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Long chain fatty acids degradation in anaerobic digester: Thermodynamic equilibrium consideration

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ABSTRACT

The biological oxidations and reductions occurring in batch anaerobic digesters may approach equilibrium. The approach depends strongly on the activities of the micro-organisms present. The thermodynamics of linear long chain fatty acid degradation in a batch reactor was modeled. The substrates considered are the saturated fatty acids from acetic acid to stearic acid. From the thermodynamic perspective, the fermentation (acidogenesis and acetogenesis), decomposing the long chain saturated fatty acids to acetic acid though shorter chain acids, could not proceed spontaneously ($\Delta H \gg 0$ and $\Delta G \gg 0$). However the model suggests that the major driving force for the fermentation may be found in the methanogenesis. The model results show two distinct cases: ($\Delta S > 0$ and $\Delta H > 0$) and ($\Delta S < 0$ and $\Delta H < 0$), relating to spontaneous but endothermic and non-spontaneous but exothermic processes respectively. Where, spontaneous digestion is associated with high initial concentrations of LCFA and endotherm. This implies that the digestion of this type of substrate might be better facilitated by the supply of supplemental heat. The digestion of very low concentrations of LCFA is found to be non-spontaneous due in large part to the solubility of carbon dioxide. This implies that the digestion of this type of substrate might be enabled by selectively removing carbon dioxide.

1. Introduction

Lipids, typically the tri-glyceride esters of long chain fatty acids (LCFAs), represent an important fraction of the organic matter in dairy wastewater [1–3], fish waste [4,5], ice-cream wastes [6], oil/fat wastewater [7], slaughterhouse wastewater [8–10] and vegetable waste [11] from food processing industries. The lipids are neither easily decomposed biologically, nor by other conventional means due to their floating on the surface of the wastewater [7]. Alternative disposal through incineration incurs heavy costs due to the energy required to evaporate the high water content.

Anaerobic digestion has been used for many decades to treat the strong organic wastes and to simultaneously produce renewable energy from biogas. The anaerobic digestion of the tri-glyceride esters is achieved by a combination of hydrolytic, fermentative, syntrophic acetogenic (SAB) and methanogenic microorganisms [10,12–14]. The tri-glyceride esters are hydrolyzed to glycerol and LCFA. Vavilin et al. [15] and Batstone et al. [16] set out in some detail a mechanism for the hydrolysis in which anaerobes (effective catalysts) attach to a complex particle, where they produce extra-cellular enzymes to hydrolyze the solid matter and then they use the soluble products released as substrates. Glycerol is fermented to a variety of short chain fatty acids and alcohols. Novak and Broughton [17,18] suggest that SAB degrade LCFAs to acetate via shorter chain fatty acids (β-oxidation) and then require methanogenic bacteria to remove inhibitory levels of acetate, formate and hydrogen produced.

In recent years much attention has focused on LCFA degradation due to its perceived status as the "limiting step" [18] of the anaerobic digestion processes. Many researchers [19–23] explained that the limiting step is closely related to initial concentration of LCFAs and therefore high concentration of LCFA leads to the failure of anaerobic digesters. Some researchers [8,24–26] attribute the failure mainly to the microbial flocs floating on the surface and LCFAs inhibition of anaerobic microorganisms. The inhibition mechanism described by a few researchers [10,27,28] is the result of the adsorption of the LCFAs onto the cell wall and membrane affecting the metabolic processes of transportation.

A few researchers [20,29–36] reported anaerobic short chain fatty acids degradation showing product inhibition when the system is close to the equilibrium point ($\Delta G = 0$). The observations suggest that a thermodynamic study needs to demonstrate the equilibrium condition more generally. Thus we are in particular concerned with the thermodynamics for linear saturated fatty acid degradation.

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In the present work, thermodynamic laws are applied to the anaerobic digestion process so that a quantitative study of the energy transformations that occur between functional living organisms and the physicochemical processes of their environment can be made. This thermodynamic analysis will highlight fundamental reasons for "inhibition" by substrate and product. Linear saturated fatty acid degradation is modeled and we assume the biological oxidations and reductions occur in a 1 l, batch anaerobic digester and progress to equilibrium.

2. Model development

The thermodynamic equilibrium model of anaerobic digestion is built up from fundamental stoichiometric foundations. The stoichiometric foundations are linked by equilibrium relationships which are quantified by relationships between activity/fugacity and observable concentrations. Three types of model for the relationships can be considered: Ideal model; Debye–Hückel model and Pitzer model. Their applicability relating to ionic strength is shown in Table 1. We assume a two-phased (solution/gas) digester which the solution phase is "ideal" whilst the gas phase is "non-ideal". This assumption results from the observation of Oh and Martin's [37], which showed that end-products, non-polar and high polar gases, are vaporised and that the vaporisation is key to substrate degradation. The substrate is almost completely degraded leaving few residuals. This explicitly means that the value of ionic strength at equilibrium is also very small and is close to that required by the ideal dilute solution model.

