Anaerobic co-digestion: a critical review of mathematical modelling for performance optimization

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Abstract

Anaerobic co-digestion (AcoD) is a pragmatic approach to simultaneously manage organic wastes and produce renewable energy. This review demonstrates the need for improving AcoD modelling capacities to simulate the complex physicochemical and biochemical processes. Compared to mono-digestion, AcoD is more susceptible to process instability, as it operates at a higher organic loading and significant variation in substrate composition. Data corroborated here reveal that it is essential to model the transient variation in pH and inhibitory intermediates (e.g. ammonia and organic acids) for AcoD optimization. Mechanistic models (based on the AMD1 framework) have become the norm for AcoD modelling. However, key features in current AcoD models, especially relationships between system performance and co-substrates' properties, organic loading, and inhibition mechanisms, remain underdeveloped. It is also necessary to predict biogas quantity and composition as well as biosolids quality by considering the conversion and distribution of sulfur, phosphorus, and nitrogen during AcoD.

Keywords: Anaerobic co-digestion; Biosolids quality; Mathematical modelling; Process stability; Nutrient recovery; Sewage sludge.

1 Introduction

The past 10 years have seen a substantial expansion in anaerobic digestion (AD) applications, particularly co-digestion. The term co-digestion refers to the simultaneous digestion of two or more organic substrates. In comparison to mono-digestion, anaerobic co-digestion (AcoD) offers several advantages such as the

improvement of the balance of nutrients and C/N ratio, alleviation of inhibitory effects due to toxic substances and other inhibitors via dilution and enhancement of methane production kinetics (Mata-Alvarez et al., 2011; Xie et al., 2011). AD plants can co-digest a variety of solid waste substrates to increase biogas production. However, inappropriate selection of co-substrates, co-substrate composition and operating conditions can lead to process instability and significant reduction of methane production. Although pilot-scale and even full-scale AcoD experiments can be designed and performed strategically to provide practical guidelines, there is enormous time required for the start-up of these systems and to reach steady state conditions, letting alone significant capital costs. Therefore, a general co-digestion model is necessary to support full-scale design and operation decisions as well as to assist lab scale and pilot co-digestion research.

Qualitative and quantitative aspects of physico-chemical and biochemical reactions can be included in process models. These range from hydrodynamics and mass transfer to microbial population dynamics in different reactor configurations under different environmental and operating conditions. However, estimating the kinetic constants is a challenging task because AD is a complex multi-stage dynamic process that involves a consortium of microorganism groups. In addition, the microbial community structure can vary in response to changes in substrate composition, intermediates inhibition, organic loading rate (OLR), hydraulic retention time (HRT), sludge retention time (SRT), temperature and reactor configuration. In the case of insoluble substrates, it is further complicated by the lack of a reliable method for quantifying microbial biomass (Yu et al., 2013b). To better understand the status and relative capacity of each model, we undertook a critical review of the literature to characterize the demonstrated model applications on energy production and volatile solid (VS) reduction by AcoD and critical barriers to AcoD technologies that have the potential to contribute to energy-positive wastewater management. Based on available data, the typical performance of the technologies linked with models in terms of operating conditions and process stability was quantified. Seeking a deeper understanding of the mathematical modelling used in each model category, the capacity of existing models to optimize AcoD operation for on-demand bioenergy production, VS reduction and biosolids quality were also evaluated. Furthermore, key knowledge gaps for optimising existing models and the development of new models were identified and discussed. On this basis, a research roadmap for future model developments to comprehensively simulate the AcoD process and its impact on downstream process were proposed. This review aims to provide further insight to the scientific audience interested in the fundamental aspects of AcoD, its

impact on process performance, and its optimisation through mathematical modelling, as well as practitioners interested in AcoD technologies.

2 AcoD of sewage sludge with organic waste

2.1 Current status

Driven by energy security, resource recovery, and environmental protection, scientific and commercial interest in AcoD has grown significantly in recent years. Preferable co-substrates with sewage sludge, digester capacity, operation conditions and process performance in full-scale AcoD studies have been systematically reviewed by Shen et al. (2015). They highlighted a range of potential benefits of co-digestion including higher methane yield, more efficient digester volume utilization, and reduced biosolids production (Shen et al., 2015). In some cases, co-substrate addition can also result in synergistic enhancement of biodegradation of both the main and co-substrate. Nevertheless, data from full scale anaerobic digesters are very scarce. Indeed, most AcoD investigations to date are from laboratory scale studies and their results cannot be readily transferable to full scale operation. Besides, there have been very few pilot and full scale studies on this topic.

The limited number of pilot and full scale studies available in the literature is a major hurdle to the transfer of technological know-how to full scale AcoD implementation. More importantly, there is currently very little capacity in the available models to guide pilot and full scale investigation efforts to strategically target key research needs for full scale implementation. Indeed, AcoD differs significantly from mono-digestion in process intensity (e.g. OLR) as well as substrate composition (e.g. temporal variation, nutrient content, sulfur content, and co-substrate biodegradability).

In the context of wastewater treatment, the primary function of AD is to stabilize sewage sludge prior to land application or landfilling. Biogas production is an attractive component but not always essential in AD plants. As mono-digestion of sewage sludge is usually operated at a low OLR (typically < 1.0 kg VS/m^3/d), the modeling requirements for mono-digestion of sewage sludge are often simplified to include only organic (i.e. COD fractionation and OLR) and hydraulic loading (i.e. HRT) as key inputs while key outputs are VS reduction and biogas production (Figure 1A). As a result, the need to assess process stability is limited, although several indicators (e.g. pH and alkalinity) and intermediate products (e.g. VFAs) have been successfully used to model mono-digestion. As a typical example to illustrate the current mathematical modelling capacity for mono-digestion of sewage sludge, Mendes et al. (2015) conducted a sensitivity analysis to evaluate kinetic parameters, followed by an evaluation of organic shock loading. However, in most mono-digestion studies to date, only pH

inhibition has been incorporated in the mathematical modelling (Mendes et al., 2015). This leads to an oversimplification of complex inhibition mechanisms, and thus most current models cannot accurately predict the AcoD process.

AcoD operation is inherently more complex than mono-digestion. Several critical factors including co-substrate properties and composition, co-substrate induced inhibitions, and OLR can significantly affect the AcoD process. When adding sulfur-rich co-substrates, an unfavorably high H_2S content in biogas can be expected, which can negatively influence subsequent biogas utilization. Such high level of H_2S is due to sulfate reduction processes outcompeting methanogenesis for carbon and energy sources under anaerobic conditions (Barrera et al., 2013). In addition, several inhibitory intermediates can coexist in anaerobic digesters. Recent studies have highlighted the significance of the interplay amongst these inhibitory intermediates, particularly during AcoD operation (García-Gen et al., 2013; Jensen et al., 2014; Zonta et al., 2013). Furthermore, AcoD process generally operates at a much higher OLR and thus is more susceptible to process instability compared to mono-digestion.

In light of the current AD model development and practical applications, necessary inputs and outputs to describe the AcoD process are depicted in Figure 1B. In general, to accommodate co-substrates induced inhibitions and to predict AcoD system performance, co-substrates characterization, co-substrates organic loadings and various inhibition terms are required as key inputs. As such, the AcoD model is expected to produce a large range of outputs, including recommended maximum OLR, optimal main substrate/co-substrate ratios, biogas quality, and process stability related parameters.

2.2 Effect of co-substrate addition on AcoD

Substrate properties and composition are key factors governing the AcoD process. Some substrates such as crude glycerol, fat-oil-grease, and most food waste are readily biodegradable, while several others such as silage and crop residuals have much slower degradation kinetics (Nghiem et al., 2014; Xie et al., 2011). Thus, in some cases, co-digestion can result in a higher methane yield (per unit of VS or COD input) than mono-digestion due to the synergistic effect of the co-substrates (Mata-Alvarez et al., 2011). This synergistic effect is classified as either a boost in specific methane yield or an increase in biogas production kinetics. The former is exemplified by a study by Aichinger et al. (2015), who investigated the AcoD process of sewage sludge and whey. They demonstrated that co-digestion yields more biogas than the sum of the biogas produced from mono-digestion of each substrate (Aichinger et al., 2015). The increase in biogas production kinetics without changing

the ultimate biodegradability during AcoD has also been reported by Astal et al. (2014). They reported that the mitigation of inhibitory compounds, such as long chain fatty acids (LCFA), contributes to such kinetics improvement (Astals et al., 2014). The improvement in biogas production kinetics observed by Astals et al. (2014) is likely associated with dilution of fats due to the addition of co-substrates.

Antagonistic or neutral effects have both been observed during AcoD of sewage sludge and organic waste. Silvestre et al. (2014) reported that increasing grease waste from 27 to 37% at the same OLR (on a COD basis) decreases methane production by more than 40% during thermophilic AcoD of sewage sludge. Their results demonstrate an antagonistic effect possibly due to LCFA inhibition (Silvestre et al., 2014). In a subsequent study when adding co-substrate to more than 1% (v/v), they did not observe any changes in the specific methane yield during mesophilic AcoD of sewage sludge and crude glycerol (Silvestre et al., 2015). This antagonistic effect is not directly related to organic overloading or temperature. Indeed, it is associated mainly with co-substrates' properties and composition (Silvestre et al., 2014).

Co-substrate selection through an enhanced modelling capacity can be an avenue to facilitate synergistic effects and avoid antagonistic effects during AcoD. Preferable co-substrate properties include (i) high buffering capacity to avoid pH shock (Xie et al., 2011), (ii) sufficient nutrients and a balanced C:N ratio to maintain an active methanogenic activity (Wang et al., 2012) and (iii) higher readily biodegradable organic fraction to boost the kinetics of biogas production (Astals et al., 2014). In addition, a low concentration of nitrogenous matter to reduce free ammonia (NH_3) inhibition (Yenigün & Demirel, 2013), and a relatively low sulfur content to suppress the activity of sulfur reducing bacteria (Chen et al., 2008) are also highly desirable co-substrate properties.

