# **Process Evolution of Dry Anaerobic Co-digestion of Cattle Manure with Kitchen Waste**

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Knowledge of the effect of kitchen waste on dry anaerobic mesophilic digestion of cattle manure is important for understanding and controlling the anaerobic co-digestion process. In this study, laboratory scale (Volume = 5 L) performance was evaluated using six different ratios of cattle manure to kitchen waste: 1:0, 11:1, 9:1, 7:1, 5:1 and 3:1. The selected conditions were: 10 % inoculum, 20 % total solids, and 35 °C temperature, optimum in the mesophilic range. The six ratios showed an initial start-up phase in the range between 1 and 4 days, and the initial methane generation began within 2 days of operation. After 22 days, 14.98 % of Volatile Solid was removed for reactor 4 (R4) at the ratio of 7:1 of cattle manure to kitchen waste, and the reactor showed higher volumetric average daily biogas generated of 10.47 mL g<sup>-1</sup> VS day<sup>-1</sup> and 54.51 % methane content. The methane yield for R4 reached 0.1223 L CH<sub>4</sub> g<sup>-1</sup> VS, followed by the other two ratios (11:1 and 5:1) with the value of 0.1213 and 0.1208 L CH<sub>4</sub> g<sup>-1</sup> VS, respectively. And the methane yield of cattle manure with no kitchen waste was 0.1033 L CH<sub>4</sub> g<sup>-1</sup> VS during 22 days of operation. The result indicated that kitchen waste could improve the digestion process for methane production provided that the total solid ratio of cattle manure to kitchen waste was no less than 5.

Key words:

Cattle manure, kitchen waste, dry anaerobic digestion, methane

# Introduction

Manure residues have been identified as a major source of environmental pollution. Traditionally, the waste has been disposed directly or after composting, as soil amendments in the agricultural industry. Since this practice has resulted in the degradation of air, soil, and water resources, new regulations for protecting the environment have been promulgated to control land application of animal manure.<sup>1</sup> As such, livestock industries and regulatory agencies are seeking alternative technologies to manage manure residues in an environment-friendly manner.<sup>2</sup>

Anaerobic digestion is an attractive treatment strategy and shows great potential from an environmental point of view and for social benefit by providing a clean fuel.<sup>3–5</sup> Anaerobic digestion of complex wastes in liquid form (<5 % total solids) is a mature technology that has been well studied and successfully implemented at full-scale.<sup>6</sup> However, digestion in liquid form produces excessive fermented liquid, the disposal of which is difficult. Anaerobic digestion of high-solid substrates ( $\geq 20$  % total solids), referred to as 'dry digestion', has been proven feasible.<sup>7–9</sup> In addition, dry anaerobic digestion has become attractive because it requires relatively simple pre-treatment and addition of less water before digestion than in liquid form.<sup>10</sup> High efficiency dry anaerobic digestion has attracted attention owing to the increasing generation of municipal solid wastes (MSW). The state-of-the-art of dry anaerobic digestion has been reviewed by De Baere<sup>10</sup> for digestion of MSW and by Qi<sup>11</sup> *et al.* for digestion of lignocellulosic substrate.

Kitchen wastes (KW) contain a high concentration of biodegradable organic compounds.<sup>12</sup> But the single-phase anaerobic digestion of KW is not straightforward for the accumulation of intermediary compounds occurs easily, giving rise to an unbalanced fermentation, and consequently, diminishing the stability of the process.<sup>13</sup> On the other hand, the soluble organics are converted rapidly to volatile fatty acids (VFAs) at an early stage of the digestion process,<sup>14</sup> resulting in a drastic pH drop if no sufficient buffering capacity is present.<sup>15</sup> As a result, anaerobic treatment of KW is often performed at low organic loading rates (OLR) of 2–3 g COD L<sup>-1</sup> d<sup>-1</sup> to prevent process failure.<sup>16</sup> Therefore, it is important to investigate the optimum conditions and efficiencies of digesters by examining VFAs.<sup>17</sup> Moreover, the quantity of KW

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is likely to increase with the growing population and improvement of the living standard. Consequently, alternative KW disposal technologies have become a major concern in past years.<sup>18</sup> There is some literature about the anaerobic digestion of KW in liquid form.<sup>16,19</sup> This study investigates the development of dry anaerobic co-digestion of cattle manure with kitchen wastes.

