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Development of a Modified Three-Stage Methane Production Process Using Food Wastes

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Abstract

A modified three-stage system was developed for the rapid production of methane from food wastes. The primary stage was a semianaerobic hydrolysis/acidogenic system, in which approx 4100 mg/L of volatile fatty acids (VFAs) was produced at a hydraulic retention time (HRT) of 2 d. The operation temperature and pH were 30°C and 5.0–5.5, respectively. The nondegraded materials were removed through a hole at the bottom of the reactor. The secondary stage was an anaerobic acidogenic system equipped with an upflow anaerobic sludge blanket (UASB) type of fermentor. VFA was accumulated up to 6100 mg/L by the addition of *Clostridium butyricum* to the reactor at an HRT of 2 d. The optimum temperature and pH range were 35°C and 5.0–5.5, respectively. The tertiary methanogenic stage produced CH_4 and CO_2 from the VFA in the UASB reactor. Methane content was 72% of the total gas volume, and the yield was 0.45–0.50 m^3/kg of volatile solids at an HRT of 12 d. The operation temperature and pH were 41°C and 7.6–7.9, respectively. The three-stage process exhibited an unusually high total chemical oxygen demand reduction rate up to 95%. Total nitrogen decreased to 96% and <10 mg/L of total phosphorus remained in the final effluent.

Index Entries: Anaerobic digestion; volatile fatty acid; modified three-stage methane production process.

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Introduction

The disposal of food wastes has become a major concern. Because of the high moisture content (75–80%) of Korean food wastes, they are easily putrefied and emit unpleasant odors. Landfilling creates serious environmental pollution, and it is difficult to find land on which to dispose of the food wastes. An alternative treatment is anaerobic digestion, which has recently been developed to utilize food wastes for the production of energy and materials. In this system, the organic compounds contained in food wastes are decomposed to volatile fatty acids (VFAs) by hydrolytic and acidogenic bacteria at the first stage (acidogenic phase). VFAs are further decomposed to methane and carbon dioxide by methanogenic bacteria at the second stage (methanogenic phase). The microbial consortia in the two phases have substantially different physiological properties and nutrient requirements. If the microbial growth conditions change, the growth balance between acetogenic and methanogenic bacteria can be destroyed. As a result, cell growth is severely inhibited. To overcome these problems, a two-phase anaerobic digestion process has been developed to separate acid- and methane-producing phases *(1–3)*.

In a conventional one-phase system, acid and methane are produced simultaneously, and it is difficult to maintain optimal conditions for the fermentation. Moreover, fermentation stability tends to be lowered by changes in influent properties. However, a two-phase system can provide optimal conditions for the process. In this system, syntrophic bacteria grow well even with excessive amounts of organic compounds because hydrogen is maintained at low levels *(4)*. Therefore, the two-phase anaerobic system has been studied intensively. However, the studies were focused mainly on easily biodegradable carbohydrates such as glucose. Hanaki et al. *(5)* reported that phase separation is not effective for the degradation of complex substrates consisting of carbohydrates, proteins, and lipids. Over the last 20 yr, a number of notable process configurations have been proposed: the leached-bed two-phase or LanFilgas Process *(6–8)*, the National Renewable Energy Laboratory high-solids system *(9)*, the Valorga Process *(10)*, the Dranco Process *(11)*, and the BTA Process *(12)*.

We report here a modified three-stage system that can produce methane effectively from easily biodegradable food wastes. This system efficiently reduced the hydraulic retention time (HRT) by increasing the rates of hydrolysis and acid production, and produced larger amounts of methane than those by conventional systems. Nondegradable materials such as shellfish and plastics in the food wastes could be easily removed from the primary digestion reactor without additional processes.

