Mathematical modeling of solid-state anaerobic digestion: a review

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Abstract: Solid-state anaerobic digestion (SS-AD) technology for the conversion of solid organic wastes to renewable energy has been widely studied and applied during the past decades. Due to the nature of the solid medium, the SS-AD process is significantly different from the traditional liquid anaerobic digestion in many aspects, such as the distribution of microbes and substrates in the reactors, mass transfer, and reaction kinetics. Extensive efforts have been dedicated to developing mathematical models for understanding SS-AD mechanisms, predicting its performance, and improving process control. In this review, SS-AD mathematical models derived from theoretical, empirical, and statistical approaches are critically reviewed and discussed regarding their different assumptions, structures, applications, and limitations. Based on this review, it was concluded that significant efforts should be devoted to experimental verification of the model assumptions, measurement of important kinetic parameters specific for SS-AD, and generation of sufficient data for model validation. It is necessary to synergistically improve modeling and experimental approaches in order to gain deeper insight into the SS-AD

21 mechanism. Several promising research directions for the future development of experimental and
22 modeling approaches in SS-AD are proposed.

23 **Keywords:** kinetics, ADM1, SS-AD, bioenergy, methane, biogas

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47 **Abbreviations**

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1 D	One-dimensional
3D	Three-dimensional
AD	Anaerobic digestion
ADM1	Anaerobic Digestion Model No. 1
ANN	Artificial neural network
CFD	Computational fluid dynamics
COD	Chemical oxygen demand
DOC	Dissolved organic carbon
FISH	Fluorescence in situ hybridization
L-AD	Liquid anaerobic digestion
LCFAs	Long chain fatty acids
MLR	Multiple linear regression
NIR	Near infrared spectroscopy
OFMSW	Organic fraction of municipal solid waste
SS-AD	Solid-state anaerobic digestion
SSTR	Semi-continuous stirred tank reactor
TS	Total solids
VFAs	Volatile fatty acids

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50 List of Symbols

a_0, a_m, a_{mm}, a_{mn}	Regression coefficients	
a_i	Model parameters	
A	The surface area of a “reaction front”	cm^2
b_i	Model parameters	
B	The concentration of microbes	g L^{-1}
B_i	The concentration of microbe i	g L^{-1}
D_e	The effective diffusion coefficient of solute in the medium	$\text{cm}^2 \text{d}^{-1}$
D_B	The diffusion coefficient of microbes	$\text{cm}^2 \text{d}^{-1}$
D_G	The diffusion coefficient of biogas	
D_S	The diffusion coefficient of soluble substrate (e.g. acetate)	$\text{cm}^2 \text{d}^{-1}$
D_X	The diffusion coefficients of solid substrate	$\text{cm}^2 \text{d}^{-1}$
$f(s)$	Inhibition of acetate (or total VFAs) to hydrolysis	d^{-1}
F	The expansion rate of a reaction front	m d^{-1}
$g(s)$	Inhibition of acetate (or total VFAs) to microbial growth	d^{-1}
G	The methane production from the system;	g L^{-1}
h	The maximum microbial cell mass concentration that can be reached	mgDOC L^{-1}
k_d	The microbial cell mass decay coefficient	d^{-1}
k_{hi}	The first-order hydrolysis rate constant of substrate i	d^{-1}
k_i	The hydrolysis inhibition coefficient	d^{-1}
K_{S_i}	The half saturation constant of substrate i in Monod equation	g L^{-1}
L	The diffusion length	cm
L_S	The diameter of “seed” (inoculum) particles	cm
L_W	The diameter of “waste” (substrate) particles	cm
q	The volumetric liquid flow rate per unit surface area	$\text{L cm}^{-2} \text{d}^{-1}$
r	The radius of a “reaction front”.	cm
r_d	The diffusion rate of solute	$\text{g L}^{-1} \text{d}^{-1}$
r_i	The hydrolysis rate reduction due to inhibition	$\text{g L}^{-1} \text{d}^{-1}$
$r_{B_i}^g$	The growth rate of a given microbial species i is related to the concentrations of its substrate (S_i , g L^{-1})	$\text{g L}^{-1} \text{d}^{-1}$
$r_{G_i}^f$	The production rate of the gaseous product i .	
$r_{P_i}^f$	The production rate of i (e.g. a certain type of VFAs) in acidogenesis and acetogenesis	$\text{g L}^{-1} \text{d}^{-1}$
$r_{P_i}^h$	The production rate of a given type of hydrolytic product i	$\text{g L}^{-1} \text{d}^{-1}$
$r_{P_j}^h$	The production rate of a given type of hydrolytic product j	$\text{g L}^{-1} \text{d}^{-1}$
r_{S_i}	The rate of the concentration change for a soluble substance i	$\text{g L}^{-1} \text{d}^{-1}$
$r_{S_i}^f$	The consumption rate of i in fermentation to produce VFAs	$\text{g L}^{-1} \text{d}^{-1}$

	and other intermediate products.	
$r_{X_i}^h$	The hydrolysis rate of a solid substrate i	$\text{g L}^{-1} \text{d}^{-1}$
$r_{(\text{CH}_4)\text{max}}$	The maximum methane production rate	$\text{g L}^{-1} \text{d}^{-1}$
$2R$	The initial distance between each “reaction front”	cm
S	The concentration of soluble substrate in the whole system	g L^{-1}
S_i	The concentration of a soluble substrate i in the whole system	g L^{-1}
S'	The sugar concentration inside the microflora	g L^{-1}
S_S	The solute concentrations in the “seed” particles	g L^{-1}
S_W	The solute concentrations in the “waste” particles	g L^{-1}
t	Reaction time	day
V	The volume of the substrate layer around each microflora	L
x_i, x_j	Explanatory variables	
X	The concentration of solid substrate in general	g L^{-1}
X_i	The concentration of a solid substrate i	g L^{-1}
X_{NB}	The concentration of non-biodegradable substrate	mg DOC L^{-1}
X_0	The amount of microbial accessible solid substrate in X_0^{max}	$\text{gCOD/g}_{\text{initialTS}}$
X_0^{max}	The initial value of X	$\text{gCOD/g}_{\text{initialTS}}$
y	Response variable	
Y_{B_i/S_i}	Microbial biomass growth yield coefficient, quantifying the new microbial cell mass that can grow from a unit of substrate mass i	g g^{-1}
$Y_{G/X}$	The methane yield per unit solid substrate consumed	$\text{L}_{\text{CH}_4} \text{mg}^{-1} \text{DOC}_{\text{consumed}}$
Y_{P_j/X_i}	The stoichiometric yield of a hydrolytic product j from the hydrolysis of one unit of i	g g^{-1}
Z	The vertical coordinate of the reactor	cm
α	The fraction of microbial cell mass transferred by liquid flow;	
γ	The mass fraction of methane in biogas	
$\mu_{\text{max},i}$	The maximum specific growth rate coefficient of microbial species i	d^{-1}
μ_{max}^R	The optimal maximum microbial specific growth rate	d^{-1}
χ	A stoichiometric coefficient	
ρ_{max}	The maximum acetate utilization rate	d^{-1}
ω	The actual water content	%
ω_{min}	The minimal water content required for the initiation of bioconversion	%
ω_R	The water holding capacity	%
Γ	A stoichiometric constant	
Σ	Sum	

1. Introduction

1.1 Development of solid-state anaerobic digestion (SS-AD) technology

Anaerobic digestion (AD) is a biological process in which organic matter is decomposed by an assortment of microbes in oxygen-free or oxygen-lean conditions to produce biogas (about 40-70% CH₄ and 30-60% CO₂) [1]. Since the 1990's, increased energy prices, concerns of global warming, as well as the decreasing capacity of landfills, have stimulated development of AD technology to produce renewable energy from various organic wastes, such as the organic fraction of municipal solid waste (OFMSW), sewage sludge, agricultural residues, and energy crops [2-5]. Among these, solid organic waste and lignocellulose biomass were considered to be the major source of feedstock for renewable energy production [6-8]. For example in Germany, the global leader of AD technology, solid organic material contributes two-thirds of the total biogas potential (Fig. 1) [3]. As of 2012, there were 9,766 agricultural-based biogas plants in Europe, with 7,515 in Germany, and these biogas plants mainly used maize silage, sugar beet, lawn grass, crop residues and dedicated energy crops [3;9].

Based on the operating total solids (TS) content, AD process can be divided into liquid-AD (L-AD) systems which operate at TS content of less than 15%, and solid-state AD (SS-AD) systems that operate at TS content higher than 15% [10]. L-AD has been widely applied to treat liquid organic waste, such as sewage sludge, animal manure, and food processing wastewater [11;12]; while SS-AD is suitable to handle solid organic materials, such as yard waste, crop residues, and OFMSW [10;13]. The availability and methane yields for these various substrates have been extensively reviewed [13-15]. Compared with L-AD, SS-AD has the advantages of high solid loading capacity, increased volumetric biogas productivity, and reduced energy needs

for heating the extra water [16]. Moreover, SS-AD is free of stratification problems incurred by floating of fibrous material, and also tolerates inerts, such as sand and stones [17]. Due to these reasons, SS-AD has captured a higher market share of the total installed AD capacity in Europe during the past 20 years, and its dominance has further increased since 2008(Fig. 2)[18;19].

Various SS-AD technologies have been developed during the past 20 years. Some have been successfully commercialized, while most of them are still being evaluated at lab or bench scale [13]. These digesters can be categorized based on the design (vertical, horizontal, inclined), feedstock (single, co-digestion), configurations (one-, two-, multi-stages), modes of operation (batch, continuous, semi-continuous), or operating temperature (psychrophilic, mesophilic, and thermophilic). Biogas injection, internal mechanical agitation, and pre-mixing/recirculation are three commonly adopted methods for mixing. Currently, the majority of SS-AD digesters in Europe operate in one-stage mode feeding a single feedstock at mesophilic temperatures [13;18;19]. Several predominant commercial SS-AD systems are listed in Fig. 3. More details for these technologies, such as installation location and capacity, operating temperature, and retention time, have been reviewed in previous publications [13;20].

1.2 SS-AD modeling efforts

Although believed to be a promising technology with multiple economic and environmental benefits, a major disadvantage of SS-AD compared to L-AD is the relatively low reaction rate[21;22]. One possible reason is attributed to the slow release of the soluble substrates for microbial metabolism due to the retarded hydrolysis of the solid substrate; the other reason is believed to be the difficulty of providing sufficient agitation and thus compromised mass transfer, which reduces the microbial accessibility to substrates and also the dispersion of inhibitors[23-

25]. Thus, more investigation about the mass transfer phenomena in the solid, liquid, and gas phase in SS-AD is required to improve the efficiency of the process.

To date, the operation of SS-AD systems are usually performed empirically, and there is still a lack of mechanistic tools for accurate process control [26]. Experimental studies and optimization for SS-AD are time consuming and costly due to the demand for space, equipment, and labor [27;28]. It is commonly agreed that the application of mathematical models can be used to improve the engineering process, explain the mechanisms, understand the effects and interaction of different operating parameters, and predict system performance [29-31]. Hence, more attention is required for the development of adequate mathematical models for SS-AD.

Different SS-AD models have been developed in the past decades to improve the design of the SS-AD process [29;31;32]; however, there is no review effort devoted to summarizing the mathematical models for SS-AD. Unlike the intensive research dedicated to L-AD modeling, which have converged into a unified framework, namely the Anaerobic Digestion Model No. 1 (ADM1) [33], current theoretical models proposed for SS-AD are diverse (Fig. 4). The reactor designs, mass transfer, reaction kinetics, and rate limiting steps in SS-AD are essentially different from those of the L-AD process [24;34;35]. Thus, SS-AD modeling needs to take these special features into account (Table 1). This review evaluates the mathematical approaches for each SS-AD model based on analysis of their assumptions, derivations, capacities, and limitations. An overview of the models to be discussed was summarized in Table 2. Key areas in SS-AD modeling that require further research are also discussed. It is our intention to offer deep insights into the state-of-the-art of the mathematical models for SS-AD, promote the utilization of SS-AD modeling to enhance process control and optimization, and ultimately facilitate the application of SS-AD for solid waste reduction and renewable energy production.

