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Influence of temperature on hydrolysis acidification of food waste

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Abstract

For two-phase anaerobic digestion process of food waste, degree of hydrolysis and products by acidification during hydrolysis and acidification phase directly affect the performance of methanogenesis phase. Temperature has great impact on hydrolysis and acidification of food waste. This paper monitored the dynamic change of biogas production, biogas composition, pH, soluble chemical oxygen demand (SCOD) and volatile fatty acids (VFAs) during hydrolysis and acidification stage so as to investigate specific influence of temperature on food waste. With the same inoculum and 9 days' fermentation, three different temperatures (35, 55 and 70 ºC) were taken into consideration. The results showed that cumulative gas production was 4860 mL at 70ºC, which was 129.79% and 37.87% higher than that at 35 and 55 ºC. Besides, hydrogen content at 70 ºC was 45.34%, which was the highest among the three temperatures. Hydrolysis rate was proportional to the increase of temperature. Meanwhile, total VFAs yield and composition widely differed at three different temperatures. The hydrolysis and acidification products at 35 ºC were mainly ethanol and acetic acids and the highest concentrations of ethanol at 35 ºC were 3.28 and 3.65 times of that at 55 and 70 ºC, but more acetic, isobutyric and butyric acids were generated at 55 and 70 ºC. Among three temperatures, 70 ºC had the highest acetic acids concentration while 55 ºC had the highest isobutyric and butyric acids concentration.

Keywords: Anaerobic digestion; Food waste; Hydrolysis acidification; Soluble chemical oxygen demand; Volatile fatty acids

1. Introduction

Food waste generation was increasing year by year in China and accounted for over 50% of the municipal solid waste in some big cities [1]. Food waste is perishable due to its high organic and moisture

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content. Large amounts of toxins and stench gas being produced in the process of transportation and disposition of food waste can cause pollution to the water and air. Anaerobic digestion, a technology that consume the organic component of food waste rapidly with a generation of biogas, has become an important technology for treating food waste as well as preventing pollution and obtaining renewable energy. Zhang et al. used food waste as substrate for anaerobic digestion procedure and 435 mL per gram volatile solids (VS) of biogas production rate was obtained after 28 days of digestion. The average methane content and total solids (TS) removal rate was 73% and 81% respectively [2].

Due to the high organic content of food waste, the acid accumulation appeared frequently and the digestion process suffered from the stability issues. Two-phase system split anaerobic digestion into two processes, hydrolysis/acidification and methanogenesis, which had different reactor condition requirements such as oxido-reductive activities, growth rates and pH optima (in the range 4.0-6.0 and 6.5-8.0, respectively). Thus two-phase system had several advantages over single-phase process such as increasing stability, improving microorganism specialization and promoting conversion performance. Products of hydrolysis and acidification stage were the substrates of methanogenesis stage. So the degree of hydrolysis and products by acidification (composition and yield) distinctively affected methane yield. Hydrolysis and acidification stage is influenced by environmental factors such as substrate, inoculums, pH, temperature and hydraulic retention time (HRT) [3,4]. Since temperature is an important factor in microbial activity, there are many reports focusing on the relationship between temperature and methanogenesis while the effect of temperature on the hydrolysis and acidification of food waste remains unclear. Kim et al. investigated the effects of temperature on anaerobic digestion of food waste. The operation temperature was adjusted from 30 ºC to 55 ºC and thermophilic digesters showed a higher rate of SCOD removal and methane production yield than mesophilic digesters [5]. Shin et al. studied the mesophilic and thermophilic acidification of food waste. Compared with the mesopilic acidification that acetic acids and propionic acids were the main components of VFAs, butyric acid fermentation was achieved with butyric acids accounted for 54-60% and no propionic acids produced under thermophilic acidification. The lag time of the mesophilic and thermophilic acidification was 11-23d and 0.1-3.6d respectively [6]. Ortega et al. investigated the impact of adapting mesophilic sludge to thermophilic conditions. The reactor temperature was instantaneously increased from 35 to 55 ºC and operated at this temperature until day 21. The abrupt temperature changes had no pasteurization effect, but rather lead to a biomass to acetoclastic and hydrogenophilic microorganisms. And methane production rate was 0.1-0.84 L_{STP} CH_4/gVS_{fed} [7]. There were only few reports about hyperthermophilic digestion at present. Lee et al. evaluated the performance of the co-digestion of food waste and excess sludge with an acidogenic reactor operated at hyperthermophilic (70 ºC) condition. Chemical Oxygen Demand (COD) solubilization and average protein solubilization was in the range of 22-46% and 44% respectively [8].