Materials and Methods

Design and Operation Conditions of Three-Stage System

A three-stage system was developed on the basis of the two-phase digestion system originally designed by Ghosh and Pohland *(1)* to produce

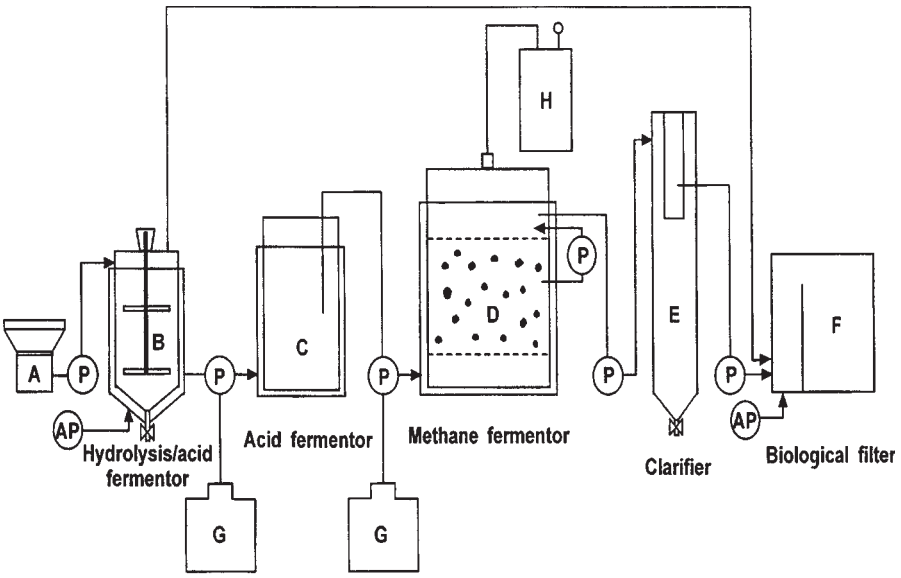

Fig. 1. Schematic diagram of a modified three-stage methane fermentation system consisting of a CSTR hydrolysis/acidogenic reactor and two upflow anaerobic sludge blanket (UASB) reactors for acidogenic and methanogenic processes. A, waste crusher; B, hydrolysis/acid fermentor; C, acid fermentor; D, immobilized-bed methane fermentor; E, clarifier; F, biological filter chamber; G, NaOH feeding bottle; H, gas reservoir tank; P, peristalic pump; AP, aerated pump.

methane at high rates (Fig. 1). It consisted of a semianaerobic hydrolysis/acidogenic process, an anaerobic acidogenic process, and a strictly anaerobic methanogenic process. The primary continuous stirred-tank reactor (CSTR) type of semianaerobic digester was designed for rapid hydrolysis and acid production from food wastes at a working volume of 20 L. Mixed household food wastes with high total solid (TS) contents were crushed and fed to the digester. The fluid was stirred at 100 rpm, and 1 vvm of air was applied to the bottom of the reactor to hydrolyze the food wastes after inoculation with a mixture of aerobic bacteria (Table 1). However, the hydrolysate still became semianaerobic because of poor oxygen dissolution owing to poor mixing in the digester. To remove nondegradable materials, a drain valve (i.e., $\phi = 10$ cm) was made in the center of the bottom of the reactor. The operation temperature and pH range were 30°C and 5.0–5.5, respectively. After a 2-d digestion, 10 L of hydrolyzed and acid-containing solution was transferred to the bottom of a secondary UASB-type digester having 20 L of working volume. In this reactor, a large amount of VFA could be produced for 2 d at a mesophilic temperature (35°C). *Clostridium butyricum* was inoculated to improve production of acids such as acetic and butyric acids. Ten liters of acid effluent was fed to the bottom of the USAB-type digester for the final step. The working volume and operation temperature were 120 L and 41°C, respectively. Methane fermentation

Table 1
Microorganisms Used for Digestion of Food Wastes

Process	Strain	Substrate
Semianaerobic hydrolysis/acidogenic	*Cellulomonas cellulans*	Cellulose, chitin, pectin
	Flavobacterium breve	Cellulose
	Bacillus amyloliquefaciens	Carbohydrates
	Bacillus licheniformis	Proteins
	Bacillus subtilis	Carbohydrates, proteins
	Bacillus alcalophilus	Fats
Anaerobic acidogenic	*Clostridium butyricum*	Sugar, amino acids, long-chain fatty acids
Anaerobic methanogenic	Methanogenic bacteria	Acetate, formate

was performed using methanogenic bacteria. The digesters were equipped with heat exchangers, gas meters, flame traps, and gas vents.