2. SS-AD models derived from theoretical approaches

The AD process involves a number of sequential and parallel biological reactions that are carried out by various microorganisms working in synergy, as well as multiple physicochemical reactions, such as ion reactions and liquid-gas mass transfer[33;36]. The function of theoretical AD models is to provide a mathematical foundation for modeling the multiple steps of the biological and physicochemical reactions in a structured way, where the concentration dynamics of the solid particulate substrates, soluble substrates, microbes, and end products (biogas) can be simulated in each step of AD.

The AD process is commonly divided into four sequential steps, namely hydrolysis, acidogenesis, acetogenesis, and methanogenesis[10;11] (Fig. 5), while some researchers also proposed to include a step named disintegration before hydrolysis to represent complex particulate substrate disintegration into small substrate particles and inert materials[11;33]. In hydrolysis, the key step in ethanol production from lignocellulosic biomass[11;37], hydrolytic bacteria excrete extracellular enzymes to break down complex polymeric organic matter composed of carbohydrates, proteins, and lipids into soluble hydrolytic products such as sugars, amino acids, and long chain fatty acids (LCFAs) through a process called hydrolysis. These hydrolytic products are subsequently fermented by acidogens into volatile fatty acids (VFAs), H_2 , and CO_2 through a process called acidogenesis[11]. Then, the VFAs and LCFAs are fermented by acetogens into acetate and CO_2 through a process called acetogenesis. Finally, the acetate and H_2/CO_2 produced from previous steps are utilized by acetotrophic and hydrogenotrophic methanogens for methane production, which is called methanogenesis[33]. Some literature did not distinguish acidogenesis from acetogenesis, which was named as a “fermentation” step in

general. This three-step process (Fig. 5) is also commonly used in AD models to reduce the model complexity [38;39] .

The complex AD process can be described by a set of differential equations (Eq. (1) to (6)). The model concept is shown in Fig. 6. The subscript i represents different substances (e.g., cellulose, glucose, acetate), which can be referred to in ADM1[33], where, for example, S_i and B_{A_i} represent the concentration of acetate and acetate consuming microbes, respectively, when i is acetate. The model can be initiated from the hydrolysis of solid substrate, whose degradation kinetics is usually simplified as a first-order equation [33;35;40], namely

$$-r_{X_i}^h = k_{h_i} X_i = \frac{1}{Y_{P_j/X_i}} r_{P_j}^h \quad (1)$$

in which $r_{X_i}^h$ (g L⁻¹ d⁻¹) is the hydrolysis rate of a solid substrate i (e.g., cellulose, protein, lipids); X_i (g L⁻¹) is the concentration of i ; k_{h_i} (d⁻¹) is the hydrolysis rate constant for i ; $r_{P_j}^h$ (g L⁻¹ d⁻¹) is the production rate of a given type of hydrolytic product j (e.g., sugars, amino acids, or LCFAs); and Y_{P_j/X_i} (g g⁻¹) is the stoichiometric yield of a hydrolytic product j from the hydrolysis of one unit of i .

The mass balance for each intermediate substance i in AD systems can be calculated by the sum (Σ) of the real-time difference between the production and consumption of i in various degradation pathways [33]. For instance, the concentration change of a hydrolytic product i (e.g., a certain type of sugars, amino acids, or LCFAs) can be described by Eq. (2),

$$r_{S_i} = \sum r_{P_i}^h - \sum r_{S_i}^f \quad (2)$$

157 where r_{s_i} ($\text{g L}^{-1} \text{d}^{-1}$) is the rate of the concentration change for a soluble substance i ; $r_{p_i}^h$ is the
 158 production rate of i from hydrolysis reaction; and $r_{s_i}^f$ is the consumption rate of i in fermentation
 159 for producing VFAs and other intermediate products.

160 Likewise, the mass balance of the fermentation intermediate i (e.g. VFAs, CO_2 or H_2) can be
 161 described by Eq. (3),

$$r_{s_i} = \sum r_{p_i}^f - \sum r_{s_i}^f \quad (3)$$

162 where $r_{p_i}^f$ and $r_{s_i}^f$ ($\text{g L}^{-1} \text{d}^{-1}$) are the production and consumption rates of i (e.g. a certain type of
 163 VFAs) in acidogenesis and acetogenesis, respectively.

164 For the final gaseous product i (e.g. CH_4 , CO_2) of AD, its production can be expressed by the
 165 sum ($\sum$) of product i from acetotrophic methanogenesis and hydrogenotrophic methanogenesis
 166 pathways (Eq. (4)).

$$r_{G_i}^f = \sum r_{P_i}^f \quad (4)$$

167 where $r_{G_i}^f$ is the production rate of the gaseous product i .

168 Traditionally, the growth rate of microorganisms in AD is expressed by Monod equation (Eq.
 169 (5)) [29],

$$r_{B_i}^g = \mu_{max,i} \frac{S_i B_i}{K_{S_i} + S_i} \quad (5)$$

170 where the growth rate ($r_{B_i}^g$, $\text{g L}^{-1} \text{d}^{-1}$) of a given microbial species i is related to the concentration
 171 of its substrate (S_i , g L^{-1}) and microbial cell mass (B_i , g L^{-1}), with a maximum specific growth
 172 rate coefficient ($\mu_{max,i}$, d^{-1}) and a half saturation constant (K_{S_i} , g L^{-1}). However, it should be

realized that the substrate for the Monod equation should be only limited to those in dissolved form such as hydrolytic products, VFAs, and H₂/CO₂[41]. Various types of inhibition can also be included into Monod equation[29;33;40;42].

Accordingly, the rate of substrate utilization ($r_{S_i}^f$, g L⁻¹ d⁻¹) by this microbial species i can be correlated to that of the microbial growth in the Monod equation (Eq. (5)), with a growth yield coefficient (Y_{B_i/S_i} , g g⁻¹) quantifying the new microbial cell mass that can grow from unit substrate mass as described in Eq.(6). The production rate of this product i ($r_{P_j}^f$, g L⁻¹ d⁻¹) can be modeled to be proportional to the substrate utilization rate with a product yield coefficient (Y_{P_j/S_i} , g g⁻¹) defining the mass of this product can be produced from unit substrate mass consumption.

$$-r_{S_i}^f = \frac{r_{B_i}^g}{Y_{B_i/S_i}} = \frac{r_{P_j}^f}{Y_{P_j/S_i}} \quad (6)$$

In fact, Eqs.(1) to (6) are basic kinetic equations that have been broadly adopted in the development of L-AD modeling systems such as ADM1. These equations also essentially influenced the development of many SS-AD models as indicated by the combinations, derivations, modifications, and simplifications of these basic equations in SS-AD literature. In the following sections, these SS-AD models are reviewed and discussed.

2.1 SS-AD models derived from Anaerobic Digestion Model No.1

The ADM1 proposed by the International Water Association is a structured model system comprising multiple steps, including biochemical and physicochemical reactions involved in AD [33]. The concept of the system is simplified as shown in Fig. 7. The biochemical processes in ADM1 include an initial disintegration step of complex particulate substrates into organic

polymers such as cellulose, proteins, and lipids, then followed by hydrolysis, acidogenesis, acetogenesis, and methanogenesis steps. The physicochemical steps in ADM1 involve the association/dissociation of ions and the mass transfer of methane and other gaseous products from the liquid to the gas phase. After its initial release, ADM1 has been verified and modified by many L-AD researchers as their basis for modeling [40;43]. However, the earliest application of ADM1 to SS-AD has only been traced back to 2011. Currently, three models derived from ADM1 are available to explain phenomena in SS-AD. The different assumptions and results of these models are discussed below.

2.1.1 Modified ADM1

Research by Abbassi-Guendouz et al. [23] attempted to modify ADM1 to study the performance of SS-AD using cardboard as a model substrate with a TS range from 10% to 35%. The modified ADM1 model was first calibrated using methane production data at TS of 10% with most of the parameters adopted from literature. The authors assumed that the first order hydrolysis rate constant in Eq. (1) decreased with the increase of TS content, because it is commonly observed in the SS-AD that the overall reaction rate decreases with TS content [44;45]. However, in order to explain the acidification that occurred at TS of 30% and 35%, the authors further proposed to reduce the volumetric liquid/gas mass transfer coefficient at high TS content to account for the pasty texture of the substrate-biomass mixture, which trapped CO₂, methane, and H₂ in the liquid phase and substantially inhibits methanogens.

Abbassi-Guendouz et al. [23] found that both the hydrolysis rate constant and the volumetric liquid/gas mass transfer coefficient had to be adjusted much lower compared with L-AD in order to fit the experimental data at high TS content. For the assumption about the volumetric

liquid/gas mass transfer coefficient, it is understandable that the lack of mixing, low biogas bubble formation, and low moisture content in SS-AD may reduce the mass transfer coefficient and the specific surface area of the solid-liquid/gas interface. However, according to the authors, the possible reason for the reduction of the hydrolysis rate constant was still unclear. The experimental results in this study revealed that there was no VFA accumulation in reactors at 25% TS or lower, thus VFA inhibition on hydrolysis was precluded. It seems that the reduced hydrolysis rate constant in this study is still hypothetical and has not been verified with third party experimental data or alternative experimental methods [23], such as a direct measurement of the hydrolysis rate and concentrations of dissolved gas in SS-AD. More research is necessary to verify this hypothesis.

2.1.2 Simplified ADM1

As one of the traditional criticisms of ADM1 is its complex model structure and large number of parameters that cannot be easily determined from experiments [46], Bollon et al. [47] simplified ADM1 to specifically address the biochemical steps, particularly acetate uptake kinetics, in SS-AD of OFMSW. The model assumed hydrolysis (Eq. 1) to be the rate limiting step and that all other steps (except for methanogenesis) described in Eqs. (2) and (3) proceeded at the same rate as hydrolysis, thus disintegration, hydrolysis, acidogenesis, and acetogenesis could be combined into Eq. (1) with acetate as the final product. The maximum growth rate and microbial cell mass concentration for methanogens were simplified into one parameter called the “maximum acetate consumption rate”, so that there was no need to determine the microbial concentration. The experiment was carried out using stabilized solid digestate as the matrix and 5 g COD kg⁻¹ acetate as the only carbon source, so that the model only focused on the effect of TS content on acetate utilization, and its calibration did not include the steps from hydrolysis to acetogenesis.

Similar to the modified ADM1 adopted by Abbassi-Guendouz et al. [23], Bollon et al. [47] also proposed that the default values of ADM1 parameters were not suitable for the SS-AD process, but adjustments were proposed for the “maximum acetate utilization rate” and half saturation constant (K_S) in the Monod kinetics (Eq.5) of methanogenesis. Model calibration suggested that the “maximum acetate utilization rate” should decrease with increased TS content, while the value of K_S should increase with the increase of TS. The authors attributed the decreased K_S at high TS content to the diffusion limitations in the solid medium. According to Monod kinetics, K_S is inversely related to the affinity between substrate and microorganisms [48]. Therefore, an increased K_S value at high TS content suggested the reduced accessibility of the substrate to methanogens, and indicated the aggravated diffusion limitation in SS-AD.

2.1.3 Adapted ADM1

Another SS-AD model was proposed by Liotta et al. [49] based on ADM1, which assumed the disintegration rate constant and substrate (i.e. acetate, propionate) uptake rate constants to be linear functions of TS content [49]. The model was calibrated using methane production data from AD of food waste (represents easily digestible substrate) at TS contents of 4.2%, 12.8% and 19.2%, and rice straw (represents recalcitrant substrate) at TS contents of 4.8%, 14.8% and 23.4%. This model was in agreement with the models developed by Abbassi-Guendouz et al. [23] and Bollon et al. [47], who proposed that the hydrolysis rate constant and the half saturation constant decreased, respectively, with the increased TS content in SS-AD. Liotta et al. [49] postulated that the reductions of these kinetic parameters might be caused by the limited mass transfer of soluble products to bacterial sites, which was caused by the lack of water at high TS content.