2.3 Process performance

2.3.1 Operating conditions

2.3.1.1 Organic loading rates

OLR applied in co-digestion is often much higher than that used in mono-digestion. Thus, OLR is an important parameter to achieve an optimized AcoD process. During mono-digestion of sewage sludge, the impact on process instability is negligible (depicted by a thin arrow in Figure 1A). In contrast, AcoD operates at a much higher OLR value and there is a considerable risk of over loading. Jabeen et al (2015) investigated co-digestion of food waste with rice husk which has low biodegradability. They observed that when increasing OLRs from 5 to 9 kg VS/m^3/d, the corresponding VFA/alkalinity ratio increased from the optimum value of

0.15 to an imbalanced value of 0.94, indicating impending process failure (Jabeen et al., 2015). An optimized AcoD process can be engineered based on optimal VS ratios between substrates under a maximum OLR. Based on an optimal VS ratio of 1:1, Li et al. (2015) recommended the maximum OLR for co-digestion of rice straw and cow manure of 6 kg VS/m^3/d. Organic loading rates greater than 8 kg VS/m^3/d could cause foaming and process instability due to higher acidification risk (Li et al., 2015; Liu et al., 2012). Therefore, there is a need for mathematical modelling to inform a maximum OLR for a stable AcoD process (Figure 1B).

It is noteworthy that the acclimation of microbial communities can be facilitated by a stepwise increase in OLRs (Xie et al., 2012), leading to successful AcoD (Owamah & Izinyon, 2015). Such acclimation may avoid a non-reversible inhibition due to by-products (VFAs or NH_3) formed in the digester at an excess OLR (Owamah & Izinyon, 2015; Xie et al., 2012). Thus uncertainties in mathematical modelling exist due to dynamics and interactions between different functional groups within a diverse microbial community.

2.3.1.2 Hydraulic retention time

HRT can significantly affect the microbial community and biogas yield. Optimum HRT can accommodate varying biochemical reaction kinetics during AD. The optimum HRT value is dependent on several factors including substrate properties and composition, operating conditions and reactor configurations. In general, the HRT needs to be long enough, typically more than 20 days to avoid process instability (e.g. accumulation of VFAs) (Dareioti & Kornaros, 2014). Nevertheless, stable methane production has been reported with HRTs even less than 20 days (Nghiem et al., 2014; Ratanatamskul et al., 2014).

In a continuous stirred tank reactor (CSTR), the biogas yield (y) can be expressed as a function of the maximum biogas yield (y_m), the first order rate constant (k), and the HRT on the basis of a mass balance and a first order kinetics:

$$\mathbf{y} = \frac{\mathbf{HRT \cdot k \cdot y_m}}{\mathbf{HRT \cdot k + 1}} \qquad \text{Eq. 1}$$

The biogas yield y can be expressed as an absolute proportion (p) of y_m (y/y_m) based on Eq. 1. Linke (2006) has derived the relationship between p of y_m and HRT under different k. It can be calculated that about 45 days of HRT is needed to obtain 80% of the maximum biogas yield at the k value of 0.09 d^{-1}.

For a CSTR at steady state, assuming (1) first order kinetics and (2) constant specific biogas production per unit substrate removed, the following equation can be derived to predict the maximum VS reduction (VS_{r0}) and first order hydrolysis rate constant (k).

$$\frac{VS_r}{VS_{r0}} = \frac{k \times HRT}{k \times HRT + 1} \qquad \text{Eq. 2}$$

For example, by curve fitting using a series of VS reduction (VS_r) and HRT, Dai et al (2013) estimated VS_{r0} to be 44.3% and 90.3%, respectively and k to be 0.17 d^{-1} and 0.5 d^{-1}, respectively for dewatered sludge and food waste from long-term semi-continuous experiments. Based on Eq. 2, the minimum HRT to achieve 80% of maximum VS reduction (VS_{r0}) is 24 days for dewatered sludge at k value of 0.17 d^{-1}. In other words, as the HRT increases beyond 24 days, the additional increase in VS reduction is marginal.

2.3.1.3 Temperature

Temperature governs the biogas yield during AD by affecting the thermodynamics of acetogenic and methanogenic reactions. The AcoD process is usually applied under either mesophilic (35~38 °C) or thermophilic (50~70 °C) conditions. At a high temperature, the formation of H_2 from organic acids oxidation becomes more energetically favorable, while the consumption of H_2 by hydrogenotrophic methanogenesis becomes less energetically favorable. The degradation of organic acids under thermophilic conditions is faster and more favorable compared with mesophilic conditions. In general, thermophilic digestion has a higher VS reduction rate and pathogen inactivation compared with mesophilic digestion. Despite these advantages, most anaerobic plants operate under mesophilic conditions due to the risk of system instability under thermophilic conditions. For instance, Montañés et al. (2015) demonstrated that the biodegradation during co-digestion of sewage sludge and sugar beet pulp lixiviation was limited due to high volatile fatty acids (VFAs) concentrations under thermophilic conditions, while complete biodegradation was realized under mesophilic conditions. Moreover, thermophilic digestion also requires more heating and sometimes is not favourable based solely on energy balance considerations.

2.3.2 Process stability: intermediates inhibition

AcoD can significantly enhance biogas production. However, the addition of unsuitable co-substrate or inadequate amount of co-substrate can deteriorate the AcoD system. This may be attributed to intermediates inhibition such as free ammonia, VFAs, and LCFA inhibition. AcoD system may recover after a prolonged periods subjected to the nature and level of inhibition and microorganisms acclimation. Xie et al.(2011) observed reversible inhibition during AcoD of grass silage and concentrated pig manure, and speculated that the phenomenon is likely associated with the combinational effects of high concentrations of NH_3, VFAs and low pH. Nevertheless, accumulation of these intermediates can disrupt the AD process. Thus, rigorous modelling to predict their concentration and inhibition mechanisms is essential particularly when these inhibitory intermediates may be enriched in AcoD process (Figure 1B).

2.3.2.1 Free ammonia

Free ammonia inhibition during AcoD has been investigated more intensively via experimental approaches than mathematical modelling. Co-substrates rich in nitrogenous matter (e.g. proteins and urea) can be degraded into two most predominant forms of inorganic nitrogen: ammonium-*N* (NH_4^+-*N*) and NH_3 during AcoD (Chen et al., 2008). Varying inhibition concentrations of NH_3 and NH_4^+-*N* has also been summarized by Chen et al. (2008). NH_3 is more toxic to methanogens than NH_4^+-*N*, as it can diffuse through the cell membrane, causing potassium deficiency and lower pH due to proton imbalance (Sung & Liu, 2003).

To date, very few studies have been conducted on mathematical modelling of NH_3 inhibition during AcoD, possibly due to the complex factors that affect the inhibition. These factors include differences in co-substrates and inocula, operating conditions (OLRs, HRT and temperature), and microbial acclimation. Modelling of NH_3 inhibition during AcoD has been performed by Angelidaki et al. (1993) with NH_3 and acetate constituting the primary modulating factors in the model, and subsequently García-Gen et al. (2013) based on anaerobic digestion model No 1 (ADM1). In the modified model by García-Gen et al. (2013), only acetoclastic NH_3 inhibition is accounted for during pilot-scale AcoD of pig manure, wine and gelatine at mesophilic conditions. Consistent prediction of gas and liquid composition was achieved (García-Gen et al., 2013). However, the inhibition mechanism used in their study may not be exhaustive as the degree and nature of inhibitions vary under various conditions and circumstances (Wang et al., 2016).

2.3.2.2 Volatile fatty acids

Similar to previous NH_3 inhibition studies discussed above, VFAs inhibition during AcoD has been primarily focused on experimental studies rather than mathematical modelling. As important intermediate products, VFAs are transformed to acetic acid before being converted to CH_4. The conversion rate is larger for butyric acid than propionic acid. The propionic acid to acetic acid ratio can be used as a reliable indicator for digester imbalance, and an propionic acid to acetic acid ratio greater than 1.4 could indicate impending digester failure (Marchaim & Krause, 1993). The activity of methanogens was inhibited to a significant extent when propionic acid and total VFA concentrations reached about 2.9 g/L and 10 g/L, respectively, but this inhibitory effect was weakened when the total VFAs concentration fell to 6.2–8.5 g/L (Wang et al., 2009).

In the available mathematical models VFAs accumulation through overloading during AcoD has been linked directly to acidic pH that causes the inhibition of the methanogens. Accordingly, VFAs inhibition can be greatly reduced in AcoD systems with a good buffering capacity. Indeed, microbial communities, particularly

the indigenous community of methanogenic archaea, can withstand high VFAs concentrations in such an AcoD system (Franke-Whittle et al., 2014). In a complex scenario where additional inhibition mechanisms may exist, an inhibition and non-competitive model for AcoD can be proposed to distinguish the inhibition effect. For example, Jensen et al. (2014) investigated the impacts of organic and hydraulic loads on process performance and microbial community during AcoD of mixed sewage sludge and highly hydrolysable crude glycerol. By using the model, they demonstrated that the inhibition was caused by VFAs accumulation from rapid fermentation of glycerol rather than the presence of toxic compounds in the co-substrate (Jensen et al., 2014).