To remove residual organic carbon, nitrogen, and phosphate contained in the effluent from the methane digester, several other processes were used. The effluent was transferred to the sedimentation tank, where the solid fractions were precipitated. The supernatant was applied to the oxic biological filter chamber (45 L) consisting of immobilized nitrifying bacteria. After 3 d, the effluent was fed to the anoxic immobilized biological filter chamber (90 L) to remove nitrogen by denitrifying bacteria. The filters were made of polyvinyl chloride bars (length = 1 m). The immobilized filters were submerged into the wastewater for 6 d. The generated gas from the primary digester was transferred to the oxic biological filter chamber to remove the odors.

Microorganisms and Culture Conditions

Table 1 gives the microorganisms used for the digestion of food wastes. In the primary semianaerobic hydrolysis process, *C. cellulans* (NCIB 8868), *F. breve* (NCTC 11099), *B. amyloliquefaciens* (ATCC 23350), *B. licheniformis* (ATCC 21418), *B. subtilis* (ATCC 21394), and *B. alcalophilus* (NCIB 10436) were introduced for the aerobic hydrolysis of carbohydrates, proteins, and fats. *C. butyricum* (NCIB 7423) was inoculated in the secondary acidogenic process for the mass production of VFAs. However, in the case of the methanogenic process, cow manure and anaerobic methane-generating landfill soil were supplied to the reactor. Nitrifying and denitrifying bacteria used in the biological filters were prepared from the activated sludge.

C. cellulans was cultured in sporulation broth *(13)* at 26°C, and *F. breve* was in the nutrient broth *(13)* at 25°C. *B. licheniformis*, *B. alcalophilus*, and *B. subtilis* were cultured in nutrient broth at 30°C. *B. amyloliquefaciens* grew in spizizen potato broth *(13)* at 37°C. *C. butyricum* was cultured in *Clostridium acetobutyricum* medium *(13)* at 35°C.

Table 2
Elemental Analysis of Collected Food Wastes

Solid content (%)	VS/TS (%)	COD/VS	Elemental composition (%)			
			C	H	O	N
17.53	91.3	0.69	47.8	6.1	40.9	5.2

Analytical Methods

The following parameters were determined: TS, volatile solids (VS), total chemical oxygen demand (tCOD), soluble COD (sCOD), biological oxygen demand (BOD), and pH. Total nitrogen (T-N), ammonia (NH_4-N) and total phosphorus (T-P) concentrations were also monitored. These parameters were analyzed by the methods described in ref. *14*, and monitored three times per week during steady state. Total VFAs (tVFAs) was determined by gas chromatographic system (HP 5890A). Analytical conditions were as follows: FFAP capillary column (Hewlett Packard, 0.2 mm × 25 m) temperature, 150°C; injector temperature, 200°C; detector (flame ionization) temperature, 250°C; H_2 flow, 30 mL/min; airflow, 317 mL/min; column head pressure, 100 kPa. Waste food composition was analyzed by an Elemental analyzer (model 240C; Perkin-Elmer). The amount of gas produced from the digesters was monitored by a wet gas meter (W-NK-5; Shinagawa), and the gas composition was analyzed by a gas chromatograph (GC-14B; Shimadzu) using a packed column (Alltech; Haysep D, 100/120 mesh, 1/8 in. × 10 ft). Temperatures for column, injector, and detector (thermal conductivity) were 150, 200, and 220°C, respectively.

Results and Discussion

Chemical Composition of Korean Food Wastes

The average TS content of food wastes was 17.5%, and the average VS/TS and COD/VS values were 91 and 69%, respectively. The elemental compositions were C: 47.8%, H: 6.1%, O: 40.9%, and N: 5.2%. The C:N ratio was 9.2 (Table 2). This means that Korean food wastes are good resources for methane fermentation.

Process Operation and Changes in Chemical Properties of Digestive Fluid

The three-stage methane production process was operated in a stepwise system. The collected food wastes were mixed with water at a ratio of 1:1 (v/v), and 10 L of the mixture was fed to the primary digester. The mixture was stirred at 100 rpm and hydrolyzed by a combination of aerobic and anaerobic bacteria for 2 d at 30°C. Each strain of the aerobic bacteria listed in Table 1 was separately cultured in the optimal medium and transferred to the substrate mixture of food wastes. After adaptation to