The main purpose of this study was to investigate the specific influence of three different temperatures (35, 55 and 70 ºC which was corresponded to temperature under mesophilic, thermophlic and hyperthermophilic anaerobic digestion respectively) on the hydrolysis and acidification of food waste with the same inoculum and 9 days' fermentation so as to offer reference for the choice of technological process of hydrolysis and acidification of food waste.

2. Materials and methods

2.1. Substrates and inoculums

Food waste used in this study was collected from student canteen at Beijing University of Chemical Technology. Bones, chopsticks, plastic bags and other raffles were picked out before shredding by a food grinder (Waste King, USA) to avoid any mechanical damages to the grinder. The food waste was finally shredded into slurry state. Anaerobic digestion sludge collected from a mesophilic anaerobic digester in Xiaohongmen municipal waste water treatment plant (Beijing, China) was used as inoculum. All the materials were then collected and preserved in a freezer at -20oC for later use. Before commencing this study, characteristics of substrates and inoculums were analyzed and shown in Table1.

Table 1.Characteristics of food waste and anaerobic digestion sludge

Item	Food waste	Sludge
TS/%	18.28	10.71
VS/%	87.48	61.67
Carbon/%	48.35	32.20
Nitrogen/%	0.76	4.14
Carbon to Nitrogen ratio(C/N)	63.62	7.42
SCOD/ $g\cdot L^{-1}$	136.59	482.86
Soluble Biochemical Oxygen Demand(SBOD) /$g\cdot L^{-1}$	46.20	/
Crude fat%	24.11	/
Crude protein%	14.42	/
Total sugar%	35.47	/

※The content of above items were judged on a dry-matter basis except for TS and VS.

2.2. Reactor and operation

A 2500 mL flask with a fluid outlet near the bottom was used as a reactor and the working volume was 2L. A 1L jar and a 1L beaker were used as the gas gathering device. Three temperatures 35, 55 and 70 ºC which were correspond to temperature under mesophilic, thermophilic and hypertheromophlic anaerobic digestion respectively were set for this test and two parallel for each temperature. Feeding load of food waste and inoculum were 45 and 15g·L-1 on a VS basis. Then filled the reactors with tap water to their working volume and adjusted pH to approximately 7.00. In order to evaluate the effects of temperature on physicochemical and microbial activities, the experiments were carried out for a relatively long period, although hydrolysis and acidification processes are known to be completed within 3-4 days. There was previous study carried out such experiment for 22 days with relatively little change in later days [9], so here we set 9 days for this experiment. Daily gas production and composition were monitored on a daily basis while dynamic change of pH, SCOD and VFAs were monitored every other day.

