{-1}), but this value was not confirmed experimentally. A study by Petersen et al. (2017) experimentally derived oxygen k_La values ranging from 400 to 3,000 h^{-1} for a pilot scale U-loop bioreactor, but the high mass transfer rates achieved required large power inputs (i.e., 7,500–29,000 Wm^{-3}).

String film reactors (SFRs) are column reactors that rely on hydrophilic strings for gas delivery, cell immobilization, and control of liquid flow. The strings are made of felt or mixtures of nylon and cotton material. Park et al. (2018) developed a system with counter-current liquid and gas flows, where the liquid is directed downward, and gas is directed upward. This system achieved significant mass transfer rates for both CH_4 and O_2 over a range of gas and liquid flow rates.

Table 2. Aerobic methanotrophic bioreactors: membrane contactors

Enrichment	Gas delivered	Application	Membrane	Temperature (°C)	Specific area, a (cm^2/cm^3)	Pressure (kPa)	Recirculation rate (mL/min)	Removal/conversion efficiency (%)	Methane utilization rate ($mol/m^2/d$)	Reference
					Dense					
Mixed	CH_4, O_2	TCE degradation	Silicone	23	0.92	69 CH_4 40 O_2	N/A	80–90	0.20	Clapp et al. (1999)
Mixed	O_2	CH_4 oxidation	Silicone	28	0.36	50	NR	NR	0.656	Casey et al. (2004b)
Mixed	O_2	CH_4 oxidation	Silicone	30	0.36	50	NR	NR	0.868	Casey et al. (2004a)
M. trichosporium OB3b	CH_4, O_2	Methanol production	Silicone	30	0.20	NR	N/A	60	NR	Duan et al. (2011)
Mixed	CH_4, O_2	Denitrification	Silicone	—	0.04	150	N/A	NR	3.25	Modin et al. (2008)
					Porous					
M. trichosporium OB3b	CH_4, O_2	Methanol production	PES	25	12	$12–31 \times 10^3$	37	NR	NR	Pen et al. (2014)
M. trichosporium OB3b	CH_4, O_2	Methanol production	PES	25	12	12×10^3	37	NR	NR	Pen et al. (2016)
Mixed	CH_4	SCFA production	CHF	22	48	130	12.5	N/A	NR	Chen et al. (2018)
Methanosarcina	CH_4, CO_2	Bromate reduction	CHF	22	181	150	100	100	NR	Chen et al. (2018)
Candidatus methylomirabilis	CH_4, CO_2	Denitrification	CHF	22	181	150	100	>80	NR	Luo et al. (2018)
Mixed	CH_4, O_2	Denitrification	PVDF	22–25	22	150	N/A	97	NR	Sun et al. (2013)
M. trichosporium OB3b	CH_4	MTE	PVDF	30	12–30	NR	N/A	N/A	NR	Kim et al. (2016a)
Mixed	CH_4	Perchlorate reduction	PE	29	0.10	170	100	100	NR	Luo et al. (2015)
Mixed	CH_4	Chromate reduction	PE	29	0.90	170	100	95	NR	Lai et al. (2016b)
Methylomonas	CH_4	Denitrification/Selenate reduction	PE	29	0.90	205	100	100	NR	Lai et al. (2016a)
Methylocystaceae	CH_4, O_2	Denitrification	PE	24	35	150	10	19–39	NR	Alrashed et al. (2018)

Note: All studies are lab-scale unless otherwise noted. PES = polyethersulfone; CHF = composite hollow fiber; PVDF = polyvinylidene fluoride; and PE = polyethylene.

Table 3. Reactor configurations that enhance delivery of sparingly soluble gases (CO, O_2, H_2, CH_4)

Reactor type	Gas	Application	Membrane material	Temp (°C)	k_La (h^{-1})	Est. CH_4 k_La (h^{-1})	Reference
Membrane contactor	CO	SF	CHF	25	950	800	Munasinghe and Khanal (2012)
	CO	SF	PP	37	1,100	1,100	Shen et al. (2014)
	O_2	SF	PDMS	25	1,100	900	Orgill et al. (2013)
	CO	EP	PVDF	37	570	570	Jang et al. (2018)
	CO	SF	PDMS	25	420	360	Orgill et al. (2019)
	H_2	SF	PDMS	25	840	480	Orgill et al. (2019)
	H_2	MP	PVDF	55	430	380	Díaz et al. (2015)
Bubble stirred column	CH_4	MD	N/A	30	15	—	Rocha-Rios et al. (2010)
	CH_4	MD	N/A	25	12	—	Ordaz et al. (2014)
	CH_4	MTE	N/A	30	100	—	Lee et al. (2015a)
	H_2	PHA production	N/A	25	3,000	1,700	Ishizaki et al. (2001)
Forced Loop	CH_4	MTE	N/A	30	70	—	Yazdian et al. (2010)
	O_2	MTE	N/A	30	120	120	—
	O_2	MTE	N/A	25	400–3,000	340–25,00	Petersen et al. (2017)
String	CH_4	MTE	N/A	30	400	—	Park et al. (2018)
Film	O_2	MTE	N/A	30	880	840	—