2.2“Two-particle” model

Unlike the aforementioned ADM1 approaches that treated SS-AD as a homogenous system, the “two-particle” model proposed by Kalyuzhnyi et al. [50] considered SS-AD to be heterogeneous, and postulated the existence of two different types of particles inside the solid mass of SS-AD, namely “seed” and “waste” particles(Fig. 4).The “seed” particles were inoculum with low biodegradability but high methanogenic activity, and the “waste” particles were substrates with high biodegradability but low methanogenic activity. All “seed” and “waste” particles were assumed to be homogenous inside and tightly attached to each other. Hydrolysis and acidogenesisoccurred in the “waste” particles and provided VFAs to the “seed” particles by diffusion of solute (e.g. VFAs, alcohol) in the liquid phase (Fig. 8), while the authors assumed no microbial exchange between particles in this model due to the assumption that no leachate flow occurs in the reactor, thus there is minimal microbial translocation in the solid matrix.

It is noteworthy that this is the first SS-AD model that attempted to incorporate the equation of solute diffusion into the basic model structure. The diffusion rate of VFA was assumed to follow Fick’s law and to be affected by concentration gradientsof VFAs and diameters of “seed” and “waste” particles, as suggested by Eq. (7):

$$r_d = \frac{2D_e(S_S - S_W)}{L_S^2 + L_W^2} \quad (7)$$

where r_d (g L⁻¹s⁻¹) is the diffusion rate of solute; D_e (cm² s⁻¹) is the effective diffusion coefficient of solute in the medium; L_S and L_W (cm) are the diameters of “seed” and “waste” particles, respectively;and S_S and S_W (g L⁻¹) are the solute concentrations in the “seed” and “waste”

particles, respectively. The diffusion coefficient for all solutes was assumed to be $2.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, and L_S and L_W were both chosen to be 0.5 cm.

In this research, the authors concluded that the rate of solute transport and the biodegradability of waste are the two most important factors that influence SS-AD process stability. High diffusion resistance in a solid medium was considered beneficial in reducing the rate of VFAs entering the “seed” particles and, in turn, could mitigate the inhibition of VFA to methanogens. Based on the model simulation, the authors also predicted that a 10% increase in the digestibility of the substrate would cause a substantial pH drop and acidification. As a result, the authors suggested that reactor acidification could be prevented by either reducing the biodegradability of substrates through dilution with poorly degradable materials, or limiting the transport of solute from “waste” to “seed” particles by spatial separation of the two types of particles [50]. This was pioneering work on a qualitative study of SS-AD modeling, although the existence of “seed” and “waste” particles has not been experimentally validated.

2.3 “Reaction front” model

Martin [51;52] proposed a “reaction front” model to describe the poor seeding situations in SS-AD. Similar to the “two-particle” model, the “reaction front” model also depicted a spatial separation of acidogenic zones and methanogenic zones. However, Martin proposed that a “seed” particle is not homogenous but actually a “reaction front” composed of multiple layers (Fig. 4). The outside of the “reaction front” is solid substrate that has been rapidly acidified and its further hydrolysis is inhibited by low pH. Interfacing with the acidified waste is a thin acetogenic zone, in which VFAs are broken down into acetate under severe acid inhibition. Next to the acetogenic zone is a pH buffer zone where methanogenesis is completely inhibited [53]. Inside

300 the buffer zone is a methanogenic zone, where acetate is converted to methane. Finally, inside
301 this methanogenic zone is a core comprised of fully stabilized organic waste. Solutes are
302 assumed to diffuse between zones following Fick's law, and the mass transfer between zones
303 could be rate-limiting for methane production[52].

304 To mathematically calculate the methane production rate in the whole SS-AD reactor with
305 various "reaction fronts", Martin [54] made the following assumptions: (1) the methanogenic
306 "seed" particles are initially evenly distributed in the organic waste on a cubic grid before reaction
307 starts (Fig. 9); (2) the initial diameter of a "seed" particle approximates to zero; (3) the "reaction
308 front" has a constant thickness; (4) the "reaction front" advances at a constant rate; (5) the rate of
309 SS-AD reaction is proportional to the volume of all "reaction fronts".

310 According to this concept model, SS-AD reaction rate should experience an acceleration phase
311 and a deceleration phase due to the changes of the total surface area of "reaction fronts". Martin
312 [54] set the radius of a "reaction front" at time (t) to be r (cm) and the initial distance between
313 each "reaction front" to be $2R$ (cm) (Fig. 9a). Thus, the surface area (A , cm^2) of each "reaction
314 front" can be calculated as $A = 4\pi r^2$. During the acceleration phase ($r < R$), the total "reaction
315 front" surface area increases with the increase of r (Fig. 9a), and so does the overall methane
316 production rate. During the deceleration phase, r exceeds R and each "reaction front" in a cubic
317 seeding pattern starts to merge with six others, and the remaining surface area in each "reaction
318 front" decreases with the increase of r as estimated by Eq. (8) (Fig. 9b). According to this
319 equation, the surface area of each "reaction front" will decrease with further growth of r , and the
320 methane production rate decreases correspondingly:

$$A = 4\pi r^2 - 6\pi(r^2 - R^2) \quad (8)$$

Based on this model, Martin [55] concluded that the initial distribution pattern of the “seed” particles would determine the process kinetics, and a proper seeding technique should produce “ideal seed particles” that are just large enough to accommodate a thick enough buffer layer to resist acidification, and maintain an adequate numbers of methanogenic zones. With an estimation of the maximum possible VFA concentration in AD, Martin calculated that the thickness of the “reaction front” should be over 7 cm for the methanogens to survive and grow under excessive acid production from the surrounding organic waste[56].

This model provided a useful concept to visualize the SS-AD process, especially in large scale digesters with limited inoculum. However, it should be pointed out that the existence of the “reaction front”, especially the existence of distinct zones (Fig. 4), has not been experimentally verified or reported[56]. The model fitness to other SS-AD processes remains to be tested, and further experimental effort is also needed to validate model assumptions.

2.4 Distributed model

Based on previous SS-AD models, Vavilin et al. [25;57] developed a one-dimensional (1D) distributed model that considered mass transfer by both diffusion and leachate flow. This model assumed homogeneity along the horizontal direction in the reactor vessel, while VFA concentrations dynamically changed along the vertical direction due to downward leachate flow. The distributed model employed partial differential equations to include both time and spatial variations. The model structure followed the four AD steps and adopted reaction kinetics similar to Eqs. (1) to (4). However, in this model, acidogenesis and acetogenesis were combined

341 into one step, in which the production rate of acetate is directly correlated with the concentration
 342 of hydrolytic products by a stoichiometric coefficient χ (Eqs. (9) and (10)), assuming that
 343 fermentation is fast enough to immediately convert hydrolytic products to acetate, which inhibits
 344 hydrolysis and methanogenesis at high concentrations (Fig. 10). Both acetate and microbes were
 345 considered to be mobile in this model (Fig. 11), and their concentrations along the vertical
 346 direction of the reactor vessel were modeled as the combined results of diffusion, leachate flow,
 347 substrate utilization, and microbial cell mass decay (Eqs. (10) and (11)):

$$\frac{\partial X}{\partial t} = -k_h X f(S) \quad (9)$$

$$\frac{\partial S}{\partial t} = D_s \frac{\partial^2 S}{\partial Z^2} - q \frac{\partial S}{\partial Z} + \chi k_h X f(S) - \rho_{max} \frac{SB}{K_s + S} g(S) \quad (10)$$

$$\frac{\partial B}{\partial t} = D_B \frac{\partial^2 B}{\partial Z^2} - q \alpha \frac{\partial B}{\partial Z} + Y_{B/S} \rho_{max} \frac{SB}{K_s + S} g(S) - k_d B \quad (11)$$

$$\frac{\partial G}{\partial t} = \gamma (1 - Y_{B/S}) \rho_{max} \frac{SB}{K_s + S} g(S) \quad (12)$$

348 Where X , B , and G (g L^{-1}) are the concentration of solid substrate, and microbes, and gaseous
 349 products, respectively; k_h (d^{-1}) is the first-order hydrolysis rate constant; S (g L^{-1}) is the
 350 concentration of the soluble substrate (acetate in this study) in the whole system; $f(S)$ and $g(S)$ are
 351 the inhibition of acetate to hydrolysis and microbial growth, respectively; Z (cm) represents the
 352 vertical coordinate of the reactor, with the boundary condition defined based on the total length
 353 of the effective volume L ($0 \leq Z \leq L$); D_s and D_B ($\text{cm}^2 \text{d}^{-1}$) are the diffusion coefficients of the
 354 soluble substrate (acetate in this research) and microbes, respectively; q ($\text{L cm}^{-2} \text{d}^{-1}$) is the

volumetric liquid flow rate per unit surface area; χ is the stoichiometric coefficient of different hydrolytic products to acetate; $K_S(\text{g L}^{-1})$ is the half saturation constant of acetate; α is the fraction of microbial cell mass transferred by liquid flow; $Y_{B/S}(\text{g g}^{-1})$ is the methanogen growth yield coefficient over acetate consumption; $\rho_{max}(\text{d}^{-1})$ is the maximum acetate utilization rate; and $k_d(\text{d}^{-1})$ is the microbial cell mass decay coefficient; γ is the mass fraction of methane in biogas.

In Vavilin's following studies, further improvements of the model were proposed by using Contois kinetics for hydrolysis, and splitting the solid substrate X into easily digestible organic matter and recalcitrant organic matter with two different hydrolysis rate constants [34;35]. These two approaches did not significantly increase model complexity, but were especially suitable for lignocellulosic biomass composed of extractives, cellulose, and hemicellulose which have different hydrolysis rates, and for co-digestion systems with both easily digestible substrates and recalcitrant ones.

2.5 Spatial-temporal model

A spatial-temporal model [58] was developed to study the effect of a heterogeneous mass distribution on the SS-AD reaction rate based on the concept of the "reaction front" model and the structure of the distributed model. This model was able to simulate and visually demonstrate how the initial spatial distribution of substrate and inoculum affect the expansion of methanogenic centers in the reactor vessel, by using a three-dimensional (3D) regime with the spatial resolution fine enough to resolve each "reaction front" (Fig. 12). The transition from fresh substrate to stabilized digestate in a given region was assumed to be the result of the advancement of the "reaction front".

376 This spatial-temporal model followed the basic concept of the distributed model (Eqs.(9) to (12))
 377 and included both diffusion and leachate flow for mass transfer, and VFA inhibition was included
 378 as well (Eqs. (13) to (16)). However, Monod kinetics (Eq. (5)) was not adopted by this model to
 379 describe the microbial cell mass growth and VFA uptake for the model simplicity [58].

$$X_t = D_X \Delta X - a_1 q \nabla X - b_1 f(S) X \quad (13)$$

$$S_t = D_S \Delta S - q \nabla S + k_2 X f(S) - b_3 g(S) B \quad (14)$$

$$B_t = D_B \Delta B - a_2 q \nabla B + b_4 g(S) B - b_5 B \quad (15)$$

$$G_t = D_G \Delta G - q \nabla G + b_6 g(S) B \quad (16)$$

380 Where X , S , B , and G (g L^{-1}) are the concentration of solid substrate, soluble substrate, microbes,
 381 and biogas, respectively; t is time; X_t , S_t , B_t , and G_t are functions of t ; $f(S)$ and $g(S)$ are the
 382 inhibition of acetate to hydrolysis and microbial growth, respectively; q ($\text{L m}^{-2} \text{d}^{-1}$) is the
 383 convective velocity of leachate flow, and $q = 0$ in this model; G (g L^{-1}) is the methane production
 384 from the system; a_i and b_i are model parameters, where $a_i > 0$, $b_i > 0$; D_X , D_S and D_B ($\text{cm}^2 \text{d}^{-1}$) are
 385 the diffusion coefficients of solid substrate, soluble substrate, and microbes, respectively; and D_G
 386 (> 0) is the diffusion coefficient of biogas.

