



## Modeling of the methane production and pH value during the anaerobic co-digestion of dairy manure and spent mushroom substrate



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### HIGHLIGHTS

- ADM1 was used to predict anaerobic co-digestion of DM and SMS under different HRT.
- SMS was divided into inert part as well as biodegradation parts of SHF and RHF.
- The model assesses combined effects of HRT and DM–SMS ratio on the methane and pH.

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### ABSTRACT

A dynamic mathematical model, based on the IWA Anaerobic Digestion Model No. 1 (ADM1), was used to predict the methane production and pH value during anaerobic co-digestion of dairy manure (DM) and spent mushroom substrate (SMS) under different hydraulic retention times (HRT). In this model the degradation of DM was modeled according to classical ADM1, while SMS was divided into inert part as well as biodegradation parts of slowly hydrolysable fraction (SHF) and readily hydrolysable fraction (RHF). The data from lab-scale experiment was used to calibrate and validate this model. The results showed that the model was able to predict reasonably well the steady-state results of methane production and pH value at HRT of 12, 20 and 28 d. The results also indicated that the model suitability to assess the combined effects of HRT and substrate ratio on the methane production and pH value.

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### 1. Introduction

Mushroom, cultivated on a variety of agro-residues such as straw, saw dust and cotton seed hull, is the biggest solid-state-fermentation industry in China. According to Food and Agriculture Organization [1], there could be more than 8 million tons of spent mushroom substrate (SMS) produced in China each year. SMS is being used as soil amendment because it could improve soil structure [2], provide some nutrients [3] and biodegrade of pollutant [4]. In China, mushroom cultivation and dairy feed are usually kept in one farm due to the favorable economic benefits. The dairy manure (DM) is always used as fertilizer or feedstock for biogas production, while SMS is usually disposed anywhere.

Anaerobic digestion of organic matter has been considered as a suitable technology for organic wastes treatment and energy production in the form of biogas. Recently, more and more researchers pay attention to anaerobic co-digestion due to the fact that co-digestion could increase biogas production, buffer the capacity, provide a better nutrient balance, manage mixed wastes easily, and improve fertilizer value of digested residues [5,6]. However, anaerobic co-digestion includes a series of interrelated reactions, and experimental assessment the impacts of all involved variables on the process efficiency is time consuming and hardly possible. Therefore, a mathematical model is definitely useful to predict the behavior of anaerobic co-digestion, optimize the production and prevent process failure.

Anaerobic Digestion Model No. 1 (ADM1), developed by the International Water Association (IWA) Task Group for Mathematical Modeling of Anaerobic Digestion Processes [7], has been widely used both for lab- and full-scale anaerobic reactors. ADM1 or its modified version has been implemented in anaerobic co-digestion of various

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substrates. For example, the original ADM1 was used to model the thermophilic anaerobic co-digestion of olive mill wastewater with olive mill solid waste [8,9]. The results indicated that ADM1 was able to predict the results of gas flows, methane contents and pH values with different influent concentrations at various hydraulic retention times (HRT). A modified ADM1 was also used to simulate the methane production profiles for anaerobic co-digestion of pig manure and wastewater of glycerine in a batch test [10]. Zaher et al. [11] developed ADM1 to optimize the ratio of different wastes and HRT for maximizing the biogas production in the anaerobic co-digestion of diluted dairy manure and kitchen wastes. Furthermore, ADM1 was used to model the anaerobic co-digestion of municipal solid wastes and activated sludge in a 2000 m<sup>3</sup> anaerobic digester, operating at an average HRT of 26.9 d with an average organic loading rate of 1.01 kg TVS/m<sup>3</sup> d, at a temperature of 37 °C with an average gas production rate of 0.296 m<sup>3</sup>/m<sup>3</sup> d [12]. The above models were all used the classical disintegration process proposed by ADM1. In order to describe the dynamic behavior exactly, Esposito et al. [13] proposed a modified ADM1 for the anaerobic co-digestion of organic fraction of municipal solid waste and sewage sludge. In their model, the sewage sludge degradation was followed the ADM1 while a surface based kinetics was used to simulate the organic fraction of municipal solid waste disintegration process.

In addition, the formation of volatile fatty acid (VFA) for anaerobic digestion of lignocelluloses followed the characteristics that easily digestible portions had a relatively faster initial fermentation, followed by a slower fermentation, where the more refractory portions are consumed [14,15]. Zhao et al. [16] used ADM1 to model the anaerobic digestion of cattail, a lignocellulosic substrate, and found that the lignocellulosic substrate could be divided into slowly hydrolysable fraction (SHF), readily hydrolysable fraction (RHF) and inert part. However, this approach has not been applied in the model of anaerobic co-digestion. Furthermore, only a limited number of studies have been carried out to evaluate the effects of HRT on methane production and pH value in anaerobic co-digestion, indicating that HRT was an important operating parameter for methane production [11]. However, little information about the model of anaerobic co-digestion of lignocellulosic wastes and solid waste can be found in literatures. So taking into account the advantages of ADM1 implementations in modeling anaerobic co-digestion of more complex lignocellulosic wastes, the major objective of this study was to approach a model with an emphasis on anaerobic hydrolysis of lignocellulosic wastes, and used the modified ADM1 to describe the kinetics of anaerobic co-digestion. The model was then calibrated and validated by the results of biogas production and pH value during the anaerobic co-digestion of DM and SMS. In addition, the optimization of HRT and substrate ratio on biogas production and pH value were also explored.

