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Self-consistent liquid-to-gas mass transfer calculations

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ABSTRACT

This work develops an alternative gas transfer calculation method to the two methods currently used in anaerobic digestion modelling. The current calculation methods are problematic because one is computationally stiff, while the other introduces an artificial overpressure. The new approach began by noting that the gas partial pressures are the same as the partial flows at the liquid/gas interface, and then used the self-consistency requirement to develop gas pressure equations which were used by a search algorithm. The new approach took about three iterations to achieve a flow precision better than 2×10^{-7} mol h^{-1} l^{-1}, and was self-consistent and stable even when working with eight gases.

1. Introduction

Anaerobic digestion models have become increasingly useful for design and research, and of these, Anaerobic Digestion Model No. 1 (ADM1) is probably the most studied and widely applied (Batstone et al., 2006). Liquid-to-gas mass transfer calculations are an essential part of these models because almost all the chemical oxygen demand (COD) removal is by methane production (Speece, 1996), carbon dioxide transfer can affect the system pH (Stumm and Morgan, 1996), and dissolved hydrogen gas has a substantial regulatory effect on the range of fermentation products (Thauer et al., 1977). However, gas flow calculations are problematic because even with just four gases (methane, carbon dioxide, hydrogen and water vapour) the ADM1 gas flow calculations are highly sensitive to the integration algorithm and time step length (Rosen et al., 2005). Furthermore, as the gas flow calculation problem is very important and yet distinct from the difficulties caused by dissolved hydrogen dynamics, this problem warrants further investigation for the development of a more stable ADM1 model (Rosen et al., 2005).

Batstone et al. (2002) describe two methods for calculating gas flow. The first sums the individual flows of methane, carbon dioxide and hydrogen based on dynamic gas pressures, and then corrects for water vapour, but is problematic as the flow calculation exhibits nervous behaviour (Rosen et al., 2005) which slows the simulations (Rosen et al., 2006). The second method assumes that gas flow is restricted through an orifice (Batstone et al., 2002) and while it is more stable than the first method, it produces an artificial digester overpressure of about 5 kPa (Rosen et al., 2006) which changes the gas flows. These problems suggest that a new gas flow calculation approach is needed, because these calculation difficulties will be exacerbated, particularly when highly soluble trace gases such as ammonia and hydrogen sulphide are incorporated. The ideal calculation method would be both stable, and self-consistent, i.e. the sum of the gas pressures would be the same as the digester pressure, and this self-consistency requirement has become increasingly important, especially now that models such as ADM1 are being used for high-accuracy applications such as biokinetic parameter estimation (Batstone et al., 2003; Batstone et al., 2009), process evaluation (Koutrouli et al., 2009; Parker, 2005), and being extended to denitrification systems (Tugtas et al., 2010) where gas transfer plays a central role.

The aim of this research was to develop and evaluate an alternative gas transfer approach that is stable and self-consistent, can incorporate a broad range of gases, and is compatible with mechanistic models such as ADM1. The solution strategy was to reformulate the gas equations based on the concept that the gas *partial pressures* are the same as the *partial flows* at the liquid/gas interface, and then search for a self-consistent gas flow. The new method typically took about three iterations to find self-consistent and precise gas pressures, and was able to accommodate any number of gases.

2. Methods

2.1. Gas flow formula

Individual gas flows were calculated using the formula (Tchobanoglous et al., 2003):

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$$Q_j = K_{lj}a(C_j - P_j \times H_j) \quad (1)$$

where Q_j is the specific flow rate (mol h^{-1} l^{-1}) of gas j, K_{lj} is the liquid mass transfer coefficient of gas j (length h^{-1}), a is the specific transfer area (area volume^{-1}), C_j is the dissolved gas concentration (mol l^{-1}), P_j is the pressure of gas j (kPa), and H_j is the Henry's coefficient (mol l^{-1} kPa^{-1}).

Temperature corrected Henry's coefficients were determined for all the test gases, by fitting the IUPAC estimation formula (Lide and Haynes, 2010) to gas solubility data (Dean, 1992), while the gas mass transfer coefficients were estimated based on diffusivity coefficients (Danckwerts, 1951), and standardizing these mass transfer coefficients on carbon dioxide as in other studies (Merkel and Krauth, 1999; Pauss et al., 1990).

2.2. Equation formulation

When dissolved gases leave solution and enter a gas space such as a bubble, the gas composition at the liquid/gas interface is determined by the flow rates of the different gases. Under these conditions, the *partial pressure* of each gas is the same as its *partial flow*. Thus:

$$ps_j = P_j/P_{Sys} = Q_j/\sum Q \quad (2)$$

where ps_j is the partial pressure of gas j, P_{Sys} is the system pressure, $\sum Q$ is the sum of all the different gas flows, and P_j and Q_j are as for Eq. (1). So since $Q_j = P_j/P_{Sys} \times \sum Q$, by substitution into Eq. (1):

$$P_j = C_j/\left(\sum Q/(K_{lj}a \times P_{Sys}) + H_j\right) \quad (3)$$

As the total gas flow ($\sum Q$) was the only unknown on the right-hand side of Eq. (3) (because C_j and P_{Sys} were state variables, and H_j and $K_{lj}a$ were constants), each estimate of the total gas flow was evaluated by summing the individual gas pressures (Eq. (3)) and comparing this total with the system pressure. For each set of conditions, only one total gas flow yielded a combined gas pressure which was identical to the system pressure, and the total flow which met this criterion was self-consistent. A search algorithm adjusted the estimated total gas flow until the sum of the gas pressures was within 0.05 kPa of the known system pressure.