2.3.2.3 Long chain fatty acids

Addition of lipid rich co-substrates results in formation of intermediate products LCFAs. LCFAs have been identified as the main inhibitory factor during AcoD of sewage sludge and grease waste (Silvestre et al., 2014). At a high LCFAs level, the methanogenic microbial population can be suppressed, leading to VFA accumulation and deteriorate methane production. A key inhibition mechanism of LCFAs is biochemical inhibition on microbial cell membranes, including cell lysis, enzyme activity inhibition and electron transport chain disruption (Ma et al., 2015). The other inhibition mechanism is classified as physical inhibition due to LCFAs adsorption on the surface of microbial cell membranes, leading to mass transfer limitation (Pereira et al., 2004). Zonta et al. (2013) proposed two new LCFA-inhibition models, which can be compatible with the full ADM1 model. In the kinetics model, they include (i) adsorption of LCFA over granular biomass, and (ii) specific LCFA substrate (saturated/unsaturated) and LCFA-degrading populations. A new variable to describe the state of damage of the acetoclastic methanogens is also introduced to account for the inhibition caused by the adsorbed LCFAs. Zonta et al. (2013) successfully developed two distinctive models with the main difference being how the LCFA-inhibitory phenomena on acetoclastic methanogens are expressed: one is through a common non-competitive inhibition function, and the other is through a new variable that accounts directly for the damage of the cell functionality. It has been revealed that the acetoclastic population is more sensitive to the LCFA inhibition than the acidogenic population (Zonta et al., 2013).

3 Mathematical modelling

The available mathematical models for AD and AcoD can be divided into five categories namely basic kinetic models, ADM1, statistical models, computational fluid dynamics (CFD) models and other algorithm approaches. The advantages and limitations of these are summarized in Table 1. There is some overlap between these categories as the mass balance for specific state variables is the basis of all mathematical

models. For example, to predict the methane potential, COD, elemental composition, organic fraction composition and electron transfer can be used in the mass balance.

3.1 Basic kinetics models

AD kinetics models are based on the microbial growth and substrate consumption rates which depend on a growth-limiting substrate concentration. Nutrients are assumed to be sufficient in substrates, and expressions for inhibition can also be included. Some common kinetic expressions depicting the kinetics of AcoD processes are summarized in Table 2. These equations represent the fundamental framework for simulating the AcoD processes.

First order kinetics has been widely applied in anaerobic biodegradation of particulate matter. For example, hydrolysis of substrates in ADM1 is assumed to be a first order reaction (Batstone et al., 2002). In addition, endogenous decay processes are also modelled using first order kinetics (Batstone et al., 2002). Subsequently, the methane production from a mixture of substrates can be simulated following simplified first order kinetics (El-Mashad & Zhang, 2010). Several other kinetic models such as Gompertz and dual pooled first order have also been used to assess methane production during batch co-digestion (Dennehy et al., 2016; Xie et al., 2011). It is noteworthy that due to the high initial VFA content of some substrates, conventional first order and Gompertz models may be inappropriate for determining reaction kinetics, while a dual pooled first order model was found to provide the best fit for the data (Dennehy et al., 2016). Hydrolysis can also be modeled using Contois model, as hydrolysis is considered a biochemical reaction facilitated by extra-cellular enzyme produced by hydrolytic/acidogenic bacteria (Carrera-Chapela et al., 2016). It has been shown that Contois model, which links hydrolytic biomass growth with substrate degradation, works better than the first-order kinetics model (Ramirez et al., 2009a).

Substrate conversion in biological processes commonly applies Monod-type kinetics. The specific growth rate of microorganisms is a function of the substrate concentrations in the Monod equation. Contois expression considers that the substrate concentration in the digestate is dependent on the influent concentration, so that both parameters are independent. It is a key modification from Monod equation. Both models take into account the organic load involved in the process as a fundamental parameter for the reactor performance and have been widely used in the modelling of anaerobic processes (Lokshina et al., 2001).

Several other simplified kinetics models have also been demonstrated for AD in the literature. For instance, Lokshina et al. (2001) evaluated the kinetic coefficients and their standard deviations using the

methane accumulation curves of low-temperature acetoclastic methanogenesis by an integrated Monod and Haldane models. A better fit was obtained with the Haldane models and their exponential approximations for the wide range of initial acetate concentrations (4.2 - 84 mM; 5 - 100 mM) applied to the UASB biomass at 11 and 22 °C and for the lake sediment samples at 6 and 15°C, respectively. At the higher temperature (30 °C) no significant difference was observed between the Haldane and Monod models, thus the Monod model with a simpler expression can be adopted (Lokshina et al., 2001). Hidaka et al. (2015) developed a simplified model based on ADM1, with a few modifications including (1) the model inputs for substrates are determined in terms of degradation speed rather than components (carbohydrates, proteins and lipids), and (2) acetate and hydrogen were considered as one state variable. Given a reasonably close agreement between the model simulation and the experimental results, the authors suggested that the model can be used as a pre-evaluation tool to facilitate the introduction of co-digestion at WWTPs (Hidaka et al., 2015).

Currently available kinetics models may over-simplify the dynamics of rate-limiting steps (Table 1). In other words, the rate-limiting step can be influenced by operating conditions, thus it is unlikely to be constant (Yu et al., 2013b). In addition, in these models the intermediates inhibition cannot serve as the indicator for digester stability as it becomes difficult to estimate when only a single type of microorganism (e.g. acetoclastic methanogens) is considered. Furthermore, basic kinetics models (commonly used for laboratory-scale batch studies) cannot be used to provide direct practical knowledge for full scale AcoD implementation (Table 1). Therefore, these pitfalls prevent further practical application of such models, leading to the development of the more complex mechanistic model ADM1.

3.2 ADM1

3.2.1 Basic principles

The ADM1 model developed by the IWA AD modelling Task Group is arguably the most widely applied model in the research area. It includes five steps: disintegration, hydrolysis, acidogenesis, acetogenesis and methanogensis (Figure 2). The disintegration breaks solid complexes into carbohydrates, lipids, proteins and inert material (soluble and particulate inert). These substances are subjected to enzymatic hydrolysis, forming sugars, amino acids and LCFA. It is followed by acidogenesis, where sugars and amino acids are fermented to produce VFAs, hydrogen and carbon dioxide, and acetogenesis, where LCFA, propionic acid, butyric acid and valeric acid are anaerobically oxidized into acetate, carbon dioxide and hydrogen. The last step

involves the acetoclastic methanogenesis, where acetate is converted to methane and carbon dioxide, and hydrogenotrophic methanogenesis, where carbon dioxide is reduced by molecular hydrogen to form methane.

ADM1 includes (1) 19 biochemical processes, of which 4 equations capture particulate matter degradation, 8 equations describe soluble matter degradation and 7 equations represent biomass concentrations; (2) 6 acid/base equilibria in association with pH calculation; (3) 3 gas-liquid transfer processes (CH_4, CO_2, H_2), (4) inhibitions, and (5) a number of variables, of which 12 variables represent particulates (X_i), 24 variables represent soluble (S_i) and 3 variables represent gases. The ADM1 model starts with the disintegration of composite particulate materials (i.e. decomposition of feed or decaying biosolids according to their predefined fractions and composition of carbohydrates, proteins, fat (lipids) and inerts). The second step is enzymatic hydrolysis of disintegrated carbohydrates, proteins and fat (lipids), which is the start of the corresponding five pathways of anaerobic degradation. These first two degradation steps are modeled using uptake kinetics of different substrates by seven bacterial groups. The decay processes of the seven bacterial groups are also considered and the decaying particulates are sent back to the disintegration step.

3.2.2 Parameter estimation, calibration and model validation

Two procedures govern the successful implementation of modelling work: (1) well defined substrate composition in relation to the model input state variables, and (2) calibration process, particularly for the sensitive parameters. In ADM1, the input COD fractionation is divided into 13 components, 11 of which are associated with biodegradable components. These components are: composite substrate (X_c); polymers: carbohydrate (X_{ch}), proteins (X_{pr}), and lipids (X_{li}); monomers: sugars (S_{su}), amino acids (S_{aa}), and long chain fatty acids (S_{fa}); VFAs: butyrate (S_{bu}), valerate (S_{va}), propionate (S_{pro}) and acetate (S_{ac}); inert COD: soluble fraction (S_i) and particulate fraction (X_i). Thus rigorous determinations of the substrate characterization and kinetics parameters regarding the disintegration and hydrolysis phases can be performed prior to the numerical simulation. As such, Girault et al. (2012) proposed a framework for the numerical determination of the set of ADM1 input state variables for each substrate. Briefly, VFA-fractions were directly measured (Step 1); the concentration of the biodegradable fractions and the hydrolysis rate constant were optimized through curve fitting (Step 2); the individual COD fraction (for which hydrolysis is not rate limiting) was then calibrated based on the best simulation of the complete curve (Step 3); and the inert COD was determined by the total COD balance (Step 4) (Girault et al., 2012). Although the numerical method is easy to implement for a wide range of

substrates, fractions of solid waste mixture as ADM1 model input have been usually carried out experimentally (Klimiuk et al., 2015; Mottet et al., 2013; Razaviarani & Buchanan, 2015).