2.3. Analysis methods

Gas production for each reactor was measured by water displacement method. Gas composition was analyzed by a gas chromatograph SP-1120 (Shunyuhengping, Shanghai) equipped with a packed column (TDX-01, inner diameter of 4 mm and length of 2 m) and thermal conductivity detector (TCD), temperature of injector and detector were both maintained at 150 ºC while temperature of column was 140 ºC, the carrier gas is argon. VFAs were analyzed by a gas chromatograph GC-2014 (Shimadzu, Japan) equipped with a capillary column (DB-WAX, inner diameter of 0.320 mm and length of 30 m) and flame ionization detector (FID), temperature of injector and detector were both maintained at 250 ºC while temperature of column adopted temperature programing from 100 ºC (hold 1 min) to 180 ºC at a rate of 5 ºC/min and hold 3 min at 180 ºC, the carrier gas is nitrogen. Samples for VFAs analysis were first centrifuged at 10000 rpm for 5 min, the supernatants were then filtered through 0.22μm filters and then added phosphoric acid to the filtrates to adjust its pH below 2.0 and collected in GC sample vials for analyzing. pH was measured by a pH meter Olion 3STAR (Thermo Scientific, USA). COD was analyzed by COD analyzer DR2500 (HACH, USA) and BOD was analyzed by BOD analyzer BOD Track^{TM} II (HACH, USA). TS, VS were tested according to the standard methods.

3. Results and discussion

3.1. Biogas production and compostion

Gas production at three different temperatures all reached their peaks in the first day but differed in peak values. The maximum daily gas production was 3515 ml at 55 ºC higher than that at 35 and 70 ºC which was 1870 ml and 2475 ml respectively. Stagnant of gas production occurred at 35 and 70 ºC after they reached their peaks in the first day since there was no gas produced in the subsequent period of time. However, the gas production process lasted for 3 days at 70 ºC and then the reaction entered into a state without any gas production.

Cumulative gas productions at three temperatures were 2115, 3525 and 4860 mL respectively. It was evident that the cumulative gas production at 70 ºC was higher than the other two (129.79% higher than that at 35 ºC and 37.87% higher than that at 55 ºC). Gas contents were different at three temperatures. Carbon dioxide contributed a large proportion to biogas at 35 ºC, while hydrogen proportion was only 0.07%. At 55 and 70 ºC, biogas was composed by hydrogen and carbon dioxide while hydrogen occupied a large proportion both at 55 and 70 ºC. The maximum hydrogen percentage was 44.30% at 55 ºC and 45.34% at 70 ºC. Previous studies have shown that hydrogen is mainly generated in acidification stage, this meant that high temperature may significantly affect the acidification process of food waste.

