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Thermodynamic equilibrium model in anaerobic digestion process

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Abstract

Catabolic reactions provide the chemical energy necessary for the maintenance of living microorganisms. The catabolic reactions in anaerobic digestion process may progress close to the equilibrium state ($\Delta G = 0$) depending strongly on the microorganisms in the digester. The thermodynamic equilibrium of catabolic reactions in the anaerobic digestion process was modelled under isothermal and isobaric conditions. Three thermodynamic models were considered; the ideal, the Debye-Hückel–Praunitz, and the Pitzer–Praunitz. The models in this paper concentrate on the methanogenic equilibrium of the anaerobic digestion process. The thermodynamic equilibrium model shows that the methanogenesis step requires thermal energy and electrons, so that anaerobic digestion may achieve high substrate degradation and high conversion to methane. Some thermodynamic recommendations are suggested for the future development of the methanogenic phase of anaerobic digestion.

Keywords: Anaerobic digestion; Methanogenesis; Thermodynamics

1. Introduction

For years, simulating anaerobic digestion process was limited to enzyme kinetics such as Michaelis–Menten [1], Monod [2], and their empirical derivatives [3–9]. Today, these empirical kinetic relations are still used to simulate the behaviour of a wide range of anaerobic technologies.

Many scientists [6,8,10–12] note that the empirical kinetics in anaerobic digestion process follow thermodynamic laws, and that “inhibition” of the digestion process is said to occur when a system is actually close to the thermodynamic equilibrium [13,14]. However, in the empirical kinetics the thermodynamics of the process have been ignored.

2. Model development

2.1. Stoichiometric model

The thermodynamic model was built up from stoichiometric foundations based on feasible reactions in anaerobic digestion. The feasible reactions are categorised according to the phase transition, electrolyte dissociation, and oxidation–reduction (Redox). Table 1 shows the fundamental stoichiometric relationships of the methanogenic phase in anaerobic digestion process.

The fundamental equilibrium model further requires a strict mass balance condition. Mass balances were constituted for vapour, ion charge, and elementary balances involving carbon, hydrogen, and oxygen.

2.2. Equilibrium relationships

Equilibrium models were superimposed on the stoichiometric foundations. These are based on the fundamental thermodynamic equilibrium definition, which is the equalization of chemical potentials between reactants and products.

$$\Delta G = \sum_i v_i \mu_i = \text{zero} \tag{1}$$

where the chemical potential (μ_i) of component (i) is expressed as standard chemical potential ($\mu_i{}^\circ$) and activity (a_i) of component (i);

$$\mu_i = \mu_i^\circ + RT\ \ln(a_i) \quad \text{or} \quad \mu_i = \mu_i^\circ + RT\ \ln(f_i/f_i^\circ) \tag{2}$$

where f_i is fugacity and the standard reference fugacity (f_i°) is normally unity at 1 atm. By substituting Eq. (2) into Eq. (1) we obtain the fundamental definition of the equilibrium

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Table 1
Stoichiometric relationship for methanogenesis of anaerobic digestion process

Vapour/liquid transitions	Electrolytes transitions	Redox reaction
$C_2H_4O_2\ (g) \leftrightarrows C_2H_4O_2$	$C_2H_4O_2 \leftrightarrows C_2H_3O_2{}^- + H^+$	$C_2H_4O_2 + 2H_2O \leftrightarrows 2CO_2 + 8H^+ + 8e^-$
$H_2O\ (g) \leftrightarrows H_2O$	$H_2O \leftrightarrows H^+ + OH^-$	$CH_4 + 2H_2O \leftrightarrows CO_2 + 8H^+ + 8e^-$
$CH_4\ (g) \leftrightarrows CH_4$	$CO_2 + H_2O \leftrightarrows H_2CO_3$	$H_2 \leftrightarrows 2H^+ + 2e^-$
$H_2\ (g) \leftrightarrows H_2$	$CO_2 + H_2O \leftrightarrows HCO_3{}^- + H^+$	$2H_2O\ (l) \leftrightarrows O_2\ (g) + 4H^+ + 4e^-$
$CO_2\ (g) \leftrightarrows CO_2$	$CO_2 + H_2O \leftrightarrows CO_3{}^{-2} + 2H^+$	

constant (K).

$$\ln K = \frac{-\sum_i v_i \mu_i^\circ}{RT} = \sum_i \ln a_i^{v_i} \tag{3}$$

Examples of equilibria and their thermodynamic laws based on Eq. (3) are shown in Table 2. The equilibrium constant (K) in Eq. (3) can also be applied to the anaerobic digestion process. We categorised the equilibrium relationships in anaerobic digestion into three types: vapour/liquid, electrolyte ionisation, and Redox equilibrium.