Note: SF = syngas fermentation; EP = ethanol production; MP = methane production; MD = methane degradation; MTE = mass transfer enhancement; CHF = composite hollow fiber; PP = polypropylene; PDMS = polydimethylsiloxane; PVDF = polyvinylidene fluoride; and PHA = polyhydroxyalkanoate.

Table 4. Selected physical gas properties at 298K, 1 bar

Gas	Diffusion coefficient, D (10^{-5} cm^2 s^{-1})	Radius (Å)
CH_4[a]	1.49	1.9
CO[b]	2.03	1.73
O_2[a]	2.1	1.73
H_2[a]	4.5	1.45

[a]From Cussler (2009).
[b]From Ho and Sirkar (2002).

Table 5. Features of membrane contactors

Characteristic	Advantages	Disadvantages
Specific surface area	High specific surface area	Densely packed membranes decrease reactor liquid volume
Bubbleless	Low shear stress, minimal substrate loss; up to 100% oxygen use efficiency	Biofilm growth, decrease in mass transfer characteristics due to membrane fouling
Power	Low	—
Delivery mechanism	Physical separation of hazardous gas mixtures	May need multiple distribution modules

Table 6. Comparison of different reactor configurations

Reactor type	Advantages	Disadvantages
Bubble stirred column	Relatively simple operation, power and k_La relationship readily available to model	Substrate loss (gas), poor mixing
Forced loop	Low shear stress	Can have high power requirements
String film	Can easily scale by increasing column size or number of strings, low energy consumption	No separation of flammable gases

Fluid Contactors

Fluid contactors are defined in this paper as nonaqueous phase additives (oils or hydrophobic polymers) that self-assemble into networks with high surface area to volume ratios. They may also make use of hydrophilic additives (electrolytes, alcohols) that decrease the diameter of CH_4 gas bubbles, increasing interfacial surface area to volume ratios. A variety of fluid phase modifiers, including both hydrophobic and hydrophilic compounds, can increase mass transfer rates (Fig. 3).

Mechanisms of Operation

Fig. 3(a) illustrates how aqueous phase additives, such as an oil, create a dispersed CH_4-rich hydrophobic phase in contact with water and characterized by high surface area to volume ratios. These additives effectively behave as CH_4 shuttles. Fig. 3(b) illustrates small hydrophobic particulate shuttles loaded with CH_4 for efficient delivery to the aqueous phase; Fig. 3(c) illustrates a hydrodynamic thinning of the diffusion layer mediated by addition of alcohols or polymers; Fig. 3(d) illustrates the effects of hydrophilic electrolytes that decrease the diameter of CH_4 gas bubbles; and Fig. 3(e) shows how use suspended hydrophobic particles can collide with and rupture CH_4 bubbles, increasing interfacial area (a).

Applications Overview

Table 7 summarizes fluid contactors that use (1) nonaqueous phase materials as highways for CH_4 delivery, or (2) solutes that increase the specific surface area of CH_4 bubbles by shrinking bubble size and preventing coalescence. Fluid contactors generally have a higher affinity for hydrophobic gases such as CH_4 and O_2 (e.g., oils, hydrophobic polymers) and affect interfacial surface area by inhibiting bubble coalescence via electrorepulsive forces (e.g., electrolytes, cations) or by decreasing surface tension (e.g., alcohols). Contactors are grouped as either *hydrophobic* or *hydrophilic* depending on whether the contactors are present as a solid or nonaqueous phase or are a completely water-miscible component.

Hydrophobic Fluid Contactors

Hydrophobic contactors listed in Table 7 have been used to increase CH_4 bioavailability. Hydrophobic substances, such as oils, have high affinities for CH_4 as demonstrated by high partitioning coefficients, $K\,[C_g/C_v]$ or by an increase in CH_4 saturation levels [$CH_{4(aq)}$].