The kinetics parameters concerning the disintegration and hydrolysis phases during AcoD are also estimated and calibrated prior to the implementation of ADM1 simulation (Razaviarani & Buchanan, 2015). Derbal et al. (2009) estimated the constants for disintegration and hydrolysis of carbohydrates, proteins and lipids (K_{dis}, $K_{hyd.Ch}$, $K_{hyd.Pr}$, and $K_{hyd.Li}$) in their study, and found they were equal to typical values reported in the literature for biowaste. It is controversial to apply kinetic parameters estimated from lab-scale experiments to the modeling of full-scale digesters, as demonstrated by Batstone et al. (2009) that the first order hydrolysis rate constant (k_{hyd}) obtained from anaerobic batch tests are not appropriate when applied to continuous digester modelling. This could be largely attributed to the simple disintegration step of a homogeneous substrate (X_c) simulated by a single kinetic parameter within ADM1 model. As such, Mottet et al. (2013) modified ADM1 model using a new disintegration/hydrolysis structure and implemented two hydrolysable composite fractions of sewage sludge (i.e. a readily hydrolysable fraction and a slowly hydrolysable fraction). Mottet et al. (2013) used anaerobic batch tests to calibrate model kinetic parameters and biomass concentrations. The model was then validated against the same substrate subjected to a thermal pretreatment. They observed that the model was representative in terms of methane production following the intrinsic changes of the waste active sludge composition through the different thermal pretreatment conditions as well as in a continuous full-scale anaerobic digester (Mottet et al., 2013).

3.2.3 Extensions and modifications

Notable extensions and modifications have been made to ADM1 to broaden the capacity to predict the AcoD process and to take into account the toxic effects of inhibitory substances from co-substrates and intermediates. Modifications to the current ADM1 model are necessary to solve characterization of the substrates and definitions for disintegration and enzymatic hydrolysis steps (García-Gen et al., 2013; García-Gen et al., 2015; Shi et al., 2014; Zaher et al., 2009). Other extensions and modifications for ADM1 include degradation of new soluble fermentable substrates (García-Gen et al., 2013), organic contaminants degradation (Fezzani & Ben Cheikh, 2009), disintegration of organic waste solids using surface-based kinetics model (Esposito et al., 2011a) and VFAs inhibition (Boubaker & Ridha, 2008). Recently, Flores-Alsina et al (2016) extended the ADM1 with P, S and Fe biological and physico-chemical reactions. This important extension considers (1) potential uptake of organics by X_{PAO} to form X_{PHA} affecting overall biogas production, (2)

substrates with high S content leading to H_2S formation and (3) the proportioning of soluble and particulate P in the digester outlet affected by the cationic load, which is linked to pH and precipitation of minerals.

Co-substrates are heterogenic and dynamically changing in composition. Thus, parameter estimation problems and use of fraction parameters can be avoided through a dynamic interface to ADM1, which is a general transformer model for any combination of co-substrates. Zaher et al. (2009) employed models integrated in General Integrated Solid Waste Co-Digestion model (GISCOD). They successfully developed transformer model nodes which generate input for ADM1 by estimating the particulate waste fractions, while hydrolysis nodes were modeled separately for each substrate. The authors applied the integrated model to a co-digestion study of diluted dairy manure and kitchen wastes, demonstrating reliable simulation results in terms of process optimization (Zaher et al., 2009). The AD process was modeled using the ADM1 (Batstone et al., 2002) as a basis with phased implementation to separate the enzymatic hydrolysis of solid wastes from the metabolic reactions utilizing soluble substrates. García-Gen et al. (2015) developed a methodology to estimate disintegration and hydrolysis kinetic parameters of solid wastes and validate an ADM1-based AcoD model. Fractions of substrates were divided into readily and slowly biodegradable fractions. The model was calibrated against batch reactor experiments treating individual fruit and vegetable waste fraction of solid waste. Validation of kinetic coefficients was performed using a continuous co-digestion experiment. Finally, simulation of batch and continuous experiments was carried out with a modified ADM1-based model. It is noteworthy that GISCOD allows for a dynamic changing input, but it is quite complex. In contrast, the fractionation approach is very straightforward to implement, but it is less accurate.

3.2.4 Limitations

Several limitations in ADM1 model have been acknowledged in the literature. LCFA inhibition, which has a significant impact on the AcoD process, has been systematically investigated by Zonta et al., (2013). However, to date this feature has not been considered in the ADM1 model for AcoD. Indeed, the inherent features in the ADM1 model, such as the requirement to understand and estimate kinetic parameters for the various bacterial groups present in the reactor and a very ponderous amount of substrate characterization could hinder its practicality for full-scale simulation. Furthermore, the mechanism of the disintegration and hydrolysis of solid substrates is a notable limitation in the current AD modelling paradigm. In most cases where disintegration of solid substrate is the rate-limiting step, a criticism could be made upon the presentation of the

initial stages of AD using the proposed ADM1 model, as hydrolysis can occur even before disintegration due to the enzymatic penetration into complex materials (Batstone et al., 2015).

The challenge of maximizing energy production and resource recovery also require further development of the ADM1 model. A key feature for incorporation into the ADM1 model is to determine the fate of phosphorus and sulfur (Table 1). This additional feature should include all phosphorus species in relevant fractions of the AcoD process (Johnson & Shang, 2006). Moreover, the inherent composition and properties of co-substrates and operating conditions affect biogas and biosolids quality during AcoD of sewage sludge and organic waste. Biogas utilization considerations also reinforce the need to expand the current model capacity to predict sulfur conversion and distribution (see section 4.2). In addition, the complex interactions between substrates that may facilitate synergistic or antagonistic effects remain largely unsubstantiated. It is hypothesized that several mechanisms may benefit the synergistic effects including metal additions, reduced intermediates inhibition, sufficient nutrients and a balanced *C*:*N* ratio (Astals et al., 2014; Dennehy et al., 2016; Xie et al., 2011). However, to date, there have not yet been any laboratory studies to comprehensively elucidate these underlying mechanisms. Thus these mechanisms have not been fully accounted for in the current scope of ADM1 model.

3.3 Statistical models

Apart from main stream mechanistic models focusing on the fundamental characterization of AcoD, statistical models emphasize the interrelationship between key parameters (e.g. substrate/co-substrate ratio, C/N ratio, OLR, and temperature) and the outputs (e.g. methane yield and VS reduction) (Xie et al., 2012). There are two most frequently used statistical approaches in AcoD, namely simplex-centroid mixture design and central composite design (CCD). The former contains different combinations of substrate mixture as variables, while the latter can involve several factors, such as substrate/co-substrate ratios and *C*/*N* ratios. Both are suitable methods for optimising methane production from AcoD using a variety of substrates (Wang et al., 2013).

It is noteworthy that the simplex-centroid mixture design approach can establish the surface model of continuous variables to optimize the proportions of all components for a target response variable. When analysing the effect of substrates, mixtures are expressed on a VS basis, and visualisation of the effects of subtrates on the dependant variables (typically specific methane yield) is achieved using a triangle whose vertices are corresponded to a pure blend (mixture that is 100% single substrate). The standard forms of the widely used mixture models are linear, quardratic, special cubic, full cubic, and special quartic models (Rao &

Baral, 2011). Pagés-Díaz et al. (2014) used a four factor mixture design (a special cubic model with 14 coefficients) to optimise mixture composition and correlated biological processes and statistical results. Similarly, CCD approach utilises response surface methodology (RSM) to optimise the studied paramters.

Functional relationships between responses (Y) and a set of factors (X_1 and X_2) can be described by estimating coefficients of the following second-order polynomial model based on experimental data.

$$Y=\beta_0+\beta_1X_1+\beta_2X_2+\beta_{11}X_1^2+\beta_{22}X_2^2+\beta_{12}X_1X_2 \quad \text{Eq. 3}$$

where Y represents the predicted response of methane potential, X_1 is the ratio ofM_1/M_2; X_2 is the ratio of C/N; β_0 is a constant; β_1 and β_2 are linear coefficients; β_{12} is interaction coefficients and β_{11} and β_{22} are quadratic coefficients. In some cases, it may be more appropriate to employ CCD approach to design the experimental conditions, such as OLR, HRT, and temperature (McLeod et al., 2015).

Numerous studies have investigated the effect of operating conditions on AcoD processes. However, they focused mostly on quantitative sensitivity, neglecting any qualitative aspects. Statistical models can inform the design of initial conditions and parameters to achieve optimum output for full-scale operation of AcoD system (Table 1). The predictive limitation of this methodology varies from one study to another subjected to the sensitivities of multiple variances reported in each case study. The degree of similarity of the reaction kinetics, sensitivities, and inhibition between lab-scale and full-scale digesters determines the accuracy for predicting the full-scale measurements (McLeod et al., 2015). It may therefore be acknowledged that there are some limitations of applying statistical modelling to predict a highly complex relationship in AcoD.

3.4 CFD models

Mixing allows for intimate contact between active microorganisms and feed substrates, and enhances the mass transfers of intermediate byproducts within digesters for effective AD processes. CFD models offer a versatile approach to study flow and velocity fields, turbulence, particle trajectories, rates of energy dissipation, transport of dissolved components and to determine volumes of high mixing intensity and stagnant zones, based on digester geometry, feed locations and operating conditions (Yu et al., 2013b). These models can be implemented in the following procedures: (1) constructing the geometry of the digester studied in a computer aided design type program, (2) fitting a mesh to divide up the entire domain into smaller cells, (3) setting boundary conditions such as inlets, outlets, and walls, (4) defining the properties of different phases (gas, liquid and solids), and (5) selecting different solvers and turbulence models to calculate how the phase/phases are affected by the geometry and boundary conditions in each individual cell defined by the mesh (Lindmark et al.,

2014). Once validated, the CFD model can be used to design, evaluate, and optimize the AcoD process. Zhang et al. (2016) applied the CFD model to investigate the mixing mode and power consumption in anaerobic mono- and co-digestion of cattle manure and corn stover. They observed that for different mixing modes, the optimum feedstock ratio for co-digestion changed with net power production and the best option of CM/CS ratio for continuous mixing and intermittent mixing were 1:1 and 1:3, respectively.