2.2.1. *Vapour/liquid equilibrium*

The vapour/liquid equilibrium is defined by the equality of the chemical potentials (μ_i) for component (i) in the two phases.

$$\mu_i^{\text{Vapour}} = \mu_i^{\text{Liquid}} \tag{4}$$

Substituting Eq. (2) into Eq. (4) yields the definition of the equilibrium relation. The vapour/liquid equilibrium constant corresponds to Henry's law coefficient (K^{H}) and is defined by Eq. (5).

$$K^{\text{H}}_{i-\text{W}}\ (\text{atm l/mol}) = \exp\left\{\frac{-(\mu_i^{\circ-\text{Vapour}} - \mu_i^{\circ-\text{Liquid}})}{RT}\right\} = \frac{f_i}{a_i f_i^\circ} \tag{5}$$

where subscript i–W indicates that the Henry's law constant ($K^{\text{H}}_{i-\text{W}}$) is for solute ($i$) in solvent (water). Relevant Henry's law constants in anaerobic digesters are shown in Table 3.

Table 3
Henry's law constants in anaerobic digesters

Substances name	T (°C)	Henry's law constants			References
		(mol/l atm)	(atm l/mol)	$\log(K^H_{i-\text{W}})$	
H_2	25	1164.224	0.000858	3.066	[25]
O_2	25	716.764	0.0014	2.855	[25]
CO_2	25	21.82	0.0458	1.338	[26]
CH_4	25	640.0	0.0016	2.806	[27]
$C_2H_4O_2$	25	0.0012	850.0	−2.920	[26]

Furthermore solvent water also exhibits a vapour/liquid equilibrium. When the water activity (a_{W}) is unity, the solvent phase equilibrium corresponds *Raoult's law* for pure ideal solvent (water).

$$K^{\text{H}}_{\text{W}} = \frac{f_{\text{W}}}{a_{\text{W}} f^\circ_{\text{W}}} \cong P^{\text{sat}}_{\text{W}} \tag{6}$$

where the fugacity of water (f_{W}) in gas phase becomes saturated water pressure ($P^{\text{sat}}_{\text{W}}$).

2.2.2. *Electrolyte ionisation equilibrium*

The equilibrium relation is described by the ion association, in which the chemical potential (μ_i) of component (i) equals the summation of chemical ion potentials (μ_j^+ and μ_k^-) of its constituent ions (j) and (k) for the component (i).

$$v_i \mu_i = v_j \mu_j^+ + v_k \mu_k^- \tag{7}$$

The electrolyte ionisation equilibrium in anaerobic digesters is characterised by dissociation constants (K_{a}) for reactions of the ion composites. The dissociation constants are expressed by Eqs. (2) and (7).

$$K_{\text{a}} = \exp\left\{\frac{v_i\mu_i^\circ - v_j\mu_j^{\circ+} - v_k\mu_k^{\circ-}}{RT}\right\} = \frac{(a_j^+)^{v_j}(a_k^-)^{v_k}}{a_i{}^{v_i}} \tag{8}$$

Table 2
Examples of equilibria and their associated thermodynamic laws

	Examples of reactions	Remarks
Homogeneous reaction		
In the gaseous phase	$2H_2O\ (g) = 2H_2\ (g) + O_2\ (g)$	Güldberg and Waage's law of dissociation (law of mass action) chemical equilibrium constant (K)
In the liquid (aqueous) phase	$H_2O\ (l) = H^+\ (aq.) + OH^-\ (aq.)$	Oswald's dilution law of electrolyte dissociation
Heterogeneous reaction		
Of solid/solution	$Fe(OH)_2\ (s) = Fe^{2+}\ (aq.) + 2OH^-\ (aq.)$	Solubility product law
Of gas/solution	$CO_2\ (g) + H_2O\ (l) = H_2CO_3\ (aq)$	Henry's gas solubility law
	$As_2O_3\ (s) + H_2O\ (l) = 2HAs_2O\ (aq)$	Solubility
Conversion from condensed phase to gaseous phase	$H_2O\ (l) = H_2O\ (g)$	Vapour pressure law

This table was based on the Atlas of electrochemical equilibria in aqueous solutions [24].