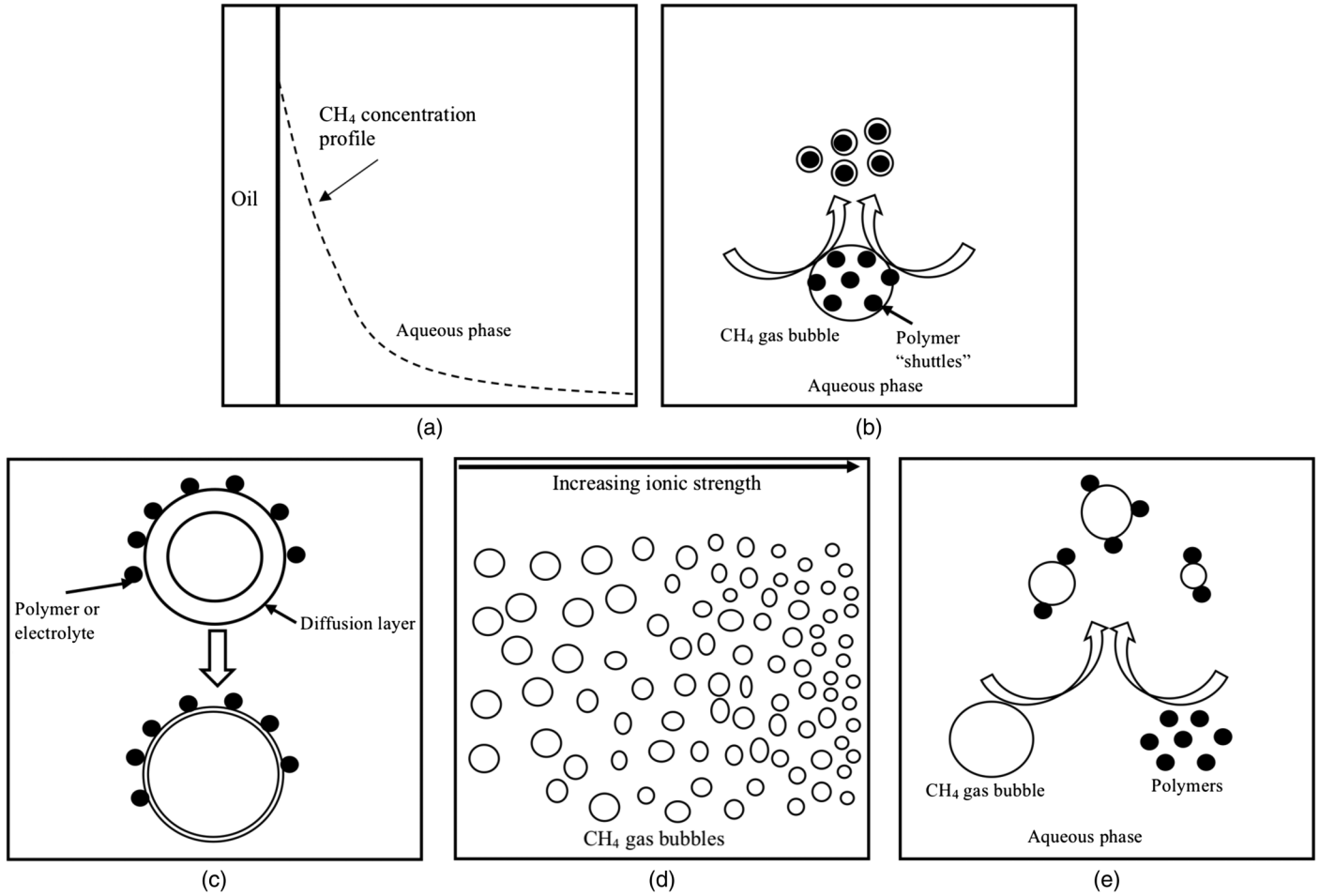

Fig. 3. Fluid contactors: (a) hydrophobic shuttle (oil); (b) hydrophobic shuttle (polymer); (c) thinning of the water boundary layer; (d) hydrophilic electrolytes; and (e) bubble rupture (polymer).