387 In order to mathematically depict the changes of substrate and microbial concentrations at each
 388 point within the 3D structure of the SS-AD reactor vessel, the concentrations of X , S , and B at
 389 each time step were calculated separately using an outer iteration loop without simultaneously
 390 solving the partial differential equations [58;59]. This study simulated the expansion of the

“reaction front” in a 3D space for the first time, and demonstrated how initial inoculation size and distribution affect the overall degradation rate of solid waste in SS-AD. While the model simulation is impressive and inspiring, the simulation results were not validated with experimental data.

2.6 Diffusion limitation model

Considering TS to be an essential factor governing SS-AD kinetics, Xu et al. [24] developed a mathematical model to interpret the effect of TS content on AD of lignocellulosic substrates. The foundation of this model was in line with the “two-particle” and “reaction front” concepts as it assumed SS-AD is initiated from numerous pinpoint microflora inoculated into the substrate. During AD, each microflora releases extracellular hydrolytic enzymes into the surrounding substrate layer and converts cellulose and hemicellulose into sugars. These sugars diffuse from the lignocellulosic biomass particles toward the microflora due to concentration gradients, and are consumed by the synergistically congregated microbial communities in each microflora (Fig. 13).

Hydrolysis of lignocellulosic biomass (Eq.(1)) was assumed to be inhibited by hydrolytic products such as glucose, and an empirical equation (Eq. (17)) was proposed for hydrolysis inhibition:

$$r_i = -k_i S \quad (17)$$

where r_i ($\text{g L}^{-1} \text{d}^{-1}$) is the hydrolysis rate reduction due to inhibition; k_i (d^{-1}) is the hydrolysis inhibition coefficient; and S (g L^{-1}) is the concentration of soluble hydrolytic products such as sugars.

411 After hydrolysis, sugars diffuse from the substrate layer to the microflora based on Fick's law
412 (Eq.(18)),

$$r_d = \frac{D_e A}{LV} (S - S') \quad (18)$$

413 in which $r_d(\text{g L}^{-1}\text{d}^{-1})$ is the diffusion rate of sugars; $D_e(\text{cm}^2 \text{s}^{-1})$ is the diffusion coefficient; A
414 (cm^2) is the surface area of the microflora; $L (\mu\text{m})$ is the thickness of the effective zone of
415 enzymatic hydrolysis; $V(\text{L})$ is the volume of the substrate layer around each microflora; and $S'(\text{g}$
416 $\text{L}^{-1})$ is the sugar concentration inside the microflora.

417 Recognizing that model verification was a challenge in all previous SS-AD modeling studies, Xu
418 et al.[24] were able to validate the volumetric methane production rate of the model using
419 experimental data collected from three independent sources. Based on this model, Xu et al. [24]
420 concluded that there is a TS content threshold between 15% and 20%, below which the
421 volumetric methane production rate tends to increase with TS content as governed by the Monod
422 kinetics, but decreases when the TS content exceeds the threshold, due to hydrolysis inhibition
423 caused by the diffusion limitation of sugars. It should be pointed out that, even though Xu et al.
424 [24] exploited multiple sets of experimental data for indirect model verification, some of the
425 assumptions still need to be validated experimentally.

426 Generally, all SS-AD theoretical models need a series of inputs, such as the values of some
427 model-specific initial conditions (e.g., X_0 , B_0 , S_0 , X_0/B_0 ratio) that can be determined from
428 experiments, and kinetic constants (e.g., K_s , μ_{max} , D_e) that can be obtained from model calibration
429 or from literature. The popular kinetics used in these models include the first-order kinetics for
430 hydrolysis (Eq. (1), (9), and (13)), and equations derived from Monod kinetics for microbial

growth/substrate uptake/products generation (Eq. (5), (10-12)). However, these kinetic equations are only mathematical simplifications of complex SS-AD steps and additional modifications are required based on model assumptions. Many publications before 2005 (section 2.2-2.5) proposed various VFA inhibition functions and mass transfer of VFA and microbes in liquid-phase by diffusion or leachate flow [35;57]. All of these models (the “two-particle”, “reaction front”, distributed model, and spatial-temporal model) tried to emphasize the necessity of initial spatial separation of the methanogenic centers from active acidogenic areas at high organic loadings [60;61]. Based on model simulation results in these studies, highly dispersed inoculum and vigorous mixing and leachate recirculation were shown to be unfavorable for SS-AD, because under these conditions, the inoculum particles are more easily to be acidified by the excessive VFAs produced [60]. Following these models, the recent models are mostly focused on the interpretation of the effect of TS content on the methane production rate and ultimate yield, and several important kinetic rate constants are proposed to be influenced by the TS content (section 2.1 and 2.6). Generally, these models emphasized the importance of mass transfer process in SS-AD, and the necessity of incorporating mass transfer in an SS-AD tailored model beyond the scope of previous AD models such as ADM1.

3. SS-AD models derived from empirical approaches

3.1 Logistic model

Most of the SS-AD models introduced above tried to give a theoretical but complex description of the bioconversion mechanism with multiple biochemical reactions and mass transfer processes. However, criticism has arisen that limited experimental measurements cannot lead to reliable determination of so many model parameters [44]. Thus, a much simpler SS-AD model with a

limited number of parameters was proposed by Pommier et al. [44] to predict methane production from SS-AD.

The simplification was made by assuming that (1) only the microbial concentration (B) is responsible for methane production; (2) the growth of microbes is limited by some factors such as the hydrolysis rate and substrate availability; (3) inhibition and the decay of microbes are not considered. The model was developed based on a logistic equation (Eq. (19)) that fits the global shape of the biogas production kinetics in batch SS-AD (Fig. 14), i.e., an initial exponential increase and a final stabilization at a maximal methane production level.

$$\frac{dB}{dt} = \mu_{max} B \left(1 - \frac{X_0^{max} - X}{X_0} \right) \quad (19)$$

where $\mu_{max}(\text{d}^{-1})$ is the maximal specific growth rate; $X(\text{gCOD/g initial TS})$ is the concentration of solid substrate; $X_0^{max}(\text{gCOD/g initial TS})$ is the initial value of X ; and $X_0(\text{gCOD/g initial dry matter})$ is the amount of microbial accessible solid substrate in X_0^{max} .

Pommier et al. [44] postulated that inside the solid substrate, the portion of water that is physically adsorbed to the solid surface and capillaries is not available for biological metabolism and solute transport, thus only the portion of substrate saturated with water is accessible for methane production. Accordingly, they assumed two parameters to be linearly related to moisture content: the microbial maximal specific growth rate μ_{max} , and the amount of accessible organic matter X_0 . The water content (ω) was empirically correlated to μ_{max} and X_0 in Eq. (19) via Eqs. (20) and (21).

$$\mu_{max} = \tau \mu_{max}^R \quad (20)$$

$$X_0 = \tau X_0^{max} \quad (21)$$

Where τ is a function that if $\omega < \omega_{min}$, $\tau = 0$; if $\omega_{min} < \omega < \omega_R$, $\tau = \frac{\omega - \omega_{min}}{\omega_R - \omega_{min}}$; if $\omega > \omega_R$, $\tau = 1$. ω_R is the water holding capacity; μ_{max}^R (d⁻¹) is the optimal maximum specific growth rate; and ω_{min} is the minimal water content required for the initiation of bioconversion.

These equations suggests that if the actual water content ω exceeds the water holding capacity ω_R , all the solid substrate X_0 is accessible to microbes, and the optimal maximum specific growth rate μ_{max}^R can be reached. While below the minimal water content ω_{min} , no bioconversion is possible ($X_0 = 0$ and $\mu_{max} = 0$). When ω ranges between ω_{min} and ω_R , both X_0 and μ_{max} cannot reach their optimal values and are directly proportional to the water content.

This model provided a new perspective on the effect of TS content on SS-AD. The model was calibrated using paper and cardboard as the substrate with TS content ranging from about 6% to 80%. Results showed that the water holding capacity (ω_R) of the substrate was 34% water content, and the minimal water content required for bioconversion (ω_{min}) was 60%. However, some assumptions such as the reduced amount of accessible substrate at low water content need direct validation.

3.2 General kinetic model

Due to the good fit to AD experimental data, a general kinetic model was recently adopted by Fernández et al. [62] and Fdez-Güelfo et al. [31] for SS-AD research (Fig. 14). This model was

488 first proposed for a general fermentation process, and the foundation of this model was based on
 489 the simplified biochemical reaction rate law (Eq.(22))[63]:

490 where k is the rate constant of the process; $X(\text{mgL}^{-1})$ is the concentration of dissolved organic
 491 carbon in solid substrate; $B(\text{mgL}^{-1})$ is the concentration of microbes expressed in dissolved
 492 organic carbon; and Γ is a stoichiometric constant. Accordingly, the following equations can be
 493 derived,

$$\frac{dB}{dt} = (\Gamma - 1)kXB \quad (23)$$

$$-\frac{dX}{dt} = kXB \quad (24)$$

494 With this concept, a general kinetic equation was derived as Eq. (25),

$$-\frac{dX}{dt} = \mu_{max} \frac{(h - X)(X - X_{NB})}{X_0 - X_{NB}} \quad (25)$$

495 where $X_0(\text{mgDOC L}^{-1})$ is the initial solid substrate concentration (DOC stands for dissolved
 496 organic carbon); $X_{NB}(\text{mgDOC L}^{-1})$ is the concentration of non-biodegradable substrate; and h
 497 (mgDOC L^{-1}) is the maximum microbial cell mass concentration that can be reached.

498 By associating the substrate utilization rate in the reactor with the methane production rate, this
 499 integrated model can provide a general kinetics for methane generation in AD as shown in Eq.(26):

$$G = Y_{G/X} \left(\frac{\exp(\emptyset t) - 1}{(1/(h - X_0)) + \exp(\emptyset t)/(X_0 - X_{NB})} \right) \quad (26)$$

500 where $\emptyset = \mu_{max} \frac{h - X_{NB}}{X_0 - X_{NB}}$; G (L L⁻¹) is the total methane produced; and $Y_{G/X}$ (L_{CH₄} mg⁻¹DOC_{consumed})
501 is the methane yield per unit substrate consumed.

502 This model was adopted by Fernández et al. [62] to study the effect of TS content on the SS-AD
503 process. By fitting the model to methane production data from SS-AD experiments with OFMSW
504 at TS of 20% and 30%, Fernández et al. [62] found that μ_{max} at 20% TS (0.265 d⁻¹) was
505 significantly higher than that at 30% TS (0.147 d⁻¹). This mechanism is similar to the models
506 proposed by Abbassi-Guendouz et al. [23], Liotta et al. [49], and Pommier et al. [44], who
507 assumed the TS content to affect the coefficients of microbial growth kinetics. Further studies
508 are required to validate these assumptions.

509 Fdez-Güelfo et al. [31] modified the general kinetic model to study the SS-AD of OFMSW at
510 thermophilic temperature, based on a semi-continuous stirred tank reactor (SSTR). The objectives
511 of this research were to obtain the kinetics parameters under the steady state of SSTR at
512 thermophilic temperature, and then verify the model at non-steady state conditions. Two types of
513 substrates and four different organic loading rates were used for model validation and the
514 ultimate goal of this research was to use the verified model for further process design and
515 optimization. This model might be the first attempt to develop an SS-AD model for a
516 thermophilic and continuous process.

517 The SS-AD empirical models discussed above are modifications of the logistic equation or the
518 modified Gompertz equation, which are two common models used for bioenergy production that

involves microbial growth such as AD, fermentation, and biohydrogen production[64-66]. Both models can obtain important process kinetic parameters such as the lag phase time, maximum growth rate, and ultimate yield potential. However, the modified Gompertz model is purported to have obtained a better fit to experimental data than other sigmoidal microbial growth models such as the Logistic, Richards, Schnute, and Stannard kinetics [64;65;67]. As a result, the modified Gompertz model seems to be more widely used for AD. Currently there have been no direct comparison of the aforementioned sigmoidal microbial growth models for their fit to SS-AD data.

