Investigation of methane concentration distribution during anaerobic sludge digestion: a thermodynamic approach

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Anaerobic digestion is certainly one of the options that can help solve the dilemma of energy demand, waste management and climate crisis mitigation mainly in developing countries. Although full-scale application of this biological treatment route is already a reality in many countries such as Mexico, Brazil, Colombia and India, the risk of fugitive emissions still deserves attention.

Under ideal conditions, it is expected that all methane (CH_4) present in the biogas will be transferred from the liquid to the gas phase, ensuring maximum recovery. Considering the effluent as an ideal solution, it is possible to use Henry's law to represent the phase equilibrium. This hypothesis is particularly acceptable for reactors that treat domestic wastewater due to the high degree of effluent dilution. However, for concentrated wastewater or complex organic waste blends composed of functional groups with different sizes, the molecular interactions (polar, apolar, non-apolar, electrolytic) become important since the system is not only biphasic.

Most reports in the scientific literature relate dissolved methane losses with operating conditions such as: temperature, organic load, sludge age and hydraulic retention time (Souza et al., 2011; Yeo and Lee 2013; Yeo et al, 2015; Crone et al., 2016). However, since the formation and transfer of CH_4 to the vapor phase is related to the equilibrium condition, a thermodynamic approach can help to estimate the degree of variation of CH_4 distribution between the liquid phase and gas phases. Through mathematical modeling, considering the substrate as a non-ideal solution, it is expected to obtain supersaturation concentration values in the liquid phase closer to those reported by experimental research. That is, in practical terms, is it possible to predict the loss of dissolved methane in the liquid effluent through the equations of thermodynamic models?

The validity of the hypothesis was tested by applying the extension of Anaerobic Digestion Model (ADM1) proposed by Mendes et al. (2015), which uses Henry's Law to obtain the distribution of methane in the different phases. The substrate used was sewage sludge. For mathematical modeling, it was assumed that anaerobic digestion occurred in a CSTR reactor submitted to mesophilic temperatures without limitation of macro or micronutrients. The ADM1 was implemented in Matlab® environment.

The mathematical model proposes a numerical integration of the ADM1's ordinary differential equations with Aspen Plus® thermodynamic software. Through this procedure, the biogas composition obtained from ADM1 was instantly sent to the Aspen Plus® environment and analyzed by two thermodynamic methods (The *Electrolyte Non-Random Two Liquid Model* – eNRTL and the Ideal). Five simulations were performed in Aspen Plus® environment considering acid-base equilibrium equations in conjunction with other reactions. Table 1 shows the boundary conditions assumed in mathematical simulations.

Table 1. Boundary conditions of mathematical modeling

Simulation	Reactions considered	Method
1	Equilibrium, acidogenesis, acetogenesis, and methanogenesis,	. Ideal and eNTRL
2	Acid-base, equilibrium for volatile acids: butyric, valeric and propionic	Ideal
3	Equilibrium reactions	Ideal
4	Equilibrium reactions for volatile acids: butyric, valeric and propionic	eNTRL
5	Equilibrium reactions for CO_2, H_2O e NH_3	eNTRL

Table 2 shows the results obtained for each simulation regarding to the total concentration of CH_4 and the percentage of dissolved gas. In first line, the predicted result by ADM1 is exposed. It can be observed that thermodynamic modeling was not able to represent CH_4 supersaturation concentrations reported in experimental studies. Although it has been tested different methods, the choice of eNTRL did not result in a relevant difference when compared to the values obtained by ADM1. Therefore, it can be stated that Henry's Law simplification in ADM1 model is valid to represent the phenomenon investigated. Although little differences in phase distribution may occur, the total gas concentration predicted was the same by the two software. The non-ideal method was not relevant to check considerable variations in results, which confirms that the substrate (sewage sludge) may be considered as an ideal solution.

Table 2. Results of the simulations

	CH4 total*	Dissolved CH_4 (%)
ADM1	0.2088	2.97
Simulation 1	0.2100 (Ideal method)	0.68
	0.2090 (eNRTL)	1.82
Simulation 2	0.2088	0.69
Simulation 3	0.2088	0.36
Simulation 4	0.2088	0.0036
Simulation 5	0.2088	3.73

* Expressed as $kgCOD.m^{-3}$

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