Table 7. Fluid contactors that enhance methane delivery

Enrichment	Application	Contactor	Amount	Stir rate (rpm)	Temperature (°C)	$k_L a$ (h^{-1})	Da	$K C_g/C_v$	$CH_{4(aq)}$ (mg/L)	Reference
					Hydrophobic					
Mixed	MD	Silicone	10% (v/v)	800	30	NR	—	3.2	—	Rocha-Rios et al. (2009)
Mixed	MD	Silicone	10% (v/v)	250	30	40–250	—	2	—	Rocha-Rios et al. (2011)
Abiotic	MD	Heptamethyl-nonane	—	250	30	NR	—	2.1	—	Rocha-Rios et al. (2011)
Mixed	MD	Silicone	10% (v/v)	NR	30	3,600–7,200	—	—	—	Rocha-Rios et al. (2013)
OB3b	MTE	Paraffin	5% (v/v)	NR	30	NR	—	NR	20	Chen et al. (2009)
OBBP	MTE	fluoro-carbon	80% (v/v)	—	30	1.2	0.6	NR	13	Myung et al. (2016)
Abiotic	MTE	Silica nano-particles	0.25% by weight	200	28	40	—	NR	8	Lee et al. (2015b)
Abiotic	MTE	Silica nano-particles	0.5% by weight	200	30	130	—	NR	25	Lee et al. (2016)
Abiotic	MTE	Kraton	—	250	30	NR	—	4	—	Rocha-Rios et al. (2011)
Mixed	MD	Desmopan	10% (v/v)	250	30	40–250	—	5.4	—	Rocha-Rios et al. (2011)
					Hydrophilic					
Abiotic	MTE	$MgSO_4$	5% by weight	200	30	700	—	NR	15–20	Kim et al. (2016b)
Abiotic	MTE	Na_2SO_4	5% by weight	200	30	620	—	NR	NR	—
Abiotic	MTE	K_2SO_4	5% by weight	200	30	610	—	NR	NR	—
Abiotic	MTE	Ethanol	1 molal	300	30	430	—	NR	30	Kim et al. (2017a)
OB3b	MTE	1-Propanol	1 molal	300	30	470	—	NR	30	—
OB3b	MTE	HDTAB	1 molal	100	30	70	—	NR	24	Kim et al. (2017b)

Note: MD = methane degradation; and MTE = mass transfer enhancement.

The C_g and C_v represent concentration in the headspace gas and in the vector (the hydrophobic phase), respectively.

Rocho-Rios et al. (2009, 2011, 2013) studied CH_4 bioavailability and degradation kinetics using mixed methanotrophic cultures with 10% (v/v) silicone oil. The oil was chosen as a fluid contactor because of its low partition coefficient and lack of toxicity. In a stirred tank bubble column reactor, removal of CH_4 increased by 41% compared to a control reactor without silicone oil.

Follow-up studies used silicone oil in different bioreactor configurations, with $k_L a$ values of up to 7,200 h^{-1} reported, while reducing overall power requirements.

Chen et al. (2009) used paraffin oil at a growth optimized concentration of 5% (v/v) to increase CH_4 mass transfer and methanotrophic growth. Use of paraffin oil as a modifying contactor was possible due to its lack of toxicity and compatibility with microbial cultures, and because methanotrophs are unable to use paraffin oil as a carbon source. The reported increase in CH_4 solubility was $29.16\% \pm 2.24\%$ (v/v), approximately 10 times higher than water alone [$2.37\% \pm 0.21\%$ (v/v)]. Final biomass density over the duration of the experiment (240 h) was 14 g dry weight/L, though this value is less than the bulk concentration due to cell attachment to paraffin.

Studies with hydrophobic oils often include mixing at 200–800 rpm. These systems show enhanced mass transfer, but at larger scale, energy requirements may be prohibitory. Myung et al. (2016) developed a low-energy microfluidics emulsion-based technique with a high aqueous phase volume fraction ($V_{aq}/V_{oil} = \sim 80\%$). This system was inoculated with *Methylocystis parvus* OBBP, and methane was delivered via a gas permeable and nontoxic fluorinated oil. Henry's constant (H) calculations established that CH_4 was approximately 10 times more soluble in the oil ($H_{oil,CH4} = 1.1 \times 10^{-2}$ mol L^{-1} atm^{-1}) than in water alone ($H_{H2O,CH4} = 1.2 \times 10^{-3}$ mol L^{-1} atm^{-1}). A range of uniform water droplet sizes were generated in the emulsion, but droplet size did not affect cell growth or accumulation of polyhydroxyalkanoate. A Damköhler (Da) number was estimated for this system, where $Da \gg 1$ indicates a process that is mass transfer limited and $Da \ll 1$ indicates a process that is reaction or cell metabolism limited. Average Da numbers for the emulsions were on the order of approximately 0.6, suggesting that cell growth was the rate-limiting process.