2.3. Estimating K_la

As layers of liquid slide over rising bubbles, the surface renewal model of gas transfer (Danckwerts, 1951) was apposite, justifying the use of:

$$K_{lj} = K_{CO_2}\sqrt{(D_j/D_{CO_2})} \quad (4)$$

where K_{lj} is the mass transfer coefficient of gas j, K_{CO_2} the mass transfer coefficient of carbon dioxide (Pauss et al., 1990), and D_j and D_{CO_2} are the gas diffusion coefficients of gas j and carbon dioxide. Furthermore, the area term of the K_la was neglected for this calculation because all the gases transfer across the same surface.

2.4. Estimating diffusion coefficients

The use of diffusion coefficient data is recommended wherever possible (Poling et al., 2007), however, when aqueous diffusion coefficient data were not available these were approximated using an estimation formula (Hayduk and Minhas, 1982). To account for temperature effects, diffusion coefficient data (Bruins, 1926; Ferrell and Himmelblau, 1967; Himmelblau, 1964; Sherwood et al., 1975) were also fitted to (Himmelblau, 1964):

$$D = 10^{(B-A/T)} \quad (5)$$

where A and B are constants, and T is the temperature in Kelvin.

When gas diffusion data were used to calculate the gas transfer coefficients, ammonia, hydrogen sulphide, and water vapour diffusion data presented particular problems by being either inconsistent or not available. For ammonia, two sources of data (Bruins, 1926; Himmelblau, 1964) were combined and interpolated using a least squares fit. For hydrogen sulphide and water vapour, a molar boiling volume estimation formula (Tyn and Calus, 1975) was used in conjunction with a modified diffusion coefficient formula (Hayduk and Minhas, 1982). A minor modification was made (the "Z" of Eq. (6) was changed from 1.25 to 1.3778) because the original Hayduk and Minhas (1982) formula underestimated the aqueous diffusion coefficients of ammonia, carbon dioxide, methane, nitrogen and oxygen by an average of 9.3% at 25 °C:

$$D = Z \times 10^{-8} \times (V_a^{-0.19} - 0.292) \times T^{1.52} \times \eta^{(9.58/V_a - 1.12)} \quad (6)$$

where D was the diffusion coefficient (cm^2 s^{-1}), Z a constant, V_a the molar boiling volume (cm^3 mol^{-1}), T the temperature (kelvin), and η the water viscosity (cP).

2.5. Solution steps

To find the self-consistent total gas flow an iterative procedure was used as follows:

(1) Use the system temperature to determine appropriate values for the Henry's coefficients, gas K_la (Eqs. (4)–(6)), and water vapour pressure.
(2) Calculate equilibrium gas pressures by applying Henry's law to the dissolved gas concentrations.
(3) If the sum of the equilibrium pressures is greater than the system pressure, calculate the pressure of each gas and water vapour (Eq. (3)) using an estimated[1] total flow rate, and sum these.
(4) Use the empirical formula $\sum Q = (\sum$Step 3 pressures/system pressure$)^3 \times$ Step 3 flow rate, to find a second estimated flow rate, then calculate the pressure of each gas and water vapour (Eq. (3)) and sum these.
(5) Interpolate the total flows and total pressures from steps 3 and 4, to find the total flow at the system pressure, and repeat this process using the last two sets of flows and pressures until the calculated total pressure is within 0.05 kPa of the system pressure.

Water vapour was treated as a highly soluble gas and the water vapour pressure was calculated based on the known temperature and vapour pressure relationship (Lide and Haynes, 2010). The same water vapour pressure served as the water vapour equilibrium pressure and was also used to determine an equivalent Henry's coefficient. A water vapour mass transfer coefficient was estimated using Eqs. (4)–(6).

The test gases were methane, carbon dioxide, hydrogen, water vapour, ammonia, hydrogen sulphide, nitrogen, and oxygen. Although oxygen has been reported in several operational digester samples (Wheatley, 1979), it is not normally anticipated in an anaerobic digester, however, a trace quantity was included to test the calculation method. Dissolved methane, carbon dioxide, hydrogen and ammonia concentrations (C_j in Eqs. (1) and (3)) were based on the pseudo steady state values reported for ADM1 (Rosen and

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[1] In practice, the gas flow from the previous time step of the numerical solver would be used as an initial flow estimate, but this study used an empirical correlation; $\sum Q = 4.1796 \times 10^{-6} \times \sum P_{Eq} - 4.235 \times 10^{-4}$, where $\sum P_{Eq}$ is the sum of the equilibrium pressures. This empirical formula found a flow within about 15% of the actual flow and was based on the approximately linear correlation of the all the test gas equilibrium pressure combinations and the resulting flows.