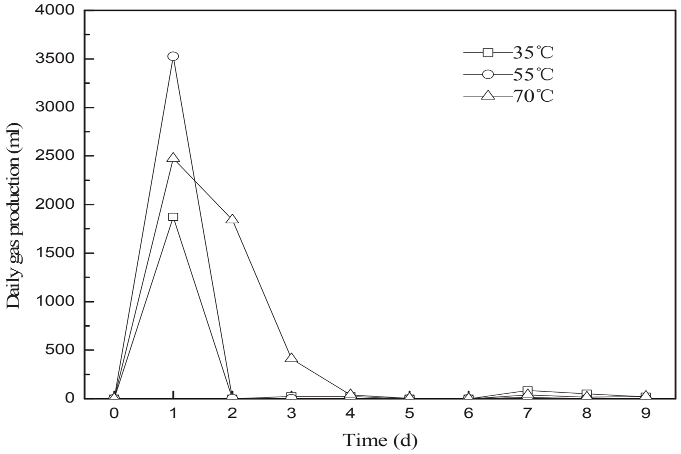

Fig 1. Daily gas production at three different temperatures

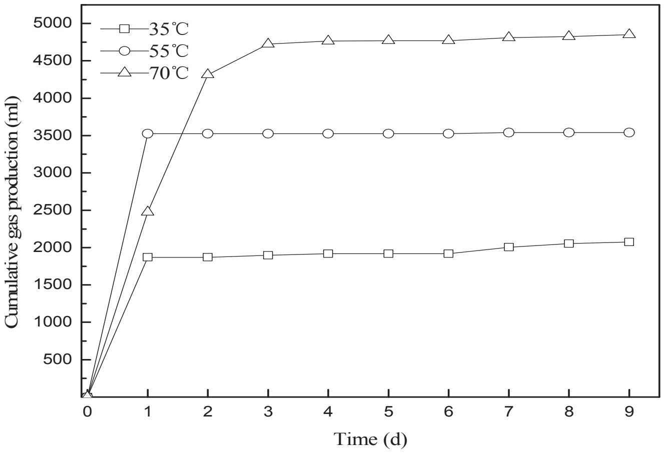

Fig 2. Cumulative gas production at three different temperatures

3.2. VFA production and composition at different temperatures

At the beginning of the reaction, the total yield of VFAs at each temperature was gradually increasing with the reaction time. But on the seventh day, the overall VFAs concentration at 35 ºC just increased a little while the overall VFAs concentration at 55 and 70 ºC dropped down. This suggested that the optimal number of days needed for VFAs production was approximately 7d for the digestion of this food waste at 55 and 70 ºC. Besides, at the end of this fermentation, 35 ºC harvested the largest VFAs production followed by 55 and 70 ºC.

Composition of VFAs at different temperatures differed greatly from each other. At 35 ºC, the production of ethanol was the largest and the maximum production can be 3.28 and 3.65 times of that at 55 and 70 ºC. Combined with the data of the gas composition, it was evident to see that under the temperature of 35 ºC, the main products during the hydrolysis and acidification stage were ethanol and acetic acids which were with a proportion of more than 99% of the total VFAs but the hydrogen content was very low with a highest proportion of 0.07%. This indicated that the reaction during this stage was mainly caused by the yeast. When the temperature is lower than the freezing point of water or higher than 47 ºC, the yeast cells are generally unable to grow [10]. Thus when the temperature was 55 and 70 ºC, the growth of yeast was suppressed and caused a lower production of ethanol. The production of acetic acids which can be directly utilized in the follow-up methanogenesis stage was much different at three temperatures. Production of acetic acids shown an increasing trend along with the temperature, at the end of the fermentation, concentration of acetic acids was 5664.28 mg·L-1 at 70 ºC, which was 3.26 and 0.89 times of that at 35 and 55 ºC. For the production of isobutyric and butyric acids, it was highest at 55 ºC followed by 70 ºC and there were little isobutyric and butyric acids at 35 ºC. All in all, by comparing the VFAs at three temperatures, concentration of the total VFAs was 35 ºC> 55 ºC> 70 ºC, concentration of the ethanol was 35 ºC> 55 ºC> 70 ºC, concentration of acetic acids was 70 ºC> 55 ºC> 35 ºC, concentration of isobutyric and butyric acids was 55 ºC> 70 ºC> 35 ºC. This shown that the elevation of temperature will inhibit the production of ethanol but promote the production of acetic and butyric acids. By comparing the data at 55 and 70 ºC, it was obvious to see that when the concentration of acetic acids increased, the concentration of isobutyric and butyric acids also increased. This was because when the acetic acids production rate was high, it often brought out the coupling effect of cycle mechanism by acetic acids and butyric acids producing process. (This is because there is no reducibility during the generating way of acetic acids, when the acetic acids production rate is high, it can lead to a large surplus of NADH+H+. At the same time, acetic acids can generate excessive acidic end products which can lead to a low pH and have a reverse feedback to the generation of acetic acids. The butyric acids producing pathway can reduce the production of NADH+H+ and acidic end products [11].)