Hydrophobic polymers have a higher affinity for CH_4 and can increase both $k_L a$ and CH_4 saturation. The majority of polymer studies listed in Table 7 were carried out abiotically with mixing at 200–250 rpm. Silica nanoparticles were functionalized with methyl groups that exhibited high surface area and hydrophobicity. These characteristics were accompanied by a higher CH_4 concentration in the water phase, ranging from approximately 8 to 25 mg/L for solutions with functionalized nanoparticles versus approximately 6.2 and 22 mg/L for water alone. Rocha-Rios et al. (2011) characterized Kraton G6157 and Desmopan DP9370A polymer beads (average diameter 3 mm), and both exhibited low partition coefficients, K, for CH_4 of 4 and 5.4, respectively, which is approximately 10 times more soluble as compared to water alone ($K = 33.5 \pm 2.3$). Depending on gas recirculation rates, Desmopan enhanced $k_L a$ by factors of approximately 160%, 98%, and 136%.

Hydrophilic Fluid Contactors

Hydrophilic contactors have generally been employed as a means of enhancing $k_L a$ and CH_4 solubility. These contactors are additives that are completely water miscible at the concentrations used. Like the polymer studies, the majority of these studies have involved testing of hydrophilic contactors in the absence of microorganisms. Use of electrolytes result in the highest $k_L a$ values, whereas alcohols and the cation hexa-decyltrimethylammoniumbromide (HDTAB) exhibited greater capacity for enhancing CH_4 solubility. Propanol and HDTAB were selected for further studies with the methanotroph OB3b. In water alone, with no propanol or cation, optical density values plateaued at a value of 0.084 and growth rate of 0.001 h^{-1} (Kim et al. 2017a, b). Addition of propanol (1 molal) led to an increase in optical density and growth rate of 0.614 and 0.007 h^{-1}, respectively. Where use of the cation HDTAB (1 mM) led to an increase in optical density and growth rate of approximately 0.42 and 0.006 h^{-1}, respectively.

Fluid Contactors and Enhanced Mass Transfer

Primary benefits of fluid contactors are enhanced $k_L a$ and an increase in saturation CH_4 levels [$CH_{4(aq)}$]. These contactors increase CH_4 bioavailability and enhance mass transfer, but additional research is needed to assess impacts on microbial growth. A high mass transfer rate will not necessarily correlate with high biomass productivity, as some contactors (e.g., alcohols) can be detrimental to microbial growth (Jiang et al. 2011). While addition of electrolytes enhances $k_L a$ by altering bubble diameter, they also result in the salting-out effect in which the solute (e.g., CH_4) becomes less soluble at high electrolyte concentrations. The effects of salting out on CH_4 solubility were investigated by Kim et al. (2016c). Maximum CH_4 solubility decreased by approximately 10% as solutions of $MgSO_4$ and other electrolytes increased in concentration from 1% to 5% by weight. In the case of hydrophobic fluids, such as oils, difficulties in the physiochemical separation of contactors from biomass adds to operational and process costs. Complete biomass recovery within hydrophobic fluid contactors is difficult as biomass can become enclosed or attached (Chen et al. 2009).

Balance between Volumetric Mass Transfer Rate and the Volumetric Reaction Rate

In any gas-fed bioreactor, overall volumetric reaction rates can be limited by mass transfer or by the kinetics of the microbial reaction. The following section describes a generalized graphical method for visualization of such bioprocesses, after Criddle et al. (1991). It is applied in this study for the specific case of methanotrophs grown over a range of $k_L a$ values and with varying levels of aqueous phase CH_4 saturation that could be practically achieved using membrane and fluid contactors.

Fig. 4 illustrates a generic case of interest for coupled mass transfer and biological reaction in methanotrophic bioreactors. The analysis assumes a closed system where CH_4 is present in the gas phase, partitioning into the aqueous phase at its solubility limit [$CH_{4(aq)}$] and bioavailable at varying concentrations in the bulk solution ($CH_{4,L}$) where it is used by methanotrophs at a cell density, X.

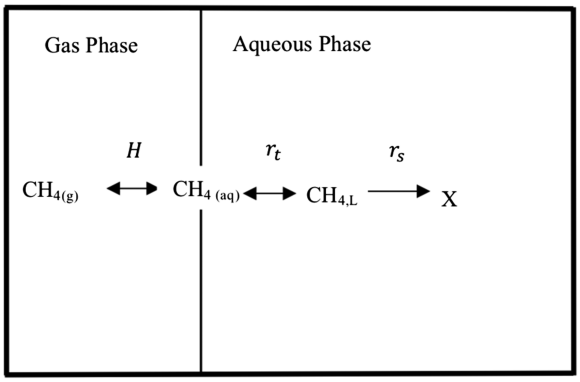

Fig. 4. Substrate delivery and consumption fluxes in a closed, two-phase system. The volumetric mass transfer rate, r_t, is equal to the volumetric rate of substrate consumption, r_s.