With more effective and intuitive visual results analysis, CFD model can be used to visualize the flow pattern and movement of particles and dissolved components in a mimic anaerobic digester (Craig et al., 2013; Vesvikar & Al-Dahhan, 2005). Separated from the kinetics of AcoD and focusing on the fluid dynamics, knowledge of the effects of mixing on the processes and criteria of optimal mixing is required (Table 1). Mixing effects within a digester is commonly unexplored in laboratory-scale reactors, where Van Hulle et al. (2014) compared a lab-scale (3.78 L) and a pilot-scale (120 L) anaerobic digester at both mixing and non-mixing conditions, and found that at lab-scale no significant difference in performance was found between these conditions, while at pilot-scale, a reduction of about 10% methane production occurred during unmixed conditions. The effect of mixing in full-scale digesters on process stability at different OLRs has been investigated by Gómez et al. (2006), who found that under low mixing conditions, the digester was able to maintain stable performance when it was overloaded. This phenomenon can be explained by a 2-D distributed model, which showed that at high OLR spatial separation of the initial methanogenic centers from active acidogenic areas was the key factor for efficient conversion of solids to methane, thus low mixing promoted the survival and expansion of most of the initiation centers for methanogenesis over the reactor volume in comparison with that of vigorous mixing (Vavilin & Angelidaki, 2005).

The addition of co-substrates with high solids (e.g. food waste) exhibit strong non-Newtonian fluid behavior, and a holistic design of the mixing system is required for such fluid rheology (Wu, 2012a). The amount and types of co-substrates used can change the rheological property and viscosity of the digestate, which means that a higher mixing intensity is needed to achieve a similar result (Lindmark et al., 2014). Considering the complex phenomena of particle segregation or aggregation (e.g. foaming or settling), multi-phase non-Newtonian models and ADM1 model were used separately to adequately simulate the complex flow behavior of heterogeneous solid substrate (Yu et al., 2013a). Despite the higher complexity in multi-phase models than for single-phase models, a greater understanding, optimisation and commercialisation of AcoD

processes can be achieved by advancing the development and application of such models in the field of AcoD (Yu et al., 2013b).

Although CFD has been extensively used to address the issue of hydraulic design in AcoD system, the inherent relationship between mixing and methane yield has not been fully elucidated. In other words, CFD models have rarely been coupled with biological models (Table 1). This is mainly due to the complexity of numerical simulation and model stability when biological rate equations are coupled. Indeed, the physical process stays stable (a small time interval required for the mixing and heat transfer) relative to the entire duration (weeks or even months) of the AcoD process. To tackle the different time step requirements between physical and biological processes, a practical approach is to develop a two-stage simulation strategy that predicts the temporal biological process using a large time step based on steady fluid flow and heat transfer. In such approach, a computational cell is treated physically as an individual bioreactor with its own residence time and temperature (Wu, 2012b). This approach unravels the intrinsic relations amongst mixing, heat transfer, and biochemical reactions (e.g. methane yield) in anaerobic bioreactors.

Distributed parameter models associated with CFD have been coupled with reactive models such as the ADM1 to evaluate process performance as impacted by non-ideal mixing (Van Hulle et al., 2014). Van Hulle et al. (2014) found a reduction of 10% in methane production during unmixed conditions due to the accumulation of undistributed VFAs. While a CSTR approach overestimated the biogas production by 10%, an application of more accurate mixing models could predict biogas production from a more complicated AcoD process (Van Hulle et al., 2014).

3.5 Other algorithm approaches

Due to the complexity of AcoD processes, the use of another approach, namely artificial neural networks, has been developed. This ‘black box’ approach does not need the information regarding the interrelationships between key variables. Gueguim Kana et al (2012) used artificial neural network (ANN) coupling genetic algorithm (GA) to model and optimize biogas production on mixed substrates of saw dust, cow dung, banana stem, rice bran and paper waste. The authors modelled the non-linear behavior of the process efficiently and derived a recipe for an optimum biogas production using these co-substrates. The specification of the network architecture and an adequate amount of consistent input data is required for the implementation of ANN. Gueguim Kana et al (2012) defined the biogas performance index by only five independent input parameters

corresponding to the concentrations of each co-substrates. This artificial intelligence based approach can significantly reduce the process development time for AcoD.

Another algorithm approach, namely Ant-Colony-Optimization (ACO), was inspired by the behavior of ants that use pheromone trails to guide their explorations. To optimize the discharge of organic waste from different waste sources in real-time, Verdaguer et al. (2016) applied the ACO algorithm that maximizes the generation of biogas through AcoD, as well as demonstrated the usefulness of the ACO approach in terms of supporting the decision making on improving the sustainability of organic waste and SWS management. The proposed approach uses an ACO algorithm which maximizes an index that quantifies the capacity to produce biogas from a sequence of waste input produced from different waste generators. Another algorithm approach was adopted by Fang et al. (2009), who used weighted non-linear least-squares and accelerating genetic algorithm to estimate the kinetic parameters of activated sludge storage.

These algorithm approaches can be advantageous, as they only require a minimum knowledge in the reaction mechanisms and experimental measurements of a number of parameters during AcoD. The drawbacks are the lacks of flexibility for reactor design and scale up, as well as the requirement of complex and diverse input-output relationships to train the method for the real-world scenario (Table 1).

4 AcoD models: applications and limitations

4.1 Capacities of current AcoD models

Several AcoD models have been developed and applied in previous AcoD studies, including the modified ADM1 model, the GISCOD transformer model in Matlab-Simulink, and the full-plant model in the process model simulator SUMO (Aichinger et al., 2015; Zaher et al., 2009; Zhou et al., 2012). Key features, aspects and outcomes of these mathematical models are summarized in Table 3.

An important aspect of current AcoD models is the capacity to identify the optimal ratio and organic loading of substrates and co-substrates for maximum energy and cost efficiency (Figure 3, Point 1), thus avoiding organic overloading (Aichinger et al., 2015; Esposito et al., 2011b; Zhou et al., 2012). These models are commonly mechanistic, linking key operating conditions (such as HRT and OLR) to digester performance (Figure 3, Point 1-4). For instance, Zhou et al (2012) investigated two important operating factors, SRT and OLR (or the mix ratio for co-substrates) based on a modified ADM1 model. The authors suggested that at a COD ratio of 1:1 AcoD of biowaste and manure yields the highest methane production and maintains the system stability at SRT of 26.7 d (Zhou et al., 2012). In another study Zaher et al. (2009) developed GISCOD

transformer model in Matlab-Simulink, where co-substrate loading ratios and HRT are optimized for maximum biogas production and VS removal efficiency by simulating hundreds of virtual experiments (Table 3). This model can be potentially applied to other AcoD processes.

Another crucial aspect of current AcoD models is the ability to simulate process failure, thus facilitating favorable operating conditions in practice (Figure 3, Point 4). Process failure commonly occurs during AcoD operation, which may be evident as irreversible pH drop and unbalanced bacterial population (i.e. elimination of active acetoclastic and hydrogenotrophic methanogenic archaea). For instance, in an ADM1 based dynamic model, Esposito et al. (2011b) predicted a maximum COD ratio between organic fraction of municipal solid waste (OFMSW) and sewage sludge to avoid an overloading condition (Table 3). Zaher et al.(2009) conducted a study to predict impact of HRT and feedstock ratio on a two-stage anaerobic digesters treating diluted dairy manure and kitchen wastes. Severe inhibition induced complete halt of methanogenesis was predicted at HRT of 10 days (Zaher et al., 2009). Recently, Arnell et al. (2016) developed a procedure to characterize and fractionate COD of co-substrates for benchmark simulation model No 2 (BSM2) and ADM1, and then applied the model to a plant-wide simulation study. Two major failure modes (i.e. ammonia inhibition mode and LCFA inhibition mode) were identified (Table 3). It is noted that some inconsistencies between simulation results and experimental results are attributed to the adoption of some sensitive parameters, which correlates with feed concentrations, HRT and reactor configurations (Gavala et al., 2002).

Additionally, the cooperative function of inhibition in AcoD model is an important aspect in some AcoD models (Figure 3, Point 5). Due to the heterogenic and dynamically changing co-substrate composition as well as lack of certain inhibition functions in original ADM1 model, AcoD models have been modified to correlate the operating parameters to process stability and optimization. For instance, Boubaker & Ridha (2008) incorporated modifications into inhibition functions of the original ADM1 model to account for a high total VFAs concentration (Table 3), which allowed for the prediction of digester failure at short HRT by the modified ADM1 model.

4.2 Recommended new features of AcoD models

4.2.1 Biogas quality

Mathematical modelling for H_2S formation and its concentration in biogas is underdeveloped (Figure 3, Point 6). As H_2S is a very corrosive gas for engines, its content in biogas determines the biogas quality and economic viability of co-digestion and co-generation. To date, no mechanistic model has been reported to

predict H_2S formation and its levels during AcoD. Nevertheless, some models have been developed based on ADM1 to reveal the bioreaction pathways for H_2S (Barrera et al., 2015; Fedorovich et al., 2003; Liu et al., 2015). For instance, Fedorovich et al. (2003) extended ADM1 with processes of sulfate reduction by the additional blocks (i.e. multiple reaction stoichiometry, microbial growth kinetics, conventional material balances for ideally mixed reactor, liquid-gas interactions, and liquid-phase equilibrium chemistry) to describe sulfate-reducing processes. However, the model could not predict H_2S content in the biogas without considering the gas-liquid transfer for H_2S (Fedorovich et al., 2003).