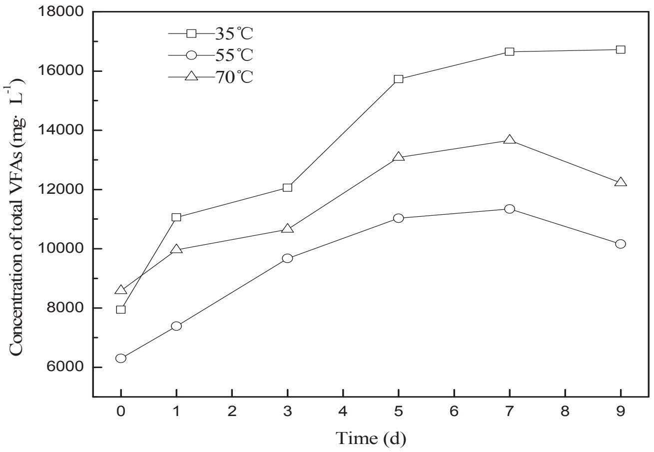

Fig 3.Concentration of total VFAs at three different temperatures

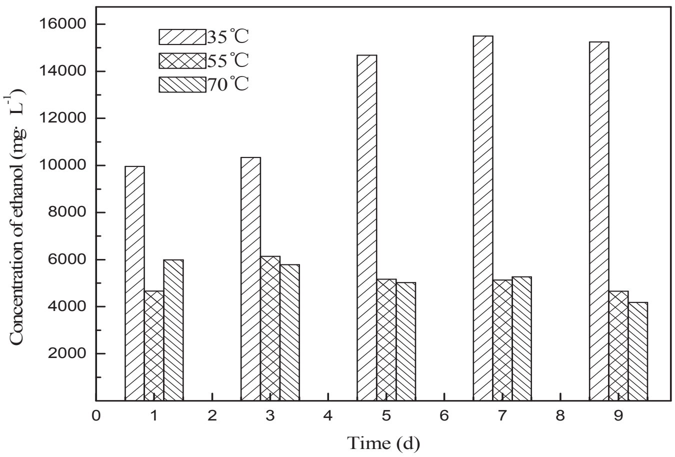

Fig 4. Concentration of ethanol at three different temperatures

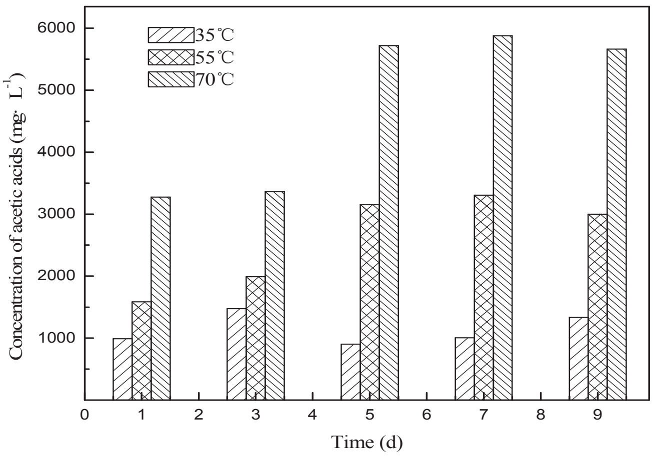

Fig 5. Concentration od acetic acids at three different temperatures

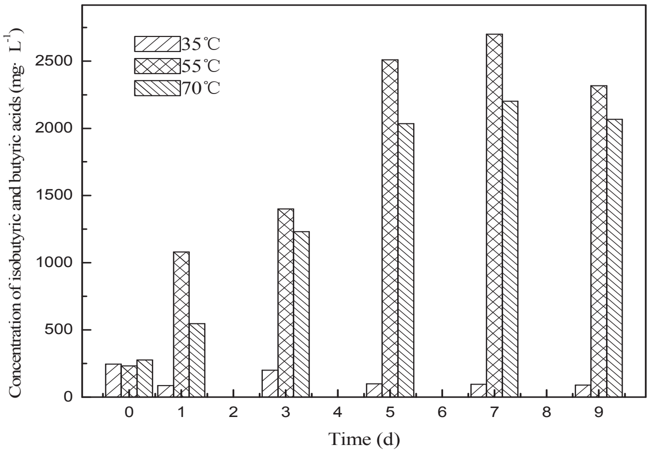

Fig 6. Concentration of isobutyric and butyric acids at three different temperatures