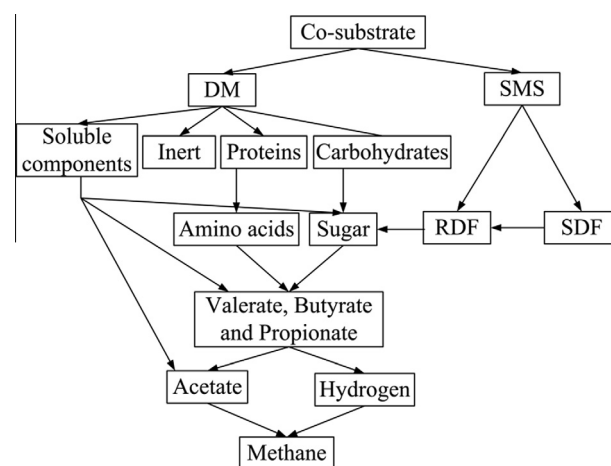
## 2. Materials and methods

### 2.1. Experimental setup

The SMS and DM used in the experiment were obtained from the same dairy farm in Gansu Province of China. Both the substrates were ground in a blender and stored at 4 °C before further use. The characteristics of SMS and DM are shown in Table 1. Anaerobically digested manure slurry was filtered and used as the inoculum, which was collected from an 800 m<sup>3</sup> size of biogas plant (Qingdao, China) operating at 32 °C with a 25 d retention time. The total solid (TS) and volatile solid (VS) contents of the slurry are 21.50% and 63.93%TS, respectively. The experiments were carried out in the semi-continuous continuous stirred-tank reactors (CSTR) fabricated from 10 mm polymethylmethacrylate sheets with a temperature-controlled water bath at 35 °C. The

**Table 1**  
Characteristics of dairy manure and spent mushroom substrate.

Substrate	Components	Unit	Value	Reference
Dairy Manure	Soluble monosaccharides	kgCOD/m <sup>3</sup>	5	[17]
	Total soluble valerate	kgCOD/m <sup>3</sup>	1.21	[18]
	Total soluble butyrate	kgCOD/m <sup>3</sup>	0.77	[18]
	Total soluble propionate	kgCOD/m <sup>3</sup>	1.3	[18]
	Total soluble acetate	kgCOD/m <sup>3</sup>	2.16	[18]
	Particulate carbohydrates	kgCOD/m <sup>3</sup>	18	[19]
	Particulate proteins	kgCOD/m <sup>3</sup>	31	[17]
	Particulate lipids	kgCOD/m <sup>3</sup>	1.7	[17]
	Particulate inert	kgCOD/m <sup>3</sup>	35.3	[19]
Spent Mushroom Substrate	Cellulose	%TS	32.0	Calculated
	Hemicellulose	%TS	15.7	Calculated
Substrate	Lignin	%TS	12.2	Calculated
	Ash	%TS	13.1	Calculated
	Readily hydrolysable fraction	kgCOD/m <sup>3</sup>	101.52	Calculated
	Slowly hydrolysable fraction	kgCOD/m <sup>3</sup>	179.35	Calculated
	Inert fraction	kgCOD/m <sup>3</sup>	95.13	Calculated



**Fig. 1.** Schematic of bioconversion pathways in the model.

CSTR, with the working volume of 2.0 L, was connected to a wet-type gas flow meter and gas sampling ports using silicone tubes. At the beginning, all digesters were inoculated and set in batch mode until the start up of biogas production. Then each digester was fed with a TS concentration of 6.0% at the HRT of 12, 20 and 28 d, respectively. The ratio of DM and SMS in the mixed substrates was fixed to 3:1 (m/m).

### 2.2. Analytical methods

The daily biogas production was recorded by the gas flow meter. Samples from the digester were daily collected for measurement of pH value and biogas components. The biogas components were analyzed by a gas chromatograph (SP 6890, Shandong Lunan Inc., China), equipped with Porapak Q stainless steel column (180 cm long, 3 mm outer diameter) and a thermal conductivity detector. The temperatures of the injector, detector and oven were 120 °C, 150 °C and 50 °C, respectively. Total lipid was determined by Soxhlet extraction with a hexane/isopropanol (60/40) mixture as a solvent. After evaporation of the solvent, the percentage of hexane extractable materials (HEM) in TS was determined by gravimetry [20]. Proteins content was based on the organic nitrogen content. The content of cellulose, hemicellulose, and lignin was estimated according to Goering and Van Soest [21]. The TS, VS, total Kjeldhal nitrogen (TKN), total ammonia nitrogen (TAN), pH and COD were determined according to the standard methods [22]. The equations for the fraction of proteins, lipid and carbohydrates in total COD were as follows.

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