# Materials and methods

## **Materials**

The cattle manure was provided from a cattle farm in Zhengzhou suburb, while the KW came from the canteens of Zhengzhou University, and the major components were cooked noodles, steamed buns, rice, fish, meat, vegetables, fruits, and so on. The inoculum was anaerobic sludge obtained from anaerobic digestion of the cattle manure. The characteristics of the initial feedstock are shown in Table 1.

Table 1 - Characteristics of initial feedstock

Analysis	Cattle manure	Kitchen waste	Inoculum
TS (wt%)	84.46±3.23	87.76±3.44	13.61±3.02
VS (%)	57.72±6.02	84.61±6.98	32.66±6.32
Organic matter (%)	62.14±6.59	66.56±6.97	38.05±6.12
pН	$8.5 \hspace{0.1in} \pm 0.2$	$3.5 \pm 0.2$	7.2 ±0.2
Total VFA (g AcH L <sup>-1</sup> )	1.16±0.79	$1.7 \pm 1.01$	6.32±1.56
$N-NH_4$ (g $L^{-1}$ )	0.72±0.23	0.18±0.31	2.08±0.59
TN (%)	$1.46 \pm 0.87$	2.68±0.96	2.24±1.12
C/N	24.72±2.68	14.41±2.54	10.63±2.01

Table	2	- Different	ratio	of	initial	feedstock
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Reactors	R1	R2	R3	R4	R5	R6
TS <sub>cattle manure</sub> :TS <sub>kitchen waste</sub>	1:0	11:1	9:1	7:1	5:1	3:1

Table 3 - Characteristics of the six reactors

#### **Experimental device**

The experiments were conducted in a laboratory-scale reactor with total capacity of 5.0 L. Operating temperature was maintained at  $35\pm1$  °C, controlled and monitored by thermostatic bath. Total solid for all the reactors was about 20 %, with inoculum of 10 % (TS). In view of C/N which was best in the range of 20–24, the ratio of cattle manure to kitchen waste is shown in Table 2, and the characteristics of six reactors are shown in Table 3.

#### **Analytical methods**

The parameters analyzed were total solids (TS), volatile solids (VS), pH, total nitrogen (TN), organic matter, total volatile fatty acid (VFA), ammonium nitrogen ( $NH_4$ -N), and the biogas production and composition.

The analytical determination of TS, VS, TN, and NH<sub>4</sub>-N was performed according to Standard Methods,<sup>20</sup> after drying, grinding and dilution of the samples. Every two days, 10 mL leachate of the reactors were sampled and analyzed for pH and VFAs. The volume of biogas was measured using a wet gas flow meter (LML-1).

The VFA levels were determined using a gas chromatography equipped with a flame-ionization detector and FFAP capillary column. The temperature of the injection port and detector was 200 °C. The temperature of column was 150 °C . Nitrogen gas at 22 mL min<sup>-1</sup> was the carrier gas. Hydrogen and air were used at the flow rate of 43.9 mL min<sup>-1</sup> and 159 mL min<sup>-1</sup>, respectively. The samples were pre-treated by adding the same volume of 3 % formic acid to adjust the pH below 3, and then centrifuged at 12000 rpm for 10 minutes. The supernatant was used in the analysis. Total VFA was calculated by addition of individual VFA levels.

Biogas composition was analyzed using a gas chromatography equipped with a thermal conductivity detector and GDX-01 column. The temperature of the injection port and detector was 100 °C. The temperature of column was 80 °C. Hydrogen at 8.78 mL min<sup>-1</sup> was the carrier gas.