The set of equilibrium relationships comprises of phase, electrolyte ionisation and redox equilibria. The three subsets of non-linear equilibrium relationships are restricted by strict elemental mass balances. The completed model consists of a set of highly non-linear simultaneous equations which was solved using an algorithm based on the Newton–Raphson technique [38]. The following sections describe the development of the individual components of the model.

2.1. Stoichiometric model

To establish the framework of the thermodynamic equilibrium model for anaerobic linear fatty acids degradation, the first step is to build up the feasible stoichiometric relationships between reactants and products. Table 2 shows the basic stoichiometric relationships for butyric acid degradation. Linear fatty acids are considered from acetic acid (CH_3COOH) to stearic acid ($CH_3(CH_2)_{16}COOH$). For each additional acid considered, stoichiometric relationships equivalent to the last line of Table 2 are added to the model. These stoichiometric relationships are categorized by three equilibrium relationships which are phase transitions, electrolytes and redox reaction.

2.2. Equilibrium relationships

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

$$\sum \nu_i \mu_i = 0 \tag{1}$$

where ν_i is stoichiometric coefficient of component i and the chemical potential μ_i is expressed as the standard chemical potential μ_i° and activity a_i of component i;

$$\mu_i = \mu_i^\circ + RT \ln a_i \tag{2}$$

where R is universal gas constant and T is absolute temperature. By substituting Eq. (2) into Eq. (1) we obtain the fundamental definition of the equilibrium constant, K.

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

The definition of K in Eq. (3) can be applied to each equilibrium in the anaerobic digestion process. We categorized the set of equilibrium relationships into three types: vapor/liquid, electrolyte ionisation and redox.

2.2.1. Vapor/liquid equilibrium

The vapor/liquid equilibrium is defined by the chemical potentials for the component i in the two phases.

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

Table 1
Individual ion activity coefficient models.

Activity coefficient	Equations	Ionic strength
Ideal model	$\ln \gamma_i = 0$	Dilute solution
Debye–Hückel model	$\ln \gamma_i = -Az_i^2\sqrt{I}$	<0.005
Pitzer model	$\ln \gamma_i = -Az_i^2\sqrt{I}\,f^r + 2\sum_{j\neq H_2O} m_j B_{ij} + z_i^2 \sum_{j\neq H_2O}\sum_{j\neq H_2O} m_j m_k B^1$	<6

Note: A: Debye–Hückel coefficient; z_i: ion charge; f^r, B_{ij} and B^1: Pitzer interaction parameters; I: ionic strength.

Table 2
Example stoichiometric model for butyric acid degradation.

Phase transitions Vapor/water	Electrolyte relations	Redox half reactions
$H_2O\ (g) \leftrightarrows H_2O\ (l)$	$H_2O\ (l) \leftrightarrows H^+ + OH^-$	
$H_2\ (g) \leftrightarrows H_2\ (aq)$		$H_2\ (aq) \leftrightarrows 2H^+ + 2e^-$
$CO_2\ (g) \leftrightarrows CO_2\ (aq)$	$CO_2\ (aq) + H_2O \leftrightarrows H_2CO_3$	
$CH_4\ (g) \leftrightarrows CH_4\ (aq)$	$CO_2\ (aq) + H_2O \leftrightarrows HCO_3^- + H^+$	$CH_4\ (aq) + 2H_2O \leftrightarrows CO_2\ (aq) + 8H^+ + 8e^-$
	$CO_2\ (aq) + H_2O \leftrightarrows CO_3^{-2} + 2H^+$	
	$C_2H_4O_2\ (aq) \leftrightarrows C_2H_3O_2^- + H^+$	$C_2H_4O_2\ (aq) + 2H_2O \leftrightarrows 2CO_2\ (aq) + 8H^+ + 8e^-$
	$C_3H_6O_2\ (aq) \leftrightarrows C_3H_5O_2^- + H^+$	$C_3H_6O_2\ (aq) + 2H_2O \leftrightarrows C_2H_4O_2\ (aq) + CO_2\ (aq) + 6H^+ + 6e^-$
	$C_4H_8O_2\ (aq) \leftrightarrows C_4H_7O_2^- + H^+$	$C_4H_8O_2\ (aq) + 2H_2O \leftrightarrows 2C_2H_4O_2\ (aq) + 4H^+ + 4e^-$