4. SS-AD models derived from statistical approaches

4.1 Simple linear regression models

Besides the theoretical and empirical approaches discussed above, statistical approaches have also been used to predict the system performance in SS-AD under different operating conditions. Compared with the aforementioned models, statistical models do not require a deep understanding of the biological or physicochemical processes, and can be much easier to develop and simpler to use [14;27].

In well controlled AD experiments that have only a few significant explanatory variables, simple linear regression is commonly used to correlate these variables to the response variables. In many previous studies about SS-AD of lignocellulosic biomass, a linear relationship was found between lignin content and methane yield[68]. Enzymatic digestibility of lignocellulosic biomass has also been correlated with methane yield, with an R^2 ranging from 0.86 to 0.99[68-70]. However, given the limited data used in these studies, the coefficients obtained might not be applicable to other studies.

4.2 Multiple linear regression model

A quadratic multiple linear regression(MLR) model was developed by Motte et al. [71]to evaluate how TS content, inoculation ratio, particle size of lignocellulosic biomass, and their interactions affect SS-AD performance (Fig. 15 a). The explanatory variables were represented by x_i and each was associated with a coefficient a_i . Their relationships with each response variables y (CH₄ production, pH, and VFAs, respectively) were analyzed according to Eq.(27). A three level Box-Behnken experimental design was implemented in an SS-AD batch study using wheat straw as a model substrate, with TS from 15% to 25%, an inoculation ratio (substrate to inoculum ratio) from 28 to 47, and particle size from 0.1 to 1.4 mm [71].

$$y = a_0 + \sum_{i=1}^k a_m x_i + \sum_{i=1}^k a_{mm} x_i^2 + \sum_{i=1}^k a_{mn} x_i x_j \quad (27)$$

Where, y is response variable which stands for methane yield, VFA concentration, or pH; x_i, x_j are explanatory variables, including a_0, a_m, a_{mm}, a_{mn}

Motte et al. [71] was able to calculate the contribution of each factor on methane production during the 270 days' SS-AD using statistical approaches. Inoculation ratio, TS, particle size, and the interaction of particle size $\times$ inoculation ratio and particle size $\times$ TS were found to be significant factors ($p < 0.05$). Intriguingly, the effect of inoculation ratio was found to be more predominant during the start-up phase (first 60 days) of SS-AD. During the growing phase, TS content became the main parameter governing methane production. This model revealed the interactions between inoculation ratio, TS, and particle size have significant effects on methane

yield and VFA production, and provided a useful method for identifying influential factors during digester operation.

Another MLR model was developed by Xu et al. [72] for SS-AD of lignocellulosic biomass based on both substrate characteristics and process parameters. In this research, 11 common explanatory variables (inoculation ratio, carbon-to-nitrogen ratio, volatile solids (VS), TS, cellulose, lignin, xylan, extractives, particle size, total ammonia nitrogen, and alkalinity of the inoculum) were analyzed for their correlations with the cumulative methane yield obtained from batch tests. Among these parameters, the inoculation ratio and the contents of lignin, cellulose, and extractives in the substrate were found to be essential in accurately determining the 30-day cumulative methane yield. The interaction between inoculation ratio and lignin content was also found to be significant by MLR analysis. This is the first statistical model in SS-AD that considered both the substrate characteristics and operating parameters. However, only the inoculation ratio was found to be significant in this study due to the limited data available for other operating parameters, such as TS content and temperature.

4.3 Artificial neural network model

Xu et al. [72] compared artificial neural network (ANN) models with MLR models for the prediction of methane yield of lignocellulosic biomass in batch SS-AD using same data sets (Fig. 15 b). Three artificial neural network (ANN) models were established using: (1) 11 commonly measured variables (inoculation ratio, carbon-to-nitrogen ratio, VS, cellulose, lignin, xylan, and extractives, particle size, TS, total ammonia nitrogen, and alkalinity of the inoculum); (2) significant variables identified by MLR, including inoculation ratio and contents of cellulose, lignin and extractives; and (3) easily measurable variables, including inoculation ratio, carbon-to-nitrogen ratio, TS, VS, and particle size. The authors found that for a satisfactory simulation,

both MLR and ANN methods have to use those significant variables, and ANN obtained a better model in terms of the lowest standard error for prediction [72]. Using large number of insignificant variables caused an over-fitting problem and obtained good results in model calibration, while the calibrated model had poor performance when tested with new data[73]. This model attempted to consider both substrate characteristics and operating parameters as explanatory variables, and was the first attempt to use ANN for SS-AD. However, essential data are missing from literature regarding TS and temperature, thus both parameters cannot be included into the model.

Multiple linear regression has been proved to be a useful tool to predict methane yields and biochemical methane potential (BMP) of different substrates based on their chemical compositions[14;28;70;74]. Most of these studies were usually under L-AD conditions with a low TS content, thus are not reviewed in this paper. Analyzing AD processes using MLR can help identify significant variables, and thus achieve the needed monitoring and prediction accuracy with reduced labor and time. According to the literature, although in some AD processes a single parameter, such as lignin content, can be dominant and a simple linear regression is good enough to predict methane yields, in most cases, AD is a complicated process where multiple parameters are required to model the process [73;75-77]. This is especially true when operating parameters of SS-AD are considered in the model.

MLR can be a good option if the explanatory variables are only a few, not significantly redundant, and have a well-understood relationship with the response variables[78]. In contrast, ANN offers the ability to predict system performance from non-linear, redundant, and complicated data inputs, as long as enough data can be obtained for each explanatory variable [73]. As a promising tool for data mining, ANN has been attracting great interest as a predictive

tool for the complicated AD system [79]. However, both linear regression and ANN are black-box models that cannot provide much understanding of SS-AD mechanisms.

5. Conclusion and remarks

5.1 Comparison of different types of models for SS-AD

Mathematical modeling is always an objective-driven exercise. In general, the three most common objectives in using a mathematical model are: (i) understanding system behavior and component interactions; (ii) quantitatively verifying a hypothesis; and (iii) predicting the behavior of the system in the future or under other similar circumstances. SS-AD models derived theoretically, empirically, or statistically have all tried to fulfill one or more of these objectives, and have improved the understanding of different aspects of the process. However, only the first two objectives have been commonly pursued, while the prediction of system behavior is relatively hard to achieve, probably due to the complexity of SS-AD processes, and the limitation of experimental and mathematical instrumentation. Statistically derived models may emphasize prediction of system behavior, and are especially useful when there are a limited number of targeting outputs, while the models are black-box models and might not provide enough information to unveil system mechanisms. On the other hand, theoretical models provide more insight into the complex system mechanism, while simplification is required to find general applications [29;80].

Different SS-AD models are classified and summarized in Table 2 and 3. SS-AD models derived from ADM1 generally assume homogenous and complete mixing in the system, while heterogeneous distribution of inoculum and substrate is assumed in other theoretical SS-AD models. In SS-AD models derived from ADM1 and empirical approaches, TS content was

considered to be an essential factor that directly affect the value of key model parameters, such as the hydrolysis rate constant [23][49], maximum microbial growth rate or half saturation coefficient K_s [44;49;62], or diffusion coefficient [23;24]. Results of statistical modeling of SS-AD also indicating the TS content was an important factor affecting methane production [71;72].

Currently, there is no universal consensus of the best modeling approach for SS-AD. The diversity in SS-AD modeling is much different from the modeling of L-AD, in which a general framework ADM1 proposed by the International Water Association has reached a broad agreement [33]. Based on this critical review, the authors would like to remark that significant progress has been made in understanding SS-AD processes. However, as pointed out by Zhu et al. [81], reaction mechanisms in SS-AD, such as the influences of TS content, substrate composition, temperature, mass transfer, and heat transfer, are still not clear [10]. Further investigation of SS-AD mechanisms is essential for the rational construction of SS-AD mathematical models.

5.2 Limitations and future research

Mathematical models have to be inferred from prior knowledge and experimental data. Hence, the experimental verification for models is of paramount importance. However, one of the major challenges for current SS-AD models is the lack of experimental data. The heterogeneous nature of SS-AD makes it difficult to collect informative experimental data by traditional experimental instrumentations. More experimental studies should be conducted based on the platform of SS-AD to give enough insight into its mechanism. In addition, databases should be established for SS-AD research to better utilize the previously accumulated knowledge contributed by researchers across the world. As can be expected, the utilization of modern experimental and

computational instrumentations is highly promising to be combined with mathematical modeling approaches to study SS-AD, and the following aspects are proposed as future studies.

Experimental verification of SS-AD model assumptions

Assumptions are the foundation of SS-AD model development, and more effective experimental methods should be explored to verify current model assumptions, such as the rate limiting steps, the spatial distribution of microbial consortia and substrate in the reactor vessel, and the changes of substrate metabolic rate constants under different TS contents. The assumption of the heterogeneity of microbial community distribution within the solid substrate of SS-AD may be determined using various 16s/18s ribosomal RNA/DNA gene based biomarkers, and the dynamic changes of the microbial community distribution in the solid substrates may be directly observed by various microscope imaging technologies [82-84]. For example, fluorescence in situ hybridization (FISH) using DNA/RNA based probes combined with epifluorescent light microscopy or confocal laser microscopy can be used to locate and quantify anaerobic microbes in the solid substrate matrix [85-87]; the changes of morphological characteristics of solid substrate during biodegradation can be observed using scanning electron microscopy, transmission electron microscopy, and atomic force microscopy [88]. Using the aforementioned technologies, assumptions about how operating conditions (e.g., TS content and temperature) affect the microbial growth kinetics can also be experimentally determined by correlating the targeted parameters with the behavior of the microbial community and feedstock degradation [22;89;90].

Another important assumption in SS-AD models is related to the rate-limiting steps and reaction pathways, which are widely used for model simplification. However, usually only the final

products (e.g., CH₄) can be measured for model calibration. To verify the model assumptions regarding rate-limiting steps, direct determination of the reaction rate of each intermediate step and substrate metabolic pathways in SS-AD can be done using isotope-labeled substrates, such as ¹H and ¹³C labeled glucose, cellulose, starch and organic acids[91;92]. Subsequently, nuclear magnetic resonance (NMR) spectroscopy can be used to trace the degradation of these isotope-labeled substrates [92;93]. The concentrations of substrates and inhibitors, such as VFAs, can be measured in situ using near infrared spectroscopy (NIR) and correlated with the in situ distribution of microbes [82;94].

It should be noted that due to the solid nature of the SS-AD medium, established analytical techniques used for similar systems, such as soil[95], rumen[85;87;88;96], solid-state fungi pretreatment of lignocellulosic biomass [84], compost[97], and solid state fermentation[98;99], could be adopted as useful experimental tools for the verification of SS-AD model assumptions.

Determination of important model coefficients

A major problem that arises is that most of the parameters in SS-AD modeling were obtained from L-AD literature without verifying the reliability, and many key parameters were arbitrarily chosen. The diffusion coefficient (D_e) of solute in SS-AD is an example. This is an essential parameter that primarily differentiates SS-AD from L-AD in kinetic modeling. However, a broad range of values have been used in current SS-AD models without experimental verification. The diffusion coefficients determined in powder technology for porous media and related methods can also be referred for the determination of D_e of solutes in SS-AD. Kalyuzhnyi et al. [50] adopted the value of $2.00 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for the diffusion coefficient; Vavilin et al. [25] used the

value of $1.73 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$; Eberl[59] chose the value to be $2.78 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$; and Xu et al. [24] estimated it to be in a range up to $10^{-7} \text{ cm}^2 \text{ s}^{-1}$ with TS increases. As a matter of fact, the work by Bollon et al. [100] might be the only study that experimentally estimated the magnitude of the effective diffusion coefficient in SS-AD. Using a potassium iodide tracer, they found the coefficient to be around $1 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, which was 200 times smaller than that in pure water ($1.98 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$). However, the diffusion coefficient of inorganic salts can be very different from that of the actual organic substances in SS-AD, such as sugars, VFAs, enzymes, and microbes. The direct measurement of the D_e of those intermediate products in SS-AD can be challenging as they are bioconvertable. Further studies are necessary to develop appropriate tracers to simulate the diffusion of organic molecules in SS-AD for accurate determination of the diffusion coefficient. Candidate tracers include those that have been used for fluorescence recovery after photo-bleaching [101;102], or radioactive tracers that measure solute migration through barriers [103].