Empirical modelling approaches have been used to predict formation and content of H_2S in biogas. Attempts to predict H_2S and NH_3 contents in biogas have been conducted by Strik et al. (2005) using a black-box approach, which employed the Matlab Neural Network Toolbox. The input includes parameters such as sulfate loading rate, H_2S content in biogas, total sulfides in reactor, biogas-productivity, pH, and OLR. The proposed model based applications well predicted H_2S and NH_3 contents in biogas, and could probably be used to foresee, control, reduce or even avoid the production of toxic H_2S and NH_3 (Strik et al., 2005). A general screening approach for the H_2S content in biogas has been developed by Peu et al. (2012) to evaluate 37 different feedstock originated from urban wastewater treatment plants, farms, agri-food facilities and municipal wastes. Total sulfur content in the feedstock ranged from 1 to 29.6 mg S/kg of total solids. A model linking H_2S content in biogas with the C:S ratio was also developed. Based on the model, a minimum C:S ratio of 40 is required in feedstock to limit the concentration of H_2S in raw biogas to less than 2% (vol/vol) (Peu et al., 2012). However, these empirical approaches ignore the physiochemical process, and cannot predict the formation of H_2S accurately during AcoD of some co-substrates such as pig slurry (Peu et al., 2011).

A mathematical AcoD model needs to be developed to monitor H_2S content in biogas from AcoD processes (Carrera-Chapela et al., 2016). It is anticipated that the new AcoD model can incorporate the competition between sulfate reducing bacteria and other bacteria such as acetogens as well as hydrogenotrophic methanogens at overloading or other inhibitory conditions (Figure 3, Point 4 and 5). Recently, a mechanistic model focusing on the H_2S generation from AD of sewage sludge was developed by Carrera-Chapela et al. (2016). The model adopted the same stoichiometry and reaction kinetics based on the work of Donoso-Bravo et al. (2009), and provided the sulfate reducing stage with a reduced number of parameters. The model is able to describe properly the dynamic behavior of AD system, particularly its gas phase composition with an accuracy of 90% for H_2S (Carrera-Chapela et al., 2016). Nevertheless, there is an urgent need to incorporate such

modifications to a generic AcoD model (Figure 3, Point 6). Indeed, current AcoD models have not incorporated the sulfate reduction pathway formulated in recent AD models, and ignore the presence of sulfur precipitants or its bound forms (e.g. sodium bisulfite) for further biochemical transformation. Without these underlying mechanisms, models cannot mechanistically describe the main biochemical and physico-chemical processes required for sulfur transformation, thus are not able to allow for plant-wide evaluation.

4.2.2 Biosolids quality

AcoD process can generate biosolids with varied quality. Digestate (biosolids) quality refers to the dewaterability, the odorous emissions, and the levels of micro-pollutants and pathogens in the water and sewage utilities. There are few comprehensive studies devoting to the effects of AcoD on the biosolids quality, the odorous emissions in particular. Jensen et al. (2014) conducted a study to co-digest sewage sludge and crude glycerol, and observed that digestate dewaterability was not affected by glycerol addition.

The impact of AcoD on odorous emissions has become an distinct and important research field (Orzi et al., 2015). The AcoD process becomes complicated by adding co-substrates rich in proteineous materials and sulfate. It is reflected by various occurrence of the sulfur related reactions and corresponding kinetics under different culturing temperatures (Du & Parker, 2012). Although biosolids odorous emissions have recently been investigated experimentally during manure composting (Zang et al., 2016), the measured biosolids odorous emissions have never been correlated to feedstock characteristics (e.g. sulfur content and feedstock composition) and operation conditions (e.g. substrates/co-substrates ratio, SRT, and temperature) to optimize the AcoD process. In addition, research on anaerobic sulfur conversions have been primarily focused on sulfide formation, mainly because it is known as the key odor causing compound (Talaiekhozani et al., 2016). Nevertheless, Higgins et al. (2006) proposed a cyclic pathway to describe the production and transformation of volatile sulfur compounds and H_2S. The pathway involves processes such as degradation of protein, generation of associated volatile organic sulfur compounds (e.g. methanethiol) and subsequent formation of H_2S (Figure 4). This could be a fundamental part to be integrated into a new biosolids odorous emissions model (Figure 3, Point 7).

The impact of co-substrates on AcoD process stability is well documented, but modelling studies regarding its impact on downstream processes are scarce (Figure 3, Point 6 and 7). Moreover, the impacts of AcoD on biosolids production and nutrients build-up have been evaluated in full-scale case studies. Aichinger et al. (2015) investigated the organic loading threshold during AcoD based on the trade-off between boosting

methane production versus increased nitrogen-return loads, biosolids production and polymer demand. The authors observed no significant increase in biosolids production and a minor increase in NH_3 release (approximately 20%) at organic co-substrate addition of up to 25% in terms of VS (Aichinger et al., 2015). In summary, a generic approach to correlate operating conditions (e.g. substrates/co-substrates characteristics and ratios, OLRs, HRT) to key state variables (e.g. methane production rates, VS removal rates, H_2S formation and its content in biogas, odorous emissions from biosolids) is essential (Figure 3, Point 1-3, 6-7). It has been demonstrated that a reduced methanogenic activity can lead to an enhanced release of these sulfur compounds (Talaiekhozani et al., 2016). Therefore it is hypothesised that an optimised AcoD system can increase methanogenic activities and consequently mitigate volatile organic sulfur and H_2S emissions under the sulfur loading rate threshold.

4.2.3 Microbial diversity

As depicted in the future research roadmap, important capacities regarding microbial analysis beyond current AcoD model studies are: (1) ability to standardize the model approach for maximum biogas production and VS removal efficiency with inhibition functions (Figure 3, Point 1 and Point 5); (2) ability to simulate H_2S formation and its content in biogas (Figure 3, Point 6); and (3) ability to predict biosolids odorous emissions (Figure 3, Point 7). Importantly, integration of mathematical models with microbial community dynamics is needed (Figure 3, Point 8).

Most studies are dedicated to the characterisation of microbial communities in anaerobic digesters. All ADM1-based models only utilize the total biomass concentration of each functional microbial consortium. The relationship between digester performance and microbial community structure has been also qualitatively studied during AcoD. In a study by Regueiro et al. (2015), microbiome changes due to changing environmental conditions as a result of the addition of three co-substrates (i.e. food waste, alkaline hydrolysate and glycerol) have been documented. It is reported that a reduced population of one species within a functional group due to system perturbation may be taken up by another species from the same group with a higher resistance (Briones & Raskin, 2003). The phenomenon is commonly referred to as functional redundancy. At the presence of functional redundancy, the relationship between digester functionality and microbial community is difficult to quantitatively model, as it lacks microbial community descriptors that may quantify, for example, functional redundancy in models (Venkiteshwaran et al., 2015). Hence, it becomes a major obstacle to improving design and operation of anaerobic digesters during AcoD. Ramirez et al. (2009b) tackled this problem by accounting

for microbial diversity in a structured model (i.e. ADM1) that could predict the adaptation of microorganisms to inhibitory substances to some extent. Thus, exploring the community response to the addition of co-substrates can offer an engineered community structure through altering co-substrates and their composition for an optimized AcoD process. Nevertheless, more studies are needed to link microbial community descriptors to AD models for the simulation, control and optimization of digesters (Figure 3, Point 8).

4.2.4 Plant wide AcoD modelling

Plant wide modelling of wastewater treatment has centered on the development of commercial software, such as BioWin computer modeling package (Batstone et al., 2015). It is well acknowledged that by the addition of co-substrates, the generation and quality of biogas and subsequent biosolids affect the overall revenue generation. AcoD also influences the subsequent wastewater (often called reject water or sludge centrate) treatment due to the release of nitrogen and phosphorous from co-substrates. Considerable progress has been made to implement AcoD in plant-wide WWTPs modelling by Arnell et al. (2016). The comprehensive method involves characterization of substrates, estimation of the substrate dependent parameters, modifications of ADM1, integration of AcoD in BSM2. In addition, the aforementioned GISCOD model was complemented by a Gaussian LCFA inhibition function to model AcoD. The impact of limiting the protein load from co-substrates was investigated to avoid NH_3 inhibition in the digester and overloading of the nitrogen removal processes in the water train. The model also included LCFA inhibition as a result of high loads of lipid rich co-substrates. Nevertheless, both ASM and ADM1 could not simulate more complex effects, such as ion activity and ion pairing implemented in physico-chemical models, and thus considered inadequate (Batstone et al., 2012). Further developments on phosphorous and nitrogen cycles during AcoD in the whole wastewater treatment plant modelling need to be carried out (Figure 3, Point 9).

5 Conclusion

Mathematical modelling of AcoD has been developed based on both empirical and mechanistic approaches, with ADM1 being the most sophisticated one. AcoD operates at high OLRs under diverse co-substrates' properties and composition; hence, its modelling requirements are more complex than mono-digestion. Compared with mono-digestion, the transient variation in pH and inhibitory intermediates are essential for AcoD optimization. New features in future AcoD models should involve interrelationships between system performance and co-substrates' properties, organic loading, and inhibition mechanisms. The conversion and

distribution of sulfur, phosphorus, and nitrogen during AcoD in a plant-wide scope is also underdeveloped in current AcoD models.

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7 References

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Table 1: Advantages and limitations of five model categories

Model categories	Advantages	Limitations
Basic kinetic models	• Easy to implement • Identify the hydrolysis rate constant	• Over-simplify the dynamics of rate-limiting steps • Cannot provide direct practical knowledge for full-scale implementation
ADM1	• Most widely applied and recognized models in the research area • Mechanistic model allowing extensions and modifications to broaden its capacity	• Require an improved practicality • Substrate characterization is ponderous • Conversion & distribution of S, P, and N are underdeveloped
Statistical models	• Qualitative analysis to aid the design of initial conditions and parameters for optimum AcoD output	• Variations in reaction kinetics, sensitivities, and inhibition determine the accuracy for the full-scale predictions
CFD models	• Effective and intuitive visual results analysis • Reveal the effects of mixing on the AcoD processes • Provide optimal hydraulic design for AcoD system	• Complex numerical simulation • Model instability when the physical process is coupled with the biological process
Other algorithm approaches	• Minimum requirements for the knowledge in the reaction mechanisms and experimental parameters measurements during AcoD	• The lacks of flexibility for reactor design and scale up • Require complex and diverse input-output relationships to train the method for the real-world scenario

Table 2: Key kinetic models applied in anaerobic (co)-digestion.