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Analysis	R1	R2	R3	R4	R5	R6
TS (wt %)	23.17±2.87	20.91±2.56	21.33±2.79	22.55±2.16	22.67±2.46	23.73±3.01
VS (%)	67.09±6.01	60.49±6.23	60.67±6.89	64.67±6.54	64.78±5.98	71.84±6.16
Organic matter (%)	62.14±6.12	62.51±6.34	62.58±6.55	62.69±6.02	62.88±6.28	63.61±6.87
pН	7.5±0.2	6.9±0.3	6.8±0.2	6.8±0.2	6.4±0.3	6.5±0.3
Total VFA (g AcH L <sup>-1</sup> )	1.16±0.89	1.21±0.92	1.22±0.76	1.23±0.82	1.25±0.94	1.35±1.03
$N-NH_4(g L^{-1})$	$0.72 \pm 0.22$	$0.68 \pm 0.32$	$0.66 \pm 0.25$	$0.65 \pm 0.34$	0.63±0.41	0.54±0.26
TN (%)	1.46±0.68	1.56±0.94	$1.58 \pm 0.85$	1.61±0.93	1.66±0.88	$1.87 \pm 1.01$
C/N	24.72±1.73	23.27±2.65	23.00±1.89	22.61±2.24	21.99±1.79	19.75±1.89

# **Results and discussion**

## Volatile fatty acids degradation

VFA was a critical parameter for operation and control of anaerobic digestion. The evolution of VFAs (g  $L^{-1}$ ) in the six reactors is shown in Fig. 1.

As evident, during 22 days of operation, hydrolytic and acidogenic stages were observed during days 0–6 with high VFAs generation, while the higher level of VFAs lasted two weeks. The evolution indicated that the substrate hydrolyzed quickly and the hydrolyzed organic matter transformed to VFAs, suggesting the start of the stabilization phase. The total VFA increased with the increase in kitchen waste during the experimental process in the six reactors. Total VFA concentration was below 10 g L<sup>-1</sup> with the main VFAs of acetic and propionic acid in R1-R5. However, total VFA value in R6 was above 16 g L<sup>-1</sup> during the experimental process, with the maximum value being 31.25 g L<sup>-1</sup>, and



Fig.1 - Reactor performance data of VFAs and accumulative methane

the VFA was mainly butyric and valeric acid. As a result, the experiment in R6 was blocked by accumulation of VFAs produced rapidly in the hydrolytic and acidogenic phases, leading to an abrupt drop in pH, unsuitable for anaerobic digestion (Fig. 2a).

The concentration of the VFAs in digester was determined by their production rate and their removal rate. Acetic acid removal rate was superior to its production rate because approximately 70 % of the digester methane originated from acetate, and the remainder of the digester methane originated mainly from the reduction of carbon dioxide with hydrogen.<sup>21</sup> The concentration of propionic acid increased with the enhancing of the ratio of KW in R1-R5 with almost no accumulation of butyric and valeric acid. The butyric and valeric acid accumulated in R6. Valeric acid firstly converted slowly to propionic acid, which converted to acetic acid and hydrogen, which transformed to methane. The butyric acid converted directly to acetic acid. Therefore, the valeric acid removal rate was inferior to its production rate.<sup>22</sup> As a result, if too much valeric acid were generated in the reactor, it would accumulate and the pH would drop rapidly to block fermentation.

#### Substrates biodegradation

The pH was stable and remained in the neutral range (between 6.5 and 7.7) until the end of the experiment for R1-R5, but the pH for R6 decreased acutely at the beginning of the digestion from 6.5 to the range of 4.5–5.0 after 4 days (Fig. 2a), which was not suitable for anaerobic digestion because the appropriate pH for methanobacteria ranges from 6.5 to 7.8.<sup>22</sup> The ammonium nitrogen values in different reactors were all below 1000 mg L<sup>-1</sup> indicating that it was in the safety range for anaerobic digestion.<sup>23</sup>

Fig. 2b showed the degradation rate of VS (%) in the six reactors with different ratios of initial feedstock. The degradation rate of VS, which indicated the microbial transformational activity, reached stability after 20 days in all reactors except R5. But the degradation in all the reactors except R6 was not over after 22 days of operation. As evident in Fig. 2b, in days 4–10 and days 12–16, the best values of VS degradation rate were for all reactors except R6. This revealed that the biogas had generated in two periods, coinciding with the change of biogas production in Fig. 3. For R6, the VS degradation took place during days 0–6, because the experimental progress was blocked after 6 days.