The volumetric rate of mass transfer of CH_4 into bulk liquid r_t [$M_s L^{-3} T^{-1}$]] is described by the mass transfer relationship

$$r_t = k_L a(CH_{4,aq} - CH_{4,L}) \quad (5)$$

where $k_L a$ = volumetric mass transfer coefficient [T^{-1}]; $CH_{4(aq)}$ = equilibrium liquid phase concentration of CH_4 [$M_s L^{-3}$]; and $CH_{4,L}$ is the liquid phase concentration of CH_4 [$M_s L^{-3}$]. The driving force for transport into the liquid medium is the concentration difference between CH_4 at its saturation limit [$CH_{4(aq)}$] and bulk liquid phase concentrations $CH_{4,L}$. $CH_{4(aq)}$ can be modified by increasing the partial pressure of CH_4 in the headspace, increasing the driving force, or using fluid contactors. The volumetric reaction rate of substrate consumption r_s [$M_s L^{-3} T^{-1}$] is given by

$$r_s = \left(\frac{\mu_{\max}}{Y_x}\right) \frac{CH_{4,L}}{K_s + CH_{4,L}} X \quad (6)$$

where $\mu_{\max}$ = observed maximum specific growth rate [T^{-1}]; Y_x = biomass yield [$M_x M_s^{-1}$]; X = active biomass concentration [$M_x L^{-3}$]; ratio $\mu_{\max}/Y_x$ is equal to $\hat{q}$, the maximum specific rate of CH_4 utilization [$M_s M_x^{-1} T^{-1}$]; and K_s is the half-saturation constant for CH_4 [$M_s L^{-3}$]. Consumption of CH_4 is modeled using saturation kinetics (Criddle et al. 1991). Saturation kinetics refers here to rate expressions that include a saturation term with a generic form $S/(K_s + S)$, where S is defined as the substrate, CH_4 for our case, and half saturation coefficient or affinity constant (K_s or K_m) defines the shape of a specific rate versus concentration curve, such as Monod kinetics for whole cells or Michaelis-Menten kinetics for enzymes. When the substrate concentration is equal to K_s, the observed specific rate is half its maximum at high values of S. For our model, we assume a constant high or low K_s value consistent with the literature where $CH_{4,L}$ is consumed by methanotrophs at varied biomass concentrations, X. Eq. (6) assumes that CH_4 is the limiting substrate and that all other nutrients (e.g., nitrogen, O_2) allow for adequate microbial growth.

To assess the rate-limiting step, Damköhler (Da) numbers can be computed to compare the reaction rate (cell metabolism) relative to the transport rate (gas delivery). The ratio of these rates indicates whether a system is limited by cell metabolism (Da $\ll 1$) or mass transfer (i.e., Da $\gg 1$). For this application, the Da number is defined as the theoretical maximum CH_4 utilization rate (MUR_{Max})