3.3. pH

pH at three different temperatures dropped to a low value within one day. Along with the reaction, pH kept on dropping but with a smaller decreasing extent. After three days of reaction, pH fluctuated in a small range and basically maintained steady. The decrease of pH was due to the decomposition of organic matters by microorganism. Organic acids generated through this process caused the decrease of pH. Throughout the reaction, the decreasing range of pH at three temperatures were different, decreasing range at 35 ºC was higher than that at 55 and 70 ºC. At the end of the fermentation, pH of the discharge at three different temperatures was 3.70, 4.15 and 4.45 respectively. Compared with the yield of VFAs, pH was higher when the content of isobutyric and butyric acids was higher. When content of organic matters is high and content of oxygen is low, organic phosphorus can be converted to gaseous phosphine by anaerobic microorganisms such as clostridium butyricum [12]. In the reaction system, more butyric acids were generated meant that the activity of clostridium butyricum was stronger, and more gaseous phosphine was generated. Gaseous phosphine was easy to enter into water and reacted with alkaline substances to generate phosphate and was converted to phosphite and hypophosphite, which resulting a higher buffer capacity and thus the decreasing change of pH was smaller at 55 and 70 ºC than at 35 ºC.

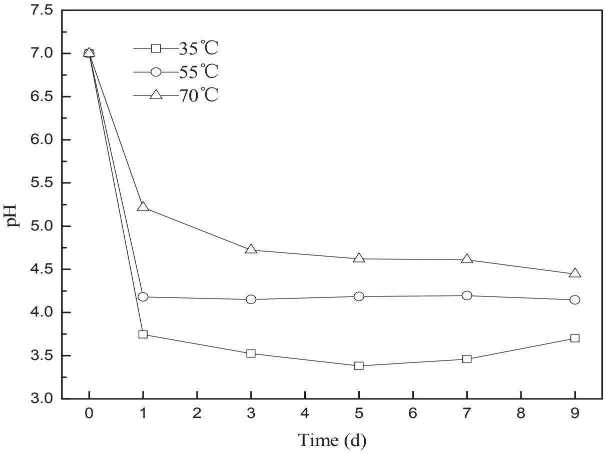

Fig 7. Change trend of pH at three different temperatures

3.4. Soluble COD concentration

The primary products of hydrolysis process are soluble monomers which can be measured as soluble COD [13]. Trends of SCOD change under three temperatures were firstly increased and then decreased gradually. The organic matter was gradually broken down into soluble monomers so as to promote the increase of SCOD at the beginning of the reaction. Based on figure 8, the increasing rate and extent of SCOD at three temperatures differed from each other. From the beginning to the first day of reaction, the growth rate and extent at 70 ºC were significantly higher than that at 35 and 55 ºC, 35 ºC has the slowest growth rate and extent. From day 2 to day 3, growth rate of SCOD at 55 and 70 ºC slightly dropped down but it increased at 35 ºC. This trend was consistent with trend of VFAs which indicated that hydrolysis and acidification were unlikely to be occurring sequentially [13]. Time to achieve maximum SCOD yield differed at different temperatures. On day 3, maximum SCOD yield was achieved at 70 ºC, which was 46758.86 mg·L-1 while it took five days for 35 and 55 ºC to reach their maximum SCOD yield. This indicated that 70 ºC promoted hydrolysis. In the later reaction, SCOD showed a downward trend. This was because acidification rate at this time was higher than that of hydrolysis. More soluble monomers were converted to small molecules and thus resulted the phenomenon that VFAs production kept on increasing but SCOD was decreasing.