The degradation rate of VS was higher for R5 than other reactors, with the value of 15.58 % after



Fig. 2 – Evolution of pH and VS in the anaerobic reactors

 

 Table 4 – Summary performance of process in different reactors after 22 days of experiment

Reactors .	VS elimination	Biogas yield	Methane yield
	%	$L g^{-1} VS$	$L CH_4 g^{-1} VS$
R1	$10.99 \pm 0.41b$	$0.2003 \pm 0.0258b$	$0.1033 \pm 0.0246c$
R2	$10.91 \pm 0.45b$	$0.2056 \pm 0.0216b$	$0.1213 \pm 0.0224$ ab
R3	$11.34 \pm 0.38b$	$0.2019 \pm 0.0286b$	$0.1178 \pm 0.0268b$
R4	$14.98 \pm 0.45a$	$0.2304 \pm 0.0245a$	$0.1223 \pm 0.0249a$
R5	$15.58 \pm 0.46a$	$0.2409 \pm 0.0288a$	$0.1208 \pm 0.0268$ ab
R6	$6.19 \pm 0.41c$	$0.0259 \pm 0.0112c$	$0.0033 \pm 0.0012d$

22 days of operation, followed by R4 of 14.98 % (Table 4). The biogas yield of R5 was the highest. However, the methane content of biogas of R5 was lower than that of R4 because the propionic and velaric acid, which changed into  $CO_2$  and acetic acid, was much higher in R5.

#### **Biogas and methane production**

Biogas was generated from the first day. The daily biogas production peaked twice during the 22 days in R2, R3, R4 and R5 (Fig. 3). The peak time of biogas production appeared later and the methane content of biogas decreased along with the enhancing of KW. The methane content of biogas exceeded 55 % in all reactors after 6 days except R6. The average daily biogas production of R4 and R5 amounted to 10.47 and 10.95 mL g<sup>-1</sup> VS day<sup>-1</sup> with the average methane content of 54.51 % and 51.55 %, respectively, which was higher than the values of other reactors.

The accumulative biogas for R5, R4 and R1 after 22 days reached 240.99, 230.38 and 200.28 mL  $g^{-1}$  VS, with the accumulative methane of 120.77, 122.32 and 103.27 mL  $g^{-1}$  VS, respectively. According to



Fig. 3 – Biogas production and methane composition in different reactors

the biogas and methane production, the ratios of cattle manure to KW in the range of 11:1–5:1, especially in the range of 7:1–5:1, could improve methane production in dry anaerobic digestion compared with dry anaerobic digestion of cattle manure with no KW.

## **Comparative process efficiency**

Table 4 shows a summary of performance data at the end of the process for all six reactors studied. Over 22 days of operation, the highest methane yield was obtained for R4, followed by R2 and R5 with values of 0.1223, 0.1213 and 0.1208 L  $CH_4$  g<sup>-1</sup> VS, respectively, which was higher than R1 (control) of 0.1033 L CH<sub>4</sub> g<sup>-1</sup> VS. This coincides with the results achieved by Forster-Cameiro<sup>24</sup> *et al.* who detected methane yields for organic fraction of municipal solid wastes (OFMSW) with different inoculum and found similar results. The highest methane yield was obtained for SLUDGE reactor, followed by SWINE/SLUDGE reactor and SWINE, with values of 0.29, 0.27 and 0.18 L  $CH_4 g^{-1} VS$  over 60 days of operation. While Fernande $z^{25}$  et al. obtained that the greatest methane yield for R20 (20 %TS) and R30 (30 %TS) in dry mesophilic anaerobic digestion of organic fraction of municipal solid waste amounted to 0.11 L CH<sub>4</sub>  $g^{-1}$  VS and 0.07 L CH<sub>4</sub>  $g^{-1}$  VS, respectively, over 45 days of operation. And the values were lower than those obtained in this experiment.

## Conclusion

The six experiments with different ratios of cattle manure to kitchen waste had performed successfully except R6. In conclusion, this showed that the ratios of cattle manure to KW from 11:1 to 5:1 could improve the digestion process for enhancing the concentration of VFAs in a safety range with the main acetic and propionic acid, suitable for methane yield. However, after adding too much KW, much more VFAs accumulated mainly of valeric and butyric acid, which degraded slowly and finally blocked digestion. Compared to digestion with no kitchen waste, dry anaerobic digestion of cattle manure with kitchen waste achieved better performance for methane yield. On the other hand, it provides a new method for using KW to produce energy by dry anaerobic digestion.

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