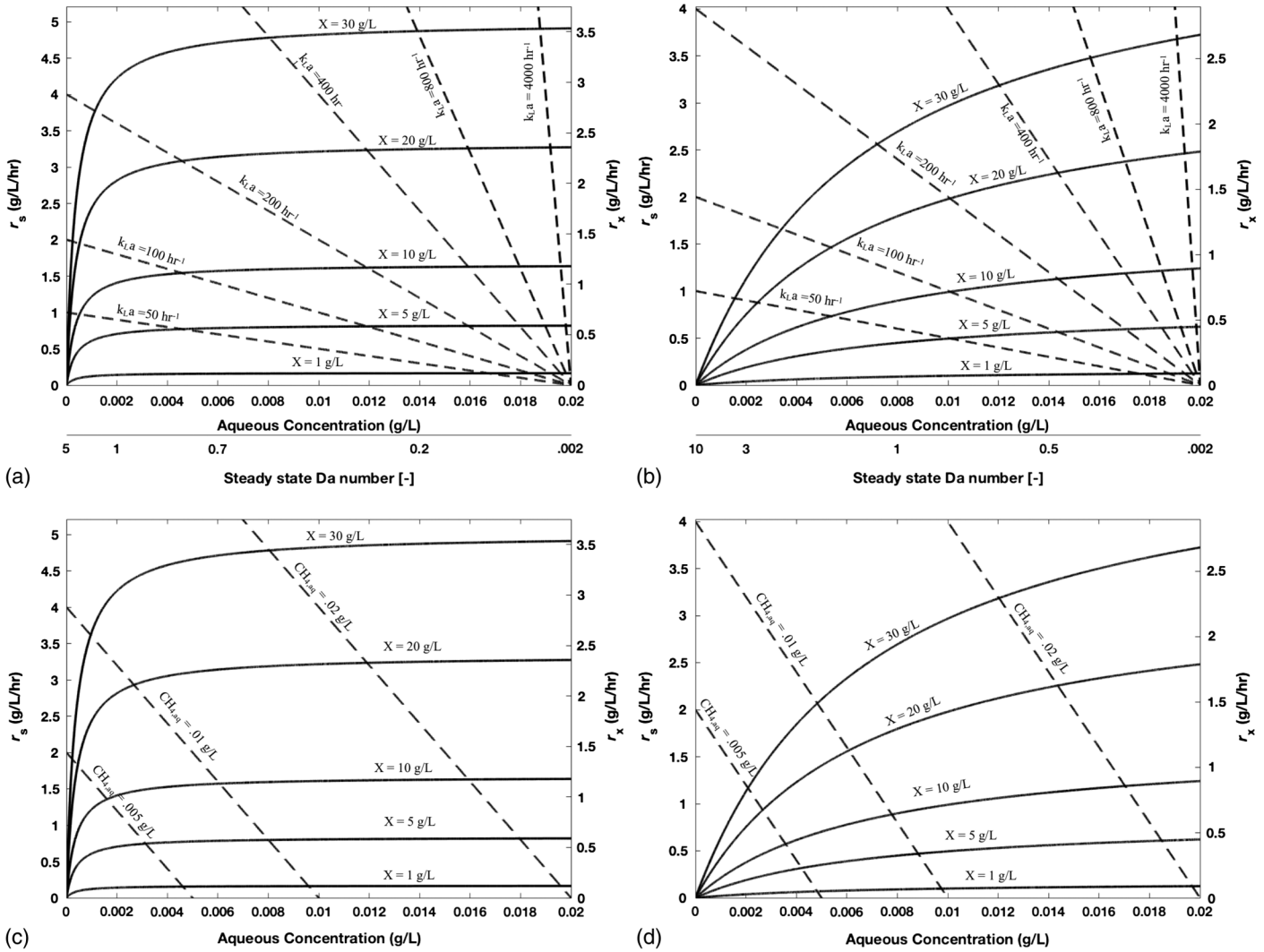

Fig. 5. Volumetric rates of reaction and mass transfer for CH_4 oxidation over a range of consumption rates ($\hat{q}X$): (a and b) CH_4 is held constant at $CH_{4(aq)} = 20$ mg/L while volumetric mass transfer rate, $k_L a$, varies; and (c and d) volumetric mass transfer rate is held constant at $k_L a = 400$ h^{-1}, while CH_4 is consumed in the aqueous phase. Assumptions: max specific growth rate = 0.12 h^{-1}, $Y_x = 0.7$ g X/g CH_4, $\hat{q} = 0.2$ g CH_4/g vss-h, pressure = 1 bar, 298K.

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divided by the maximum mass transfer rate (MTR_{Max}) (Myung et al. 2016)

$$\mathrm{Da} = \frac{\mathrm{MUR_{Max}}}{\mathrm{MTR_{Max}}} = \frac{\hat{q}X}{k_L(\mathrm{CH_{4,_{aq}}})} \tag{7}$$

Overall volumetric reaction rates can be plotted against $CH_{4,L}$ because the volumetric rates for mass transfer [Eq. (5)] and reaction [Eq. (6)] are both defined in terms of aqueous phase concentration $CH_{4,L}$. Figs. 5(a and b) illustrate a range for volumetric reaction rates [$M_s\,L^{-3}\,T^{-1}$] given that $CH_{4,L}$ is held at a maximum [i.e., $CH_{4(aq)}$] and k_La is allowed to vary. Figs. 5(c and d) illustrates volumetric reaction rates as a function of $CH_{4,L}$ given that k_La is constant and $CH_{4(aq)}$ is varied. Solid lines show saturation kinetics for CH_4 consumption (r_t) as a function of different cell concentrations on the first vertical axis, with biomass productivity (r_x) on the second vertical axis. Where biomass productivity is calculated using the cell yield value multiplied by the volumetric rate of CH_4 consumption. Dashed lines represent mass transfer curves [Figs. 5(a and b)] or maximum bioavailable CH_4 concentrations [Figs. 5(c and d)].