Models	Expressions	Examples of applications
First order kinetic model	$\frac{dS}{dt} = -K_{s,max}S$ $M(t) = P[1 - exp(-kt)]$	(Dennehy et al., 2016; Kafle & Chen, 2016; Xie et al., 2011)
Monod kinetic model	$\frac{dS}{dt} = -\frac{\mu_m}{Y}\frac{SB}{K_s + S}$	(Lokshina et al., 2001)
Contois kinetic model	$\frac{dS}{dt} = -\frac{\mu_m}{Y}\frac{SB}{K_x B + S}$	(Karim et al., 2007)
Haldane kinetic model	$\frac{dS}{dt} = -\frac{\mu_m}{Y}\frac{SB}{K_s + S + S(S/K_I)^n}$	(Carrera-Chapela et al., 2016; Senthamaraikkannan et al., 2015)
Chen and Hashimoto model	$M(t) = P \cdot (1 - \frac{K_{CH}}{HRT \times \mu_m + K_{CH} - 1})$	(Ma et al., 2013)
Modified Gompertz	$M(t) = P \cdot exp\left\{-exp\left[\frac{R_{max} \cdot e}{B_0}(\lambda - t) + 1\right]\right\}$	(Xie et al., 2011; Zhao et al., 2016)
Dual pooled first order kinetic model	$M(t) = P \cdot [1 - \alpha \cdot \exp(-K_f t) - (1 - \alpha) \cdot \exp(-K_L t)]$	(Dennehy et al., 2016; Rao et al., 2000)

Where, S is the substrate concentration (g/L); B is the microorganism concentration (g/L); $K_{s,max}$ is the maximum specific substrate uptake rate (d^{-1}); μ_m is the maximum specific growth rate (h^{-1}); Y is growth yield coefficient (dimension less); K_x is Contois kinetic constant (dimension less); K_s is the half saturation coefficient (g/L); n is the Haldane index (n=1 or 2); K_I is the inhibition constant (g/L); *M* represents the cumulative methane yield (mL/g VS); *P* stands for the ultimate methane yield (mL/g VS); HRT is digestion time or hydraulic retention time (d); K_{CH} is Chen and Hashimoto kinetic constant (dimension less); *k* is a first-order rate constant (1/d); t refers to the digestion time (d); R_{max} is the maximum methane production rate (mL/g VS/d); λ is the lag phase (d); e is the constant 2.7183; K_f is the rate constant for rapidly degradable substrate (d^{-1}), K_L is the rate constant for slowly degradable substrate (d^{-1}), and α is the ratio of rapidly degradable substrate to total biodegradable substrate.

Table 3: Current AcoD models.

Models	Features	Aspects/Outcomes	Requirements/Remarks	References
GISCOD transformer model in Matlab-Simulink	• waste composition as input • uncouple hydrolysis of the decaying biomass for ADM1 • process optimisation	• estimate accurate hydrolysis rates for each waste and particulate fraction • determine the optimal ratio between waste streams and HRT by changing OLRs • simulate a number of feedstock and flow rates using two digesters volumes	• co-substrates characterization • additional modelling, (a C-MEX S-Function)	Zaher et al. (2009)
A full-plant model in the process model simulator SUMO by Dynamita SARL	• simulate anaerobic processes under high solids concentrations or high temperatures	• identify co-substrate characteristics from a calibrated model • interpret synergistic effects in AcoD as increased hydrolysis rate constant • higher biodegradable content of co-substrates results in higher gas production	• hydrolysis rate constant is critical for synergistic effects • trace elements and nutrients or a change in microbial diversity lead to varied hydrolytic activity	Aichinger et al. (2015)
BSM2 and ADM1 based model	• a plant-wide simulation • AcoD model implemented in BSM2 • co-substrate characterisation for ADM1	• confirm the positive effects of co-digestion on methane production and operation cost • reveal the importance of protein loading limit & NH_3 inhibition prevention in the digester	• identify two major failure modes, i.e. NH_3 and LCFA inhibition through principal component analysis	Arnell et al. (2016)
Modified model based on ADM1	• a non-competitive function to represent methanogenic inhibition • the expression of inhibition for acetate uptake (I_5)	• yield similar results as observed in the experiments, including an overloading condition • predict digester failure at shorter HRT	• observe some inconsistencies between simulation results and experimental results	Boubaker & Ridha (2008)
Modified model based on ADM1	• develop an input-output feedback control system to maintain a desirable operation conditions	• investigate two important operating factors, SRT and OLR, during AcoD of (1) biowaste and corn silage, (2) manure and corn silage, and (3) biowaste and manure • identify optimum co-substrate/substrate raio	• manure/sewage sludge contributes to process stability • biowaste is preferable to be co-digested with sewage sludge or manure	Zhou et al (2012)
Modified model based on ADM1	• two substrates of different biodegradation kinetics • simulate the OFMSW disintegration process	• effects of particle size distribution and operating conditions on the COD removal and methane production • predict process failure with the combined effect of particle size distribution and OLRs	• large particle size = higher OLR to reach digester failure • slower disintegration and thus slower acidification occurs for large particle sizes	Esposito et al. (2011b)

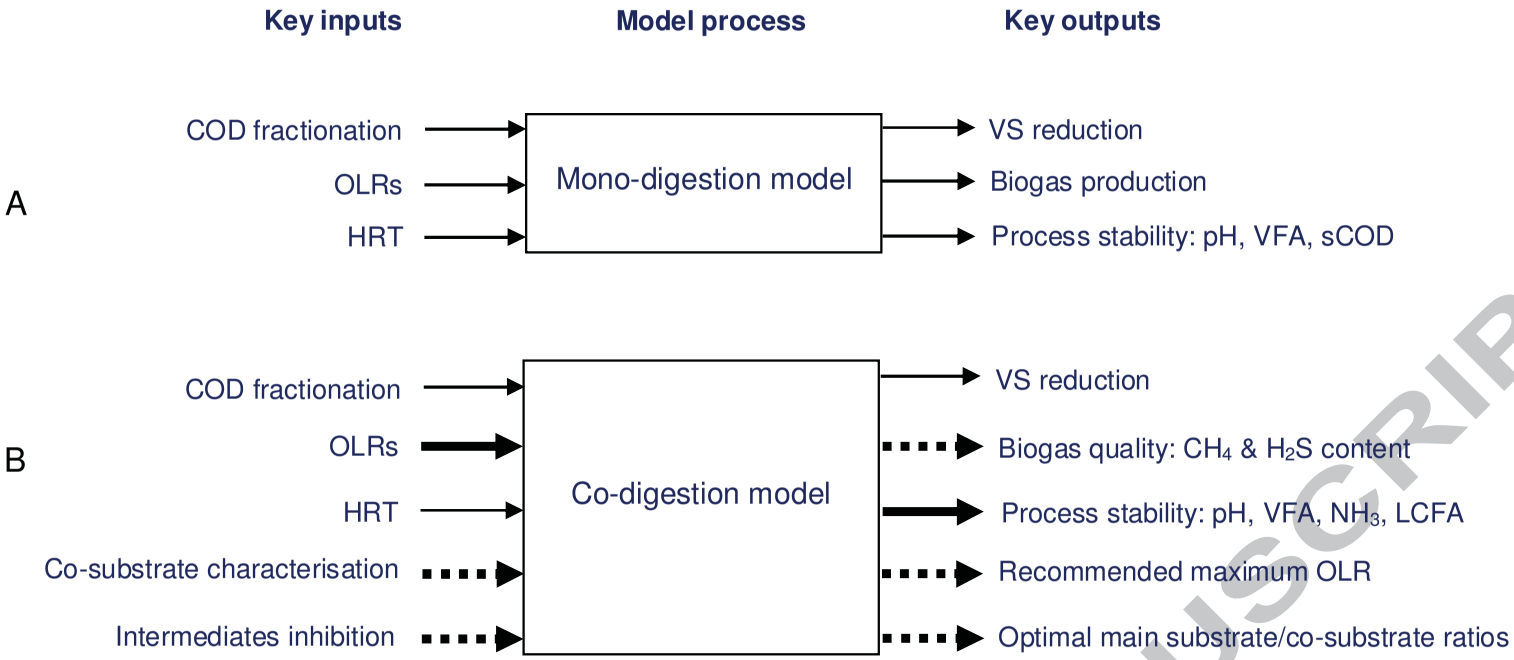

Figure 1: Comparison of mathematical models between mono-digestion of sewage sludge (A) and AcoD of sewage sludge and organic waste (B). Note: Thickened arrows indicate the need for more development of existing modeling capacity while dashed arrows indicate the need for new modelling capacity.

