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**Bing Mei[1,2,3], Linghou Zhi [1,2] and Qigu Cheng [1]**

[1] Yunnan Agricultural University,Faculty of Civil and Architectural Engineering 650000 kunming PR China;
[2] Engineering and Research Center for Industrial Biogas Technology of Yunnan Province University,Kunming 650201,China.

[3] Email: meibing11meibing@163.com

**Abstract**. The use of volatile fatty acids (VFAs) as process indicators in anaerobic digestion of FW was studied. In this paper, the anaerobic digestion of food waste (FW) at 37℃ under quasi-continuous conditions was described. The aim of this work is to determine a reliable parameter which could be used as an indicator of process imbalance during anaerobic digestion of FW. The results showed that VFAs change constitutes the most important indicator of early warning of process imbalances during anaerobic digestion of FW. During the recovery of the process, propionate could best describe the normalizing of the process.

## 1. Introduction

In recent years,FW treatment has become a serious issue worldwide. In World today, the conventional treatment for food waste is incineration, but this has some disadvantages for environment protection such as energy consumption and air pollution[1] .The attractiveness of anaerobic digestion lies in that it can reduce disposal costs and at the mean time the organic carbon in the waste can be converted to a kind of environmentally friendly energy- biogas[1].

The VFA concentration is well-known as an important indicator for monitoring the anaerobic digestion. It gives faster and more reliable information of process status, compared with other common indicators such as pH, gas production, and gas composition. In several studies of the past, VFA has been proved to be a good indicator of process imbalance during anaerobic digestion [2-4].

In the present paper, many parameters of disturbance of organic overloading were tested in the continuously stirred tank reactors (CSTR) at 37 ℃. Four parameters including methane content, gas production rate, pH and volatile fatty acids concentrations were evaluated. The aim of this work was to determine a reliable parameter which could be used as an indicator of process imbalance during anaerobic digestion of FW.

## 2. Materials and methods

### *2.1. Lab-scale digester reactor system*

The study was performed in a laboratory-scale continuously stirred tank reactor (CSTR). The total working volume of CSTR reactor was 20L (Figure 1).

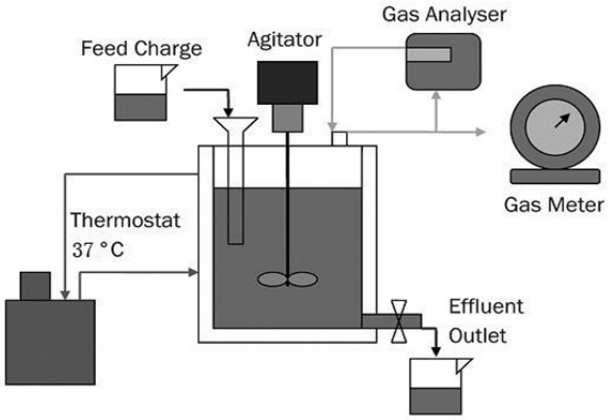


**Figure 1.** CSTR reactor.

*2.2. FW collection and preparation*

FW was collected from a student restaurant in the University .The characteristics of the FW are shown in Table.1

**Table 1.** Characteristics of food waste in the study.

| Parameters | Unit | Average value |
|---|---|---|
| Total solids(TS) | % | 24.93 |
| Volatile solids(VS) | % | 20.71 |
| Moisture content | (MC) % | 75.07 |
| Crude fat | % (Moisture weight) | 6.02 |
| $Na^+$ | g/L | 0.492 |
| C(total) | g/kg (Dry weight) | 359.37 |
| N(total) | % (Dry weight) | 2.31 |
| C/N | ---- | 15.56 |

*2.3. Experimental parameters and analytical methods*

Parameters including pH, total solids (TS), volatile solids (VS), and total volatile fatty acids (TVFA) were determined to be analyzed. All analyses were carried out in accordance with the standard methods of the APHA. Samples were stored at 4 ℃ until analysis. The samples were centrifuged at 5000 rpm for 10 min at 4 ℃.Methane in the biogas was analyzed by a Hewlett Packard GC HPn 5890A (HACH, Avondale, PA, USA).

## 3. Results

All the monitored parameters are shown in Figure 2. In the initial 4 days, TVFA concentration was decreased from 4461 mg/L to 1756 mg/L.Therefore, we conclusion that reactor stabilized gradually. From day 5 to day 21 in the first experiment, total VFA concentration relatively stable in this stage (Figure 2b). Therefore, it could be concluded that the digestion was conducted under good conditions.

During the stable period, the concentrations varied from 10.2 to 14.2 mM for acetate, 7.8 to 16.5 mM for propionate, 0.01 to 0.12 mM for iso-butyrate and 0.24 to 0.57 mM for N-butyrate. In this stage,acetate acid was the pre-dominant VFA with concentration reaching up to 14.2mM. Obviously, acetate acid was the most prevalent product. In this study, propionate acid was the second major product,which was followed by butyrate. N-valeric and iso-valeric acids could also be found in the reactor but at a low concentration. Figure 2e shows that the propionate / acetate ratio was quite stable during this stage, ranging from 0.55 to 1.47.