By focusing on points of intersection between the solid reaction curves and the dashed mass transfer curves, regions can be identified where reactions are either metabolism limited or mass transfer limited, providing insight into factors that can be manipulated to maximize biomass productivity (g/L-h), over a range of relevant k_La or $CH_{4(aq)}$ values. Points where dashed lines and solid lines cross represent steady state conditions, where volumetric rates are equal, and are mathematically defined as

$$r_t = k_La(\mathrm{CH_{4,_{aq}}} - \mathrm{CH_{4,_L}}) = r_s = \hat{q}\frac{\mathrm{CH_{4,_L}}}{K_s + \mathrm{CH_{4,_L}}}X \tag{8}$$

Biomass productivity (g vss/L-h) can be increased by increasing cell density X and/or increasing $\hat{q}$. Historically, increases in X have been achieved by increasing operational pressure (3–5 bar) (Wendlandt et al. 1993; Wendlandt et al. 2001). Fluid contactors can also be used or coupling of media recirculation systems with in-line mass transfer devices (static mixers, membrane contactors). Increases in $\hat{q}$ can also be achieved by removing inhibitors or by operating at a higher temperature.

With methanotrophs, volumetric rates are sensitive to differences in the half saturation values K_s because these values can vary over several orders of magnitude for different species and communities. Reported values range from 20 μM [assumed in Figs. 5(a and c)] to 430 μM [assumed in Figs. 5(b and d)] (El Abbadi and Criddle 2019; Anderson and McCarty 1996; Van Bodegom et al. 2001; Chang and Criddle 1997; Graham et al. 1993; Lontoh et al. 1999; Semrau et al. 2010; Speitel et al. 1993). For the low K_s values [Fig. 5(a)], a fivefold increase in X from 1 to 5 g/L results in a threefold increase in biomass productivity from ~0.2 g/L-h to ~0.6 g/L-h. However, for a methanotroph with a high K_s value [Fig. 5(b)] the same fivefold increase in X results in a much lower increase in biomass productivity, from approximately 0.2 to 0.3 g/L-h.

When mass transfer of CH_4 (r_t) is limiting (Da $\gg$ 1) at low CH_4 concentrations, system design should focus on increasing k_La values and $CH_{4(aq)}$. Increasing k_La values invariably increases energy costs, so moving from left to right across Figs. 5(a and b) illustrates tradeoffs in energy requirements, volumetric rates of CH_4 consumption, and biomass productivity, r_x.

Conclusions and Future Work

Given the energy intensive nature of GTL processes, methanotrophs are of increasing interest as biological alternatives for producing value-added and biodegradable products from natural gas and biogas. As anthropogenic methane emissions increase, new technologies are needed to increase substrate utilization rates, decreasing emissions to the atmosphere. Membrane and fluid-modifying contactors can improve the volumetric reaction rates, thereby decreasing volume requirements and cost. Methanotrophic processes are potentially limited by slow mass transfer of CH_4 into aqueous media, slow growth, or both. Damköhler numbers provide useful insight into rate limiting factors and suggest strategies for increased productivities.

The literature on methanotrophs suggests a wide range of K_s values. This characteristic of methanotrophs is consequential and merits further investigation. When volumetric rates of microbial growth are limiting (Da $\ll$ 1), high biomass levels are needed to achieve high productivities. This can be achieved by increasing $CH_{4(aq)}$ using fluid contactors or by coupling high media recirculation rates with in-line mass transfer devices (static mixers, gas permeable membranes). When mass transfer rates are limiting (Da $\gg$ 1), engineering design should focus on increasing k_La values and $CH_{4(aq)}$.

A challenge in assessing current literature on methanotrophs is a lack of standardization in reporting of microbial growth parameters. Improved estimates are needed for specific growth rates and effects of temperature, ionic strength, biomass yields, and half-saturation coefficients. Standardized reporting is needed for mass transfer characteristics of membrane and fluid contactors, such as values for k_La and $CH_{4(aq)}$. Further, productivity values and methane utilization rates for membrane contactors are virtually absent in the literature, including the information needed to compute such values (e.g., biomass density, specific growth rates, etc.)—a deficiency that should be addressed in future studies. Ultimately, dynamic, integrated models are needed that incorporate additional factors influencing methanotroph growth, such as product inhibition (say, for example, due to accumulation of methanol, low pH, and heat) and possible impacts of CO_2 and high dissolved oxygen concentrations. Models based on these principles will result in improved strategies for cultivation of methanotrophs and increase the economic viability and safety of methane bioconversions.

Data Availability Statement

Some or all data, models, or code generated or used during the study are available from the corresponding author by request, such as the script for assessment of rate limitations.

Acknowledgments

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