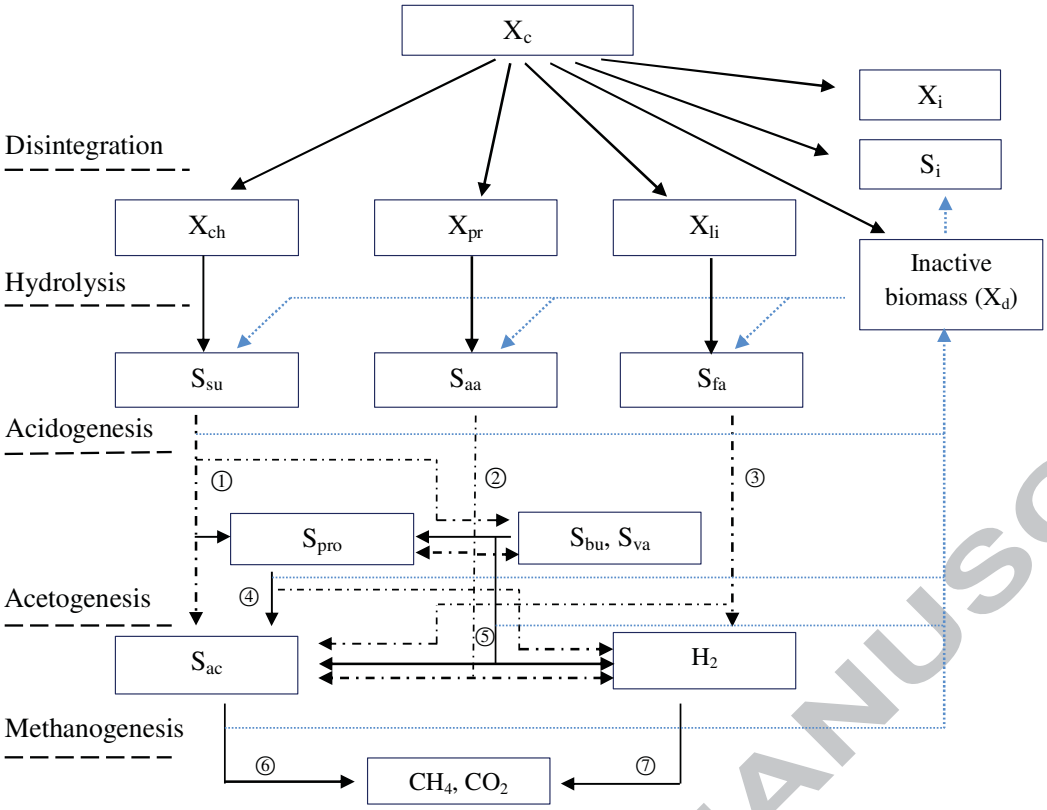

Figure 2: Anaerobic digestion model: (1) acidogenesis from sugars, (2) acidogenesis from amino acids, (3) acetogenesis from LCFA, (4) acetogenesis from propionate, (5) acetogenesis from butyrate and valerate, (6) aceticlastic methanogenesis, and (7) hydrogenotrophic methanogenesis (modified from Batstone et al. (2002)).

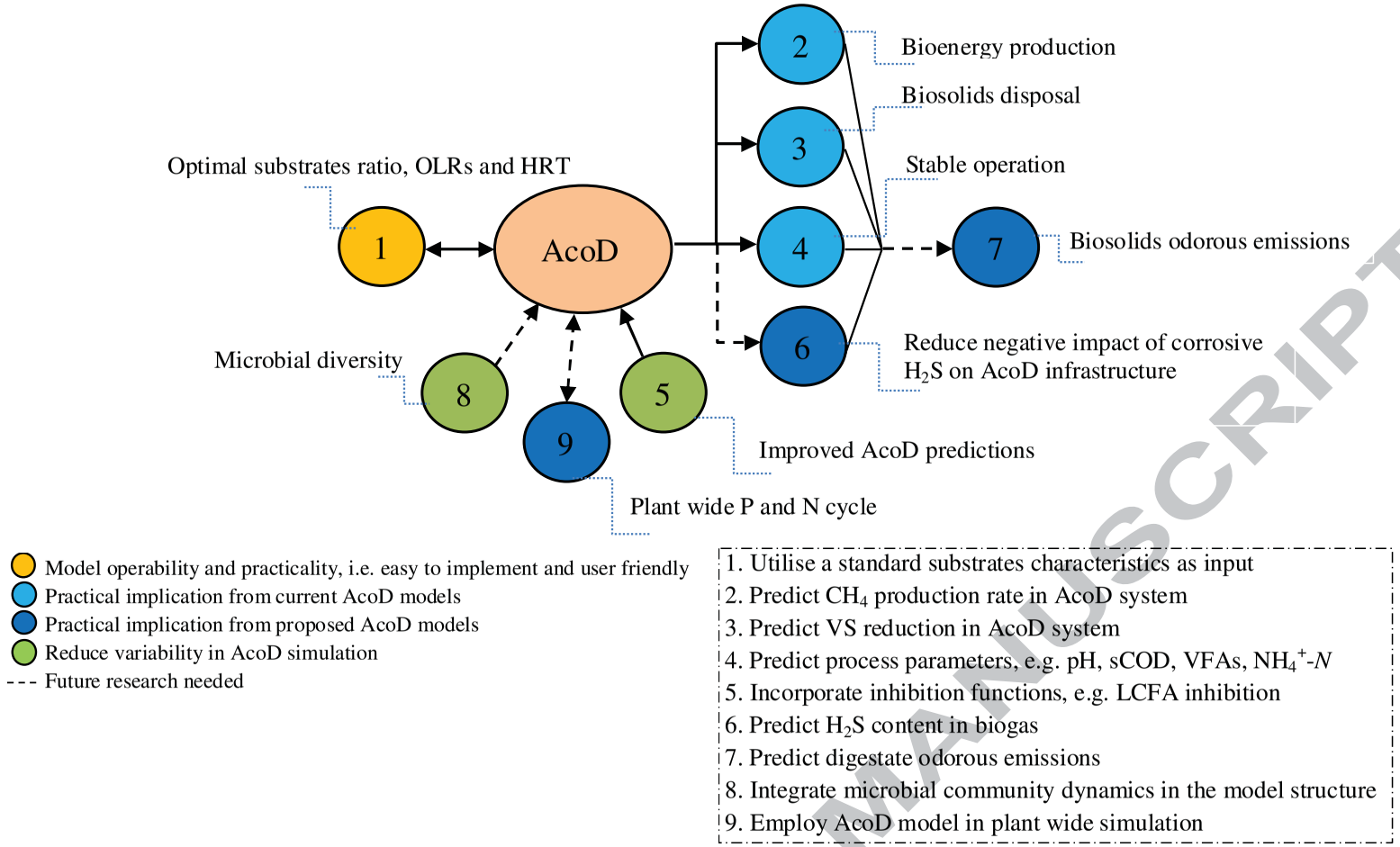

Figure 3: Future research roadmap for further development of AcoD modeling capacity.

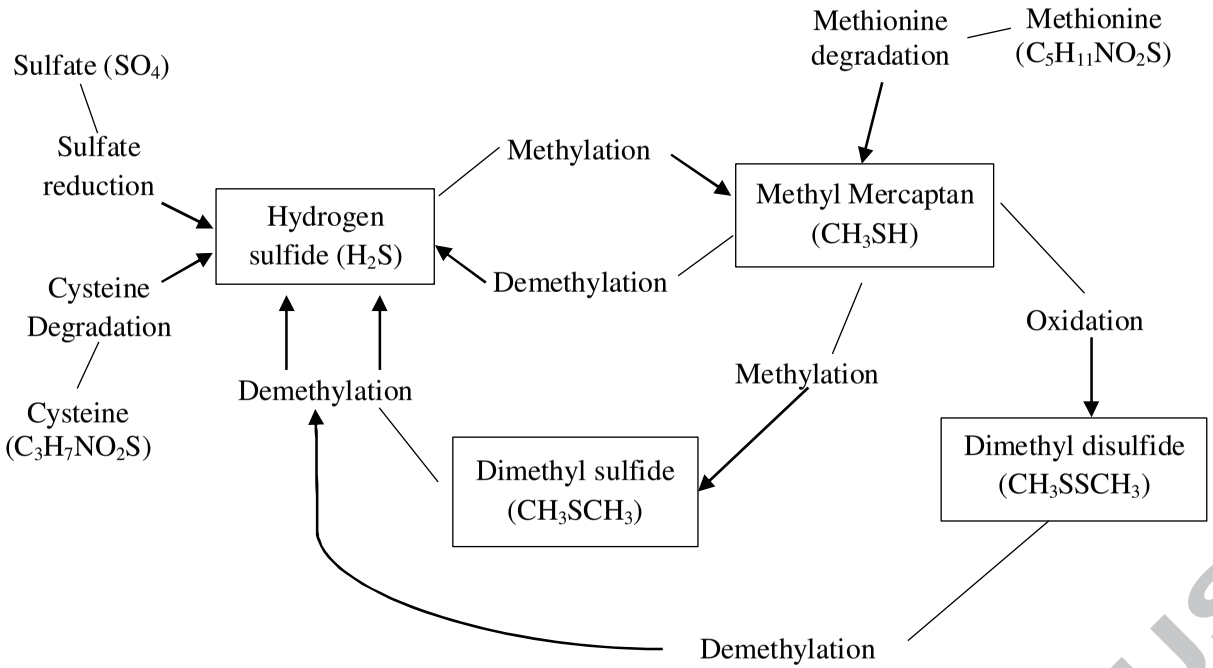

Figure 4: Cyclic pathway to describe the production and transformation of VOSCs and H_2S during biosolids storage (modified from Higgins et al., (2006)).

Highlights

- AcoD operates at high OLRs under diverse co-substrates' properties and composition
- Modelling requirements for AcoD are more complex than mono-digestion
- pH variation & inhibitory intermediate accumulation are essential for AcoD modelling
- ADM1-based model is sophisticated and an improved practicality is required for AcoD
- Conversion & distribution of S, P, and N are underdeveloped in current AcoD models