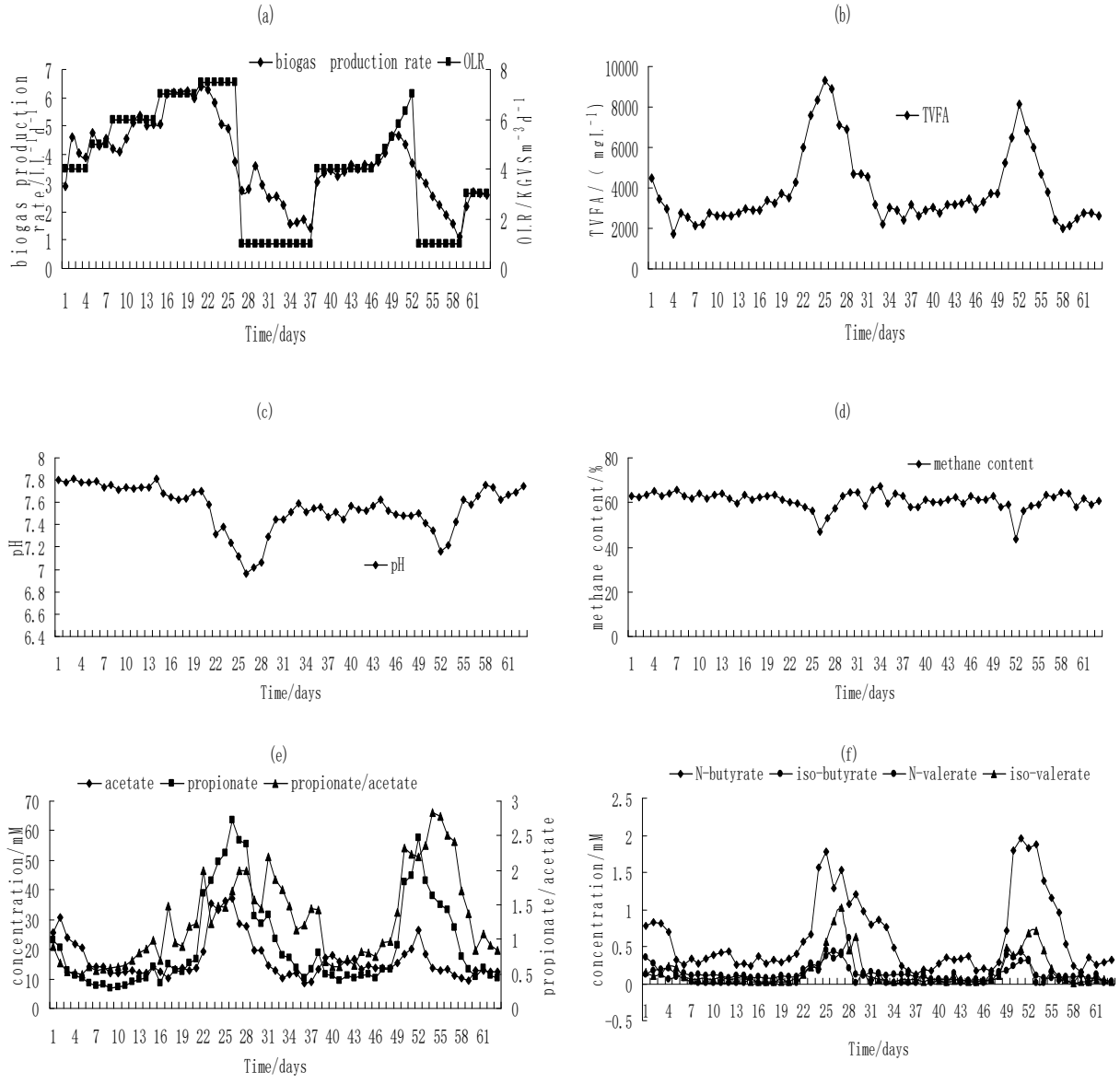


**Figure 2.** reactor results during day 1-63.(a) biogas production rate and OLR;(b)total VFA (c) pH; (d) methane content(e)acetate, propionate and propionate/acetate ;(f) N-butyrate , Iso-butyrate, N-valerate and Iso-valerate.

On day 22 of the experiment, FW was fed at an OLR of 7.5 KGVS m3d-1.In this process, The total VFA concentrations increased rapidly (Figure 2), we decided that the process of anaerobic digestion was unbalanced.

During the overloading period , the concentration was dramatically increased from 19.3 mM (day22) to37.1 mM (day 26) for acetate, 38.6 mM (day22) to 63.42 (day26) mM for propionate. And the concentrations varied from 0.57 to 1.47 mM for N-butyrate, 0.13 to 0.43 mM for iso-butyrate, 0.19 to 0.45mM for N －valerate and 0.13 to 0.85 mM for iso- valerate. Propionate, representing more than 60 % of the TVFA, was the most prevalent product in the experiment. In this stage, propionate / acetate ratio was dramatically increased from 1.45 to 1.99.