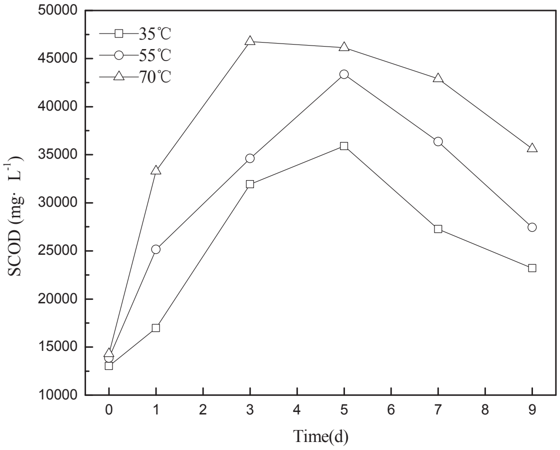

Fig 8. Concentration of soluble chemical oxygen demand at three different temperatures

4. Conclusions

Hydrolysis and acidification of food waste at three temperatures (35, 55 and 70 ºC) presented different changing trends. Cumulative gas production and hydrogen content at 70 ºC were 4860 mL and 45.34%, both reached the highest level among three temperatures. Hydrolysis rate was proportional to the increase of temperature since concentration of SCOD at 70 ºC was higher than the others and was followed by that at 55 ºC. It took 3d to reach the highest SCOD content at 70 ºC but 5d at 55 and 35 ºC. Besides, temperature had a great influence on fermentation intermediates. Total VFAs yield and composition widely differed at three different temperatures, highest methanol content reached at 35 ºC, highest isobutyric and butyric acids content reached at 55 ºC and highest acetic acids reached at 70 ºC。

Acknowledgements

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References

[1] Liang P, Huang X, Qian Y, et al. Research progress on sludge reduction technologies. Techniques and Equipment for Environmental Pollution Control 2003; 1: 44-52.

[2] Zhang R H, El-Mashad H M, Hartman K, et al. Characterization of food waste as feedstock for anaerobic digestion. Bioresource Technology 2007; 4: 929-935.

[3] Liu G Q, Zhang R H, El-Mashad H M, et al. Effect of feed to inoculum ratios on biogas yields of food and green wastes. Bioresource Technology 2009; 21: 5103-5108.

[4] Fang H H P, Liu H. Effect of pH on hydrogen production from glucose by a mixed culture. Bioresource Technology 2002; 1: 87-93.

[5]Kim J K, Oh B R, Chun Y N, et al. Effects of temperature and hydraulic retention time on anaerobic digestion of food waste. Journal of Bioscience and Bioengineering 2006; 4: 328-332.

[6]Shin H, Youn J, Kim S. Hydrogen production from food waste in anaerobic mesophilic and thermophilic acidogenesis. International Journal of Hydrogen Energy 2004; 13: 1355-1363.

[7] Ortega L, Barrington S, Guiot S R. Thermophilic adaptation of a mesophilic anaerobic sludge for food waste treatment. Journal of Environmental Management 2008; 3: 517-525.

[8] Lee M, Hidaka T, Hagiwara W, et al. Comparative performance and microbial diversity of hyperthermophilic and thermophilic co-digestion of kitchen garbage and excess sludge. Bioresource Technology 2009; 2: 578-585.

[9] Komemoto K, Lim Y G, Nagao N, et al. Effect of temperature on VFA's and biogas production in anaerobic solubilization of food waste. Waste Management 2009; 12: 2950-2955.

[10] Chen S R，Xiao X P. Yeast Biochemistry. Shangdong: Shandong Science and Technology Press; 1990, p. 83-84.

[11] Ren N Q,Wang A J. Principles and Applications of Anaerobic Biotechnology. Beijing: Chemical Industry Press; 2004, p. 83-84.

[12] Zhang Y. Research of anaerobic phosphorus removal technics of piggery wastewater. Chinese Academy of Agricultural Sciences, 2006.

[13] Yuan Q, Sparling R, Oleszkiewicz J A. VFA generation from waste activated sludge: Effect of temperature and mixing. Chemosphere 2011; 4: 603-607.