Determination of actual concentration of solutes

There are usually three physicochemical processes involved in AD: (1) liquid-liquid reactions (i.e. ion association/dissociation); (2) gas-liquid mass transfer; and (3) liquid-solid transformations (i.e. precipitation and solubilization) [33]. However, the third process is typically ignored in L-AD model development, which is understandable due to its highly diluted nature. However, precipitation might become essential in SS-AD when the water content is so low that the solutes can easily reach saturation. Calculation of the actual solute concentrations and their ionic forms in the liquid phase of the SS-AD medium might be essential for accurate determination of the medium pH and the concentrations of soluble substrates and inhibitors, which are important factors affecting biogas production of SS-AD. Due to the difference of densities between

714 substrate and inoculum, the change of inoculation ratio also affects the operational volume of
715 SS-AD reactor which should be considered in the modeling.

716 Development of inhibition functions for SS-AD

717 Another important aspect that needs further study in SS-AD is the inhibition kinetics. Most of the
718 inhibition functions in SS-AD models are adopted from L-AD studies, assuming no concentration
719 gradients within the entire reactor. In SS-AD systems, the lack of mixing may cause aggravated
720 accumulation of inhibitors in the solid medium. Hence, high concentration gradients and uneven
721 distribution of various inhibitors may exist in reactors. In this regard, the microbial tolerance to
722 inhibitors might be significantly different in SS-AD in comparison with L-AD[42;66], and the
723 inhibition functions for SS-AD need further evaluation.

724 Models for scaled-up applications

725 Further efforts should be also devoted to the modeling of scaled-up SS-AD processes. To-date,
726 most of the SS-AD models were developed based on lab-scale studies, while the scaled-up SS-
727 AD systems are expected to experience significantly more heterogeneity in mass distribution and
728 heat transfer. Although some models have considered vertical leachate flow, none of the existing
729 SS-AD models have taken heat transfer into consideration[104]. In addition, most of the current
730 SS-AD models are based on the batch process, and only one empirical model was found to
731 simulate continuous SS-AD during startup and steady state[31]. Limited information was found
732 for the kinetic parameters in the thermophilic SS-AD process, which was reported to be more
733 sensitive to environmental changes and difficult to control. As both continuous and thermophilic
734 SS-AD processes comprise a significant share in the SS-AD market[19], more modeling effort
735 should be devoted to these types of processes.

Combination of different approaches for SS-AD modelling

Theoretical, empirical, and statistical models can be combined to more accurately model SS-AD process. The empirical/statistical approaches can be used to determine some key model parameters such as the coefficients for microbial growth and mass transfer. The mechanisms obtained from the theoretical modelling can also guide the development of regression models in the empirical/statistical modeling to improve the accuracy and capability of the models. These models can be incorporated with computational fluid dynamics (CFD) models. CFD provides a useful tool to model mass and heat transfer in AD, and it is especially useful to simulate the mass transfer in a three-phase system like SS-AD, which is composed of solid, liquid, and gas phases. CFD has been successfully used for L-AD systems [105], large scale bio-ethanol fermentations [106], and solid degradation processes such as composting [107]. The theoretical and empirical models can provide the chemical and biological kinetics for each element of the CFD models. With the combination of these kinetic models with the heat and mass transfer equations in CFD models, the biogas production can be predicted to optimize the design and operating parameters of SS-AD systems. CFD could facilitate the better understanding of the SS-AD fundamentals and the application of scaled-up SS-AD systems. In addition, various modeling efforts developed for ethanol fermentation may also provide useful information for SS-AD modeling, due to the similarity of substrates and the process of initial hydrolysis, as well as the three-phases mass transfer between solid, liquid and gas [37;108].

Build-up of shared database for SS-AD modeling

Most of the SS-AD models developed so far lack of cross-verification using data from independent sources. Increased data collection is necessary for future SS-AD model development.

758 Significant amounts of data have been published for L-AD model verification and validation
759 [1;13;35;42], but information available for SS-AD is still relatively limited. Hence, the
760 publication, collection, and analysis of more SS-AD data should be helpful to provide insight to
761 SS-AD model development and validation. Coordination and data sharing between research
762 groups are essential to fully exploit the value of previously published data.

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Reference List

- [1] Frigon J, Guiot S. Biomethane production from starch and lignocellulosic crops: a comparative review. *Biofuel Bioprod Bior* 2010;4(4):447-58.
- [2] McKendry P. Energy production from biomass (part 1): overview of biomass. *Bioresour Technol* 2002;83(1):37-46.
- [3] Weiland P. Biogas production: current state and perspectives. *Appl Microbiol Biot* 2010;85(4):849-60.
- [4] Naik N, Tkachenko E, Wung R. The Anaerobic Digestion of Organic Municipal Solid Waste in California. *Chemistry* 2013;234:5.
- [5] Khalid A, Arshad M, Anjum M, Mahmood T, Dawson L. The anaerobic digestion of solid organic waste. *Waste Manage* 2011;31(8):1737-44.
- [6] Zheng Y, Zhao J, Xu F, Li Y. Pretreatment of lignocellulosic biomass for enhanced biogas production. *Prog Energ Combust Sci* 2014;42:35-53.
- [7] Zhu J, Zhuang X. Conceptual net energy output for biofuel production from lignocellulosic biomass through biorefining. *Prog Energ Combust Sci* 2012;38(4):583-98.
- [8] Bentsen NS, Felby C, Thorsen BJ. Agricultural residue production and potentials for energy and materials services. *Prog Energ Combust Sci* 2014;40:59-73.
- [9] Prządka A. State of the art and future prospects of biogas and biomethane in Europe. European Biogas Association. 2015. Link: http://energyweek.fi/wp-content/uploads/2015/03/2_2_Energy_Gases_Prządka_public.pdf. Date accessed: 6/6/2015.
- [10] Li Y, Park S, Zhu J. Solid-state anaerobic digestion for methane production from organic waste. *Renew Sust Energ Rev* 2011;15(1):821-6.
- [11] Appels L, Baeyens J, Degreè J, Dewil R. Principles and potential of the anaerobic digestion of waste-activated sludge. *Prog Energ Combust Sci* 2008;34(6):755-81.
- [12] Zhang C, Su H, Baeyens J, Tan T. Reviewing the anaerobic digestion of food waste for biogas production. *Renew Sust Energ Rev* 2014;38:383-92.
- [13] Karthikeyan O, Visvanathan C. Bio-energy recovery from high-solid organic substrates by dry anaerobic bio-conversion processes: a review. *Rev Environ Sci Biotechnol* 2013;12(3):257-84.

- [14] Angelidaki I, Alves M, Bolzonella D, Borzacconi L, Campos J, Guwy A, et al. Defining the biomethane potential (BMP) of solid organic wastes and energy crops: a proposed protocol for batch assays. *Water Sci Technol* 2009;59(5):927-34.
- [15] Appels L, Lauwers J, Degreè J, Helsen L, Lievens B, Willems K, et al. Anaerobic digestion in global bio-energy production: Potential and research challenges. *Renew Sust Energ Rev* 2011;15(9):4295-301.
- [16] Guendouz J, Buffière P, Cacho J, Carrère M, Delgenes. Dry anaerobic digestion in batch mode: Design and operation of a laboratory-scale, completely mixed reactor. *Waste Manage* 2010;30(10):1768-71.
- [17] Forster-Carneiro T, Perez M, Romero L, Sales D. Dry-thermophilic anaerobic digestion of organic fraction of the municipal solid waste: Focusing on the inoculum sources. *Bioresour Technol* 2007;98(17):3195-203.
- [18] European Bioplastic. Fact sheet: Anaerobic digestion. 2015. Link: http://en.european-bioplastics.org/wp-content/uploads/2011/04/fs/FactSheet_Anaerobic_Digestion.pdf. Date accessed: 6/8/2015.
- [19] De Baere L, Mattheeuws B. Anaerobic digestion of the organic fraction of municipal solid waste in Europe: status, experience and prospects. *Waste Manage* 2012;3:517-26.
- [20] Rapport J, Zhang R, Jenkins BM, Williams RB. Current anaerobic digestion technologies used for treatment of municipal organic solid waste. University of California, Davis, Contractor Report to the California Integrated Waste Management Board 2008.
- [21] Yang L, Xu F, Ge X, Li Y. Challenges and strategies for solid-state anaerobic digestion of lignocellulosic biomass. *Renew Sust Energ Rev* 2015;44:824-34.
- [22] Abbassi-Guendouz A, Trably E, Hamelin J, Dumas C, Steyer JP, Delgenès J, et al. Microbial community signature of high-solid content methanogenic ecosystems. *Bioresour Technol* 2013;133:256-62.
- [23] Abbassi-Guendouz A, Brockmann D, Trably E, Dumas C, Delgenès J, Steyer J, et al. Total solids content drives high solid anaerobic digestion via mass transfer limitation. *Bioresour Technol* 2012;111(0):55-61.
- [24] Xu F, Wang ZW, Tang L, Li Y. A mass diffusion-based interpretation of the effect of total solids content on solid-state anaerobic digestion of cellulosic biomass. *Bioresour Technol* 2014;167:178-85.
- [25] Vavilin V, Shchelkanov M, Rytov S. Effect of mass transfer on concentration wave propagation during anaerobic digestion of solid waste. *Water Res* 2002;36(9):2405-9.

- 834 [26] Lindmark J, Thorin E, Bel Fdhila R, Dahlquist E. Problems and possibilities with the
835 implementation of simulation and modeling at a biogas plant. International Conference
836 on Applied Energy ICAE 2012, Jul 5-8, 2012, Suzhou, China. 2012.
- 837 [27] Raposo F, Fernández-Cegri V, De la Rubia M, Borja R, Béline F, Cavinato C, et al.
838 Biochemical methane potential (BMP) of solid organic substrates: evaluation of
839 anaerobic biodegradability using data from an international interlaboratory study. J
840 Chem Technol Biotechnol 2011;86(8):1088-98.
- 841 [28] Stromberg S, Nistor M, Liu J. Early prediction of biochemical methane potential
842 through statistical and kinetic modelling of initial gas production. Bioresour Technol
843 2015;(176):233-41.
- 844 [29] Lauwers J, Appels L, Thompson IP, Degreve J, Van Impe JF, Dewil R. Mathematical
845 modelling of anaerobic digestion of biomass and waste: Power and limitations. Prog
846 Energ Combust Sci 2013;39(4):383-402.
- 847 [30] Angelidaki I, Ellegaard L, Ahring BK. A mathematical model for dynamic simulation
848 of anaerobic digestion of complex substrates: focusing on ammonia inhibition.
849 Biotechnol Bioeng 1993;42(2):159-66.
- 850 [31] Fdez-Güelfo LA, Álvarez-Gallego C, Sales D, García LIR. Dry-thermophilic anaerobic
851 digestion of organic fraction of municipal solid waste: Methane production modeling.
852 Waste Manage 2012;32(3):382-8.
- 853 [32] Álvarez J, Otero L, Lema J. A methodology for optimising feed composition for
854 anaerobic co-digestion of agro-industrial wastes. Bioresour Technol 2010;101(4):1153-
855 8.
- 856 [33] Batstone D, Keller J, Angelidaki I, Kalyuzhnyi S, Pavlostathis S, Rozzi A, et al. The
857 IWA Anaerobic Digestion Model No 1(ADM 1). Water Sci Technol 2002;45(10):65-73.
- 858 [34] Vavilin V, Lokshina L, Jokela J, Rintala J. Modeling solid waste decomposition.
859 Bioresour Technol 2004;94(1):69-81.
- 860 [35] Vavilin V, Fernandez B, Palatsi J, Flotats X. Hydrolysis kinetics in anaerobic
861 degradation of particulate organic material: an overview. Waste Manage
862 2008;28(6):939-51.
- 863 [36] Mata-Alvarez J, Macé S, Llabrés P. Anaerobic digestion of organic solid wastes. An
864 overview of research achievements and perspectives. Bioresour Technol 2000;74(1):3-
865 16.
- 866 [37] Kang Q, Appels L, Tan T, Dewil R. Bioethanol from Lignocellulosic Biomass: Current
867 Findings Determine Research Priorities. Sci World J 2014;2014.
- 868 [38] Siegert I, Banks C. The effect of volatile fatty acid additions on the anaerobic digestion
869 of cellulose and glucose in batch reactors. Process Biochem 2005;40(11):3412-8.

- 870 [39] Zhang P, Zeng G, Zhang G, Li Y, Zhang B, Fan M. Anaerobic co-digestion of biosolids
871 and organic fraction of municipal solid waste by sequencing batch process. *Fuel*
872 *Process Technol* 2008;89(4):485-9.
- 873 [40] Batstone D, Keller J, Steyer J. A review of ADM1 extensions, applications, and
874 analysis: 2002-2005. *Water Sci Technol* 2006;54(4):1-10.
- 875 [41] Wang Z, Li Y. A theoretical derivation of the Contois equation for kinetic modeling of
876 the microbial degradation of insoluble substrates. *Biochem Eng J* 2014;82:134-8.
- 877 [42] Chen Y, Cheng J, Creamer K. Inhibition of anaerobic digestion process: A review.
878 *Bioresour Technol* 2008;99(10):4044-64.
- 879 [43] Lee M, Suh C, Ahn Y, Shin H. Variation of ADM1 by using temperature-phased
880 anaerobic digestion (TPAD) operation. *Bioresour Technol* 2009;100(11):2816-22.
- 881 [44] Pommier S, Chenu D, Quintard M, Lefebvre X. A logistic model for the prediction of
882 the influence of water on the solid waste methanization in landfills. *Biotechnol Bioeng*
883 2007 Jun 15;97(3):473-82.
- 884 [45] Le Hyaric R, Chardin C, Benbelkacem H, Bollon J, Bayard R, Escudié R, et al.
885 Influence of substrate concentration and moisture content on the specific methanogenic
886 activity of dry mesophilic municipal solid waste digestate spiked with propionate.
887 *Bioresour Technol* 2011;102(2):822-7.
- 888 [46] Donoso-Bravo A, Mailier J, Martin C, Rodríguez J, Aceves-Lara C, Uwer AV. Model
889 selection, identification and validation in anaerobic digestion: a review. *Water Res*
890 2011;45(17):5347-64.
- 891 [47] Bollon J, Le-Hyarc R, Benbelkacem H, Buffiere P. Development of a kinetic model for
892 anaerobic dry digestion processes: Focus on acetate degradation and moisture content.
893 *Biochem Eng J* 2011;56(3):212-8.
- 894 [48] Liu Y. Overview of some theoretical approaches for derivation of the Monod equation.
895 *Appl Microbiol Biot* 2007;73(6):1241-50.
- 896 [49] Liotta F, Chatellier P, Esposito G, Fabbicino M, Frunzo L, Hullebusch E, et al.
897 Modified ADM1 for dry and semi-dry anaerobic digestion of solid organic waste.
898 *Environ Technol* 2014;36(7):870-80.
- 899 [50] Kalyuzhnyi S, Veeken A, Hamelers B. Two-particle model of anaerobic solid state
900 fermentation. *Water Sci Technol* 2000;41(3):43-50.
- 901 [51] Martin D, Potts L, Heslop V. Reaction mechanisms in solid-state anaerobic digestion: I.
902 The reaction front hypothesis. *Process Saf Environ* 2003;81(3):171-9.
- 903 [52] Martin D. The site of reaction in solid-State digestion: a new hypothesis. *Process Saf*
904 *Environ* 2001;79(1):29-37.

905 [53] Martin D. Mass transfer limitations in solid-state digestion. *Biotechnol Lett*
906 1999;21(9):809-14.

907 [54] Martin D. A novel mathematical model of solid-state digestion. *Biotechnol Lett*
908 2000;22(1).

909 [55] Martin D, Potts L, Heslop V. Reaction mechanisms in solid-state anaerobic digestion: II.
910 The significance of seeding. *Process Saf Environ* 2003;81(3):180-8.

911 [56] Martin D. Thickness of the buffer layer in the 'reaction front' model of solid-state
912 digestion. *Waste Manage* 2003;23(5):411-7.

913 [57] Vavilin V, Rytov S, Lokshina L, Pavlostathis S, Barlaz M. Distributed model of solid
914 waste anaerobic digestion: effects of leachate recirculation and pH adjustment.
915 *Biotechnol Bioeng* 2003;81(1):66-73.

916 [58] Eberl H. Simulation of chemical reaction fronts in anaerobic digestion of solid waste.
917 *Computational Science and Its Applications-CCSA* 2003. Springer; 2003; 503-12.

918 [59] Eberl H. The role of spatio-temporal effects in anaerobic digestion of solid waste.
919 *Nonlinear Anal-Theor* 2005;63(5):e1497-e1505.

920 [60] Vavilin VA, Angelidaki I. Anaerobic degradation of solid material: importance of
921 initiation centers for methanogenesis, mixing intensity, and 2D distributed model.
922 *Biotechnol Bioeng* 2005;89(1):113-22.

923 [61] Vavilin VA, Lokshina LY, Flotats X, Angelidaki I. Anaerobic digestion of solid
924 material: Multidimensional modeling of continuous-flow reactor with non-uniform
925 influent concentration distributions. *Biotechnol Bioeng* 2007;97(2):354-66.

926 [62] Fernández J, Pérez M, Romero L. Kinetics of mesophilic anaerobic digestion of the
927 organic fraction of municipal solid waste: influence of initial total solid concentration.
928 *Bioresour Technol* 2010;101(16):6322-8.

929 [63] Pérez M, Romero L, Sales D. Kinetics of thermophilic anaerobes in fixed-bed reactors.
930 *Chemosphere* 2001;44(5):1201-11.

931 [64] Altas L. Inhibitory effect of heavy metals on methane-producing anaerobic granular
932 sludge. *J Hazard Mater* 2009;162(2-3):1551-6.

933 [65] Mu Y, Yu HQ, Wang G. A kinetic approach to anaerobic hydrogen-producing process.
934 *Water Res* 2007;41(5):1152-60.

935 [66] Wang Z, Xu F, Li Y. Effects of total ammonia nitrogen concentration on solid-state
936 anaerobic digestion of corn stover. *Bioresour Technol* 2013;144:281-7.

937 [67] Zwietering MH, Jongenburger I, Rombouts FM, van 't Riet K. Modeling of the
938 Bacterial Growth Curve. *Appl Environ Microbiol* 1990;56(6):1875-81.

939 [68] Liew L, Shi J, Li Y. Methane production from solid-state anaerobic digestion of
940 lignocellulosic biomass. *Biomass Bioenerg* 2012;46:125-32.

941 [69] Brown D, Shi J, Li Y. Comparison of solid-state to liquid anaerobic digestion of
942 lignocellulosic feedstocks for biogas production. *Bioresour Technol* 2012;124:379-86.

943 [70] Tong X. Methane fermentation of selected lignocellulosic materials. *Biomass*
944 1990;21(4):239-55.

945 [71] Motte J, Escudie R, Bernet N, Delgenes J, Steyer J, Dumas C. Dynamic effect of total
946 solid content, low substrate/inoculum ratio and particle size on solid-state anaerobic
947 digestion. *Bioresour Technol* 2013;144(0):141-8.

948 [72] Xu F, Wang Z-W, Li Y. Predicting the methane yield of lignocellulosic biomass in
949 mesophilic solid-state anaerobic digestion based on feedstock characteristics and
950 process parameters. *Bioresour Technol* 2014;173(0):168-76.

951 [73] Mahanty B, Zafar M, Park HS. Characterization of co-digestion of industrial sludges
952 for biogas production by artificial neural network and statistical regression models.
953 *Environ Technol* 2013;34(13-14):2145-53.

954 [74] Raposo F, De la Rubia MA, Fernández-Cegri V, Borja R. Anaerobic digestion of solid
955 organic substrates in batch mode: An overview relating to methane yields and
956 experimental procedures. *Renew Sust Energ Rev* 2012;16(1):861-77.

957 [75] Sinha S, Bose P, Jawed M, John S, Tare V. Application of neural network for
958 simulation of upflow anaerobic sludge blanket (UASB) reactor performance.
959 *Biotechnol Bioeng* 2002;77(7):806-14.

960 [76] Gunaseelan V. Predicting ultimate methane yields of *Jatropha curcus* and *Morus indica*
961 from their chemical composition. *Bioresour Technol* 2009;100(13):3426-9.

962 [77] Hamed M, Khalafallah M, Hassanien E. Prediction of wastewater treatment plant
963 performance using artificial neural networks. *Environ Modell Softw* 2004;19(10):919-
964 28.

965 [78] Tobias R. An introduction to partial least squares regression. *Proc Ann SAS Users*
966 *Group Int Conf*, 20th, Orlando, FL. 1995;2-5.

967 [79] Ozkaya B, Demir A, Bilgili MS. Neural network prediction model for the methane
968 fraction in biogas from field-scale landfill bioreactors. *Environ Modell Softw*
969 2007;22(6):815-22.

970 [80] Weinrich S, Nelles M. Critical comparison of different model structures for the applied
971 simulation of the anaerobic digestion of agricultural energy crops. *Bioresour Technol*
972 2014;178:306-12.

973 [81] Zhu J, Li W, Shen R. Theoretical models of reaction mechanisms in solid anaerobic
974 digestion: a review. *Adv Mat Res* 2012;347:1247-50.

975 [82] Xu Z, Zhao M, Miao H, Huang Z, Gao S, Ruan W. In situ volatile fatty acids influence
976 biogas generation from kitchen wastes by anaerobic digestion. *Bioresour Technol*
977 2014;163:186-92.

978 [83] Gevaudan G, Hamelin J, Dabert P, Godon JJ, Bernet N. Homogeneity and Synchronous
979 Dynamics of Microbial Communities in Particulate Biofilms: from Major Populations
980 to Minor Groups. *Microbes Environ* 2012;27(2):142-8.

981 [84] Liu L, Qian C, Jiang L, Yu HQ. Direct Three-Dimensional Characterization and
982 Multiscale Visualization of Wheat Straw Deconstruction by White Rot Fungus. *Environ*
983 *Sci Technol* 2014;48(16):9819-25.

984 [85] Yue Z, Li W, Yu H. Application of rumen microorganisms for anaerobic bioconversion
985 of lignocellulosic biomass. *Bioresour Technol* 2013;128:738-44.

986 [86] Song H, Clarke WP, Blackall LL. Concurrent microscopic observations and activity
987 measurements of cellulose hydrolyzing and methanogenic populations during the batch
988 anaerobic digestion of crystalline cellulose. *Biotechnol Bioeng* 2005;91(3):369-78.

989 [87] Kong Y, He M, McAlister T, Seviour R, Forster R. Quantitative fluorescence in situ
990 hybridization of microbial communities in the rumens of cattle fed different diets. *Appl*
991 *Environ Microbiol* 2010;76(20):6933-8.

992 [88] Hu ZH, Liu SY, Yue ZB, Yan LF, Yang MT, Yu HQ. Microscale analysis of in vitro
993 anaerobic degradation of lignocellulosic wastes by rumen microorganisms. *Environ Sci*
994 *Technol* 2007;42(1):276-81.

995 [89] Shi J, Wang Z, Stiverson JA, Yu Z, Li Y. Reactor performance and microbial
996 community dynamics during solid-state anaerobic digestion of corn stover at
997 mesophilic and thermophilic conditions. *Bioresour Technol* 2013;136:574-81.

998 [90] Li Y, Nelson M, Chen P, Graf J, Li Y, Yu Z. Comparison of the microbial communities
999 in solid-state anaerobic digestion (SS-AD) reactors operated at mesophilic and
1000 thermophilic temperatures. *Appl Microbiol Biot* 2014;1-12.