Methane content increased rapidly 6 days later , showing a good recovery of activity. During the recovery of the process, the concentrations of acetate, butyrate and valerate decreased drastically. The concentration of propionate dropped at a low speed, and even 6 days later, its concentration was as high as 23.2 mM.It could be concluded that during the recovery of the process, propionate concentration could best describe the normalizing of the process.

From day 46 to day 49 in the experiment, TVFA concentration ranged from 2956 mg/L to 3723 mg/L,It could be concluded that the anaerobic digestion was conducted under good conditions .During the stable period (day 46-49), the concentrations varied from 13.8 to 15.3 mM for acetate, 10.4 to 21.3 mM for propionate, 0.13 to 0.38 mM for iso-butyrate, 0.28 to 0.43 mM for N-butyrate. In this stage, acetate was the major product with concentration reaching up to 15.3 mM, and propionate the second. These two products represented 90 % of the TVFA. Figure 2e shows that the propionate / acetate ratio was quite stable during this stage, ranging from 0.55 to 1.43.

From day 50 to 52 in the experiment, biogas production rate decreased with the increase of OLR. On day 52, the methane content dropped to 46.76%. Thereby, we could confirm that the process of anaerobic digestion was unbalanced.

During the overloading period (day 50-52), it has been observed for once that the concentration was dramatically increased from 18.3 mM (day 50) to 26.3 mM (day 52) for acetate, 42.5 (day 50) to 57.8 mM (day 52) for propionate. And the concentrations of N-butyrate, iso-butyrate, N －valerate and iso- valerate varied from 0.35 to 0.42 mM, 0.31 to 0.42mM, 0.23 to 0.32mM and 0.36 to 0.48 mM, respectively. It was found again that propionate, representing more than 60 % of the TVFA, was the most prevalent product in the experiment. In this stage, propionate/acetate ratio was dramatically increased from 0.75 to 1.39.

It was observed that methane content increased 6 days later , indicating a good recovery of methanogenic activity. During the recovery of the process, it was observed again that the concentrations of acetate, butyrate and valerate decreased drastically. The concentration of propionate dropped at the lowest speed and even 6 days later, its concentration was as high as 27.3 mM. The return of propionate concentration back to the steady-state level was 4-5 days slower than any other VFA. Consequently, it could be proved again that during the recovery of the process, propionate concentration could best describe the normalizing of the process.

## 4. Discussion

As can be seen in Figure 2, the total VFA change was too slow or too small to detect process status. Angelidaki suggested that the total VFA concentration isnt necessarily toxic to the process directly. Therefore, the increased VFA is generally the result, but not the cause of process imbalance[5].

Several volatile fatty acids showed clear response to the organic overloading. These parameters such as acetate and propionate had clear response to the organic overloading. As propionate was the most persistent one in the reactor, it could be an important indicator to determine the degree of process imbalance. During the overloading process, VFAs, especially acetate and propionate, had a high concentration. In the previous studies, it was believed that the high concentrations of propionate should be responsible for the process failure and that propionic acid at a concentration of 0.9g /l (12.5 mM) has resulted in decreased methanogenic growth rate and methane yield [6].

This could be due to the fact that propionate degradation is the most thermodynamic unfavorable among other VFA degradation, which made propionate degraders the slowest growing and most sensitive, compared with acetate and butyrate, degraders which could faster increase their degradation rate. In this experiment, propionate was a parameter to indicate process stress. However, it was found from day 50-52in the second experiment that the concentration of propionate was greatly different from that in the first experiment (day 22-26) during the overloading period. Furthermore, the experiment demonstrated that the propionate/acetate ratio could not be used as an indication of process imbalance since the propionate/acetate ratio sometimes during the stable process of anaerobic digestion was well below the limit of 1.4 suggested [7].

These results are in agreement with that reported by Ahring BK who suggested that a combined parameter reflecting the concentrations of both n-butyrate and iso-butyrate could be a reliable tool for indication of process instability [8]. Hill and Holmberg suggested that the concentration of iso-butyrate and iso-valerate higher than 0.06 mM was an indication of process instability. However, in this experiment, VFA concentrations were all well above those limits [9].

During the overloading process, analysis of the VFA concentration and composition after the disturbance of the perturbation showed a constant accumulation of acetate and propionate, but n-butyrate, iso-butyrate and iso-valerate began to accumulate only when acetate and propionate concentration reached high concentration.

Therefore, we could draw a conclusion that the concentrations of acetate,propionate,n-butyrate, iso-butyrate and iso-valerate can be used as parameters for the indication of process imbalance. But from day 50-52 in the second experiment, the concentrations of acetate,propionate,n-butyrate, iso-butyrate and iso-valerate were greatly different from those in the first experiment (day 22-26) during the overloading process.

## 5. Conclusions

(1) The concentration levels of acetate,propionate,n-butyrate, iso-butyrate, iso-valerate can be used as parameters to indicate process imbalance during the anaerobic digestion of FW.

(2) It can be concluded that VFAs changes constitute the most important indicator of early warning of process imbalance during anaerobic digestion of FW.

(3) During the recovery of the process, propionate could best describe the normalizing of the process.

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