1001 [91] Vavilin V. Equation for isotope accumulation in products and biomass as a way to
1002 reveal the pathways in mesophilic methanol methanization by microbial community.
1003 *Ecol Model* 2010;221(24):2881-6.

1004 [92] Date Y, Iikura T, Yamazawa A, Moriya S, Kikuchi J. Metabolic sequences of anaerobic
1005 fermentation on glucose-based feeding substrates based on correlation analyses of
1006 microbial and metabolite profiling. *Journal Proteome Res* 2012;11(12):5602-10.

1007 [93] Yamazawa A, Iikura T, Shino A, Date Y, Kikuchi J. Solid-, solution-, and gas-state
1008 NMR monitoring of ¹³C-cellulose degradation in an anaerobic microbial ecosystem.
1009 *Molecules* 2013;18(8):9021-33.

1010 [94] Zhang ML, Sheng GP, Mu Y, Li WH, Yu HQ, Harada H, et al. Rapid and accurate
1011 determination of VFAs and ethanol in the effluent of an anaerobic H₂-producing
1012 bioreactor using near-infrared spectroscopy. *Water Res* 2009;43(7):1823-30.

1013 [95] Machinet G, Bertrand I, Chabbert B, Watteau F, Villemin G, Recous S. Soil
1014 biodegradation of maize root residues: Interaction between chemical characteristics and
1015 the presence of colonizing micro-organisms. *Soil Biol Biochem* 2009;41(6):1253-61.

1016 [96] Yue ZB, Yu HQ, Harada H, Li YY. Optimization of anaerobic acidogenesis of an
1017 aquatic plant, *Canna indica* L., by rumen cultures. *Water Res* 2007;41(11):2361-70.

1018 [97] Dresbøll D, Magid J. Structural changes of plant residues during decomposition in a
1019 compost environment. *Bioresour Technol* 2006;97(8):973-81.

1020 [98] Xu W, Huang Z, Zhang X, Li Q, Lu Z, Shi J, et al. Monitoring the microbial
1021 community during solid-state acetic acid fermentation of Zhenjiang aromatic vinegar.
1022 *Food Microbiol* 2011;28(6):1175-81.

1023 [99] Strauber K, Schroder M, Kleinsteuber S. Metabolic and microbial community dynamics
1024 during the hydrolytic and acidogenic fermentation in a leach-bed process. *Energy*
1025 *Sustain Soc* 2012;2(1):1-10.

1026 [100] Bollon J, Benbelkacem H, Gourdon R, Buffiere P. Measurement of diffusion
1027 coefficients in dry anaerobic digestion media. *Chem Eng Sci* 2013;89(0):115-9.

1028 [101] Anissimov Y, Zhao X, Roberts M, Zvyagin A. Fluorescence recovery after photo-
1029 bleaching as a method to determine local diffusion coefficient in the stratum corneum.
1030 *Int J of Pharm* 2012;435(1):93-7.

1031 [102] Sniekers Y, van Donkelaar C. Determining diffusion coefficients in inhomogeneous
1032 tissues using fluorescence recovery after photobleaching. *Biophys J* 2005;89(2):1302-7.

1033 [103] Berne P, Pocachard J. Characterisation of diffusion/permeation properties of materials
1034 by tracer methods. 2006;26(3-4):292-311.

1035 [104] Merlin G, Kohler F, Bouvier M, Lissolo T, Boileau H. Importance of heat transfer in an
1036 anaerobic digestion plant in a continental climate context. *Bioresour Technol*
1037 2012;124:59-67.

1038 [105] Wu B. CFD simulation of mixing for high-solids anaerobic digestion. *Biotechnol*
1039 *Bioeng* 2012;109(8):2116-26.

1040 [106] Zhang HL, Baeyens J, Tan TW. Mixing phenomena in a large-scale fermenter of starch
1041 to bio-ethanol. *Energy* 2012;48(1):380-91.

1042 [107] Sobieski W. Possibility to use the diffusion equation to heat flow modeling in a
1043 composting process. J Appl Comput Sci 2011;19(2):111-23.

1044 [108] Lin Y, Tanaka S. Ethanol fermentation from biomass resources: current state and
1045 prospects. Applied microbiology and biotechnology 2006;69(6):627-42.

1046 [109] Nayono SE. Anaerobic digestion of organic solid waste for energy production. 46 ed.
1047 KIT scientific Publishing; 2010.

1048 [110] ten Brummeler E. Full scale experience with the BIOCEL process. Water Sci Technol
1049 2000;41(3):299-304.
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Figure 1 Biogas potential of AD substrates from different sources in Germany (adapted from Weiland et al. [3])

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Figure 5 Three- or four-step sequential biological reactions that are usually considered in AD models [11].

Figure 6 Basic structure of a complex theoretical model for AD with biological reactions (eq. (1) – (6)) (Adapted from ADM1 [33])

Figure 7 Illustration of SS-AD models derived from ADM1.

Assumptions:

TS content affects some important model kinetic parameters, such as

- Hydrolysis rate content
- Volumetric liquid/gas mass transfer coefficient
- “Maximum acetate utilization rate”
- Half saturation constant in Monod equation

Figure 8 Illustration of the “two particle” model

Assumptions:

- “seed” particles (inoculum B_i) and “waste” particles (substrate X_i) are adjacent to each other
- Intermediate products (S_i) diffuse from “waste” to “seed” for biogas production
- Diffusion rate follows Fick’s law

Figure 9 Illustration of the “reaction front” model at initial stage (a) and decelerating stage when the total surface area decreasing with the merge of adjacent “seed” particles (b) [54]

Assumptions:

- Inoculum are evenly distributed as sphere particles and expand in a content rate F
- Methane production rate is proportional to the total surface area of all inoculum particles

(a)

(b)

1113 **Figure 10** Simplified biological kinetic scheme of anaerobic digestion of solid substrates
 1114 (adapted from Vavilin et al. [60])

1115

Figure 11 Illustration of the distributed model

Diffusion limitation model

Assumptions:

- Microbes (B_i) and intermediate products (S_i) are mobile along the vertical direction (Z) by diffusion and leachate flow
- Homogenous in horizontal direction

1119 **Figure 12** Illustration of the spatial temporal model

1120

Assumptions:

- Heterogeneous distribution of substrate (X) and inoculum (B)
- Inoculum expand within the substrate and the mass transfer is carried out only by diffusion towards all directions

Figure 13 Illustration of the diffusion limitation model

Assumptions:

- Each microflora (B) is surrounded by substrate (X) in the form of crowded small particles
- Intermediate products diffuse in the pores between substrate particles to the microflora
- TS affects the value of effective diffusion co-efficient

Figure 14 Illustration of the empirical models

Assumptions:

- Biogas production follows a sigmoidal microbial growth curve in batch AD
- Some rate constants are affected by operating parameters such as TS and HRT.

Figure 15 Illustration of the linear regression models (a) and the artificial neural network models (b).

Assumptions:

- Linear relationship between SS-AD parameters with digester output

(a)

Assumptions:

- Complex and non-linear relationship between SS-AD parameters with digester output

(b)

1138 **Table 1.** Comparison of L-AD and SS-AD for modeling-related characteristics [10;11;13;15].

	L-AD	SS-AD
Common substrates	Liquid pumpable organic wastes (e.g., sewage sludge, manure, and food waste) usually with smaller particle sizes and higher biodegradability.	Solid organic wastes (e.g., OFMSW, yard trimming, crop residues) usually with higher recalcitrance.
Reactor design	Typical reactors (e.g., continuous stir tank reactor, plug flow reactor, upflow anaerobic sludge blanket reactor) operated at TS content less than 15% with mechanical or hydraulic mixing.	Typical reactors (e.g. single batch reactor) operated at TS content higher than 20% without effective mixing.
Phases of mass transfer	Two phases (liquid-gas)	Three phases (solid-liquid-gas)
Rate of mass transfer	Generally assumed to be homogenous and have a higher mass transfer rate.	Mass transfer is severely limited. Diffusion or convection via leachate flow is assumed as the major forms of mass transfer.
Rate limiting step	Both hydrolysis and methanogenesis can be the rate limiting step.	Hydrolysis is usually assumed to be the rate-limiting step.
Dispersion of inhibitors	More dispersion and sensitive to shock loads	Less dispersion because of less mixing

Table 2 Overview of current SS-AD models

Category	Models	Features/Assumptions	Output					
			X	S	G	B	R(CH ₄) _{max}	pH
Theoretical	• Two-particle [50]	VFAs are produced in waste particles and diffused to seeds particles for methanogenesis.	X	X	X	X		X
	• Reaction front [51;54]	Inoculum advances into the substrate as a “reaction front”, which is composed of buffer, acedogenic, and methanogenic layers.			X		X	
	• Distributed [25;34;57;60;61]	Included vertical mass transfer of VFAs and microbes through diffusion and leachate flow.	X	X	X	X		X
	• Spatial-temporal [58;59]	Simulated the 3D expansion of the methanogenic zones.	X	X	X	X		X
	• Modified ADM1 [23;47;49]	Based on ADM1 assuming homogenous system with modification of key parameters to be TS dependent.	X	X	X	X	X	X
	• Diffusion limitation [24]	Diffusion limitation causes sugar accumulation, which inhibits the hydrolysis of substrates. Effective diffusion co-efficient in SS-AD is TS dependent.	X			X	X	
Empirical	• Logistic [44]	Correlate key parameters of the empirical models with operating conditions, such as TS content, and hydrolytic retention time.	X		X	X		
	• General kinetic [31;62]							
Statistical	• Linear regression	Use extensive experimental data for model envelopment/calibration/validation.	X		X			
	• ANN [68-72]							

1140 X, S, G, B represents concentrations of substrate, intermediate products, biogas, and microbes, respectively; R(CH₄)_{max} is the
 1141 maximum methane production rate.

Table 3 Summary of SS-AD models

Basis	Models	Calibration	Validation/Application	Findings
Theoretical	• Two-particle [50]	Data and constants from literature and assumptions.	Theoretical interpretation based on batch SS-AD of OFMSW.	Reduced waste digestibility and mass transfer rate could potentially reduce the extent of seed acidification in SS-AD.
	• Reaction front [51;54]	Data and constants from literature and assumptions.	Theoretical interpretation based on batch SS-AD of Food waste and shredded paper.	A minimum thickness of the “reaction front” is required to prevent acid inhibition to methanogens.
	• Distributed [25;34;57;60;61]	Data and constants from experiments and literature.	Batch SS-AD of OFMSW, TS of about 27%, with downward leachate flow	The optimum operation strategy for SS-AD is to gradually increase the leachate recirculation rate during the startup.
	• Spatial-temporal [58;59]	Constants from literature and assumptions.	Theoretical interpretation based on batch SS-AD of OFMSW.	Spatial distribution of inoculum significantly affects the rate of substrate degradation.
	• Modified ADM1 [23;47;49]	Experimental data at 10% TS, and data from literature	Theoretical interpretation based on batch AD of cardboard, OFMSW, food waste, rice straw, with TS of 4% to 30%.	Some mass transfer or microbial growth related kinetic coefficients in L-AD need to be adjusted with TS content to fit SS-AD data.
	• Diffusion limitation [24]	Data and constants from experiments and literature	Theoretical interpretation based on batch SS-AD of corn stover with TS range from 1% to 28%, cardboard with TS range from 10% to 35%, and wheat straw with TS range from 15% to 25%.	Reaction rate increases with TS following Monod kinetics until a threshold is reached and then decreased due to diffusion limitation.
Empirical	• Logistic [44]	Data and constants from experiments and literature	Batch/semi-continuous AD of paper, cardboard, and OFMSW, with TS range from 6% to 80%. Experimental data from steady state of semi-continuous SS-AD of OFMSW	The maximal specific growth rate of microbes and substrate accessibility to microbes are related to TS content.
	• General kinetic [31;62]			
Statistical	• Linear regression	Experimental data	Batch SS-AD of lignocellulosic biomass, TS range from 1% to 40%.	Both substrate characteristics and operating parameters affect SS-AD. Operating parameters have complicated relationships with reactor performance.
	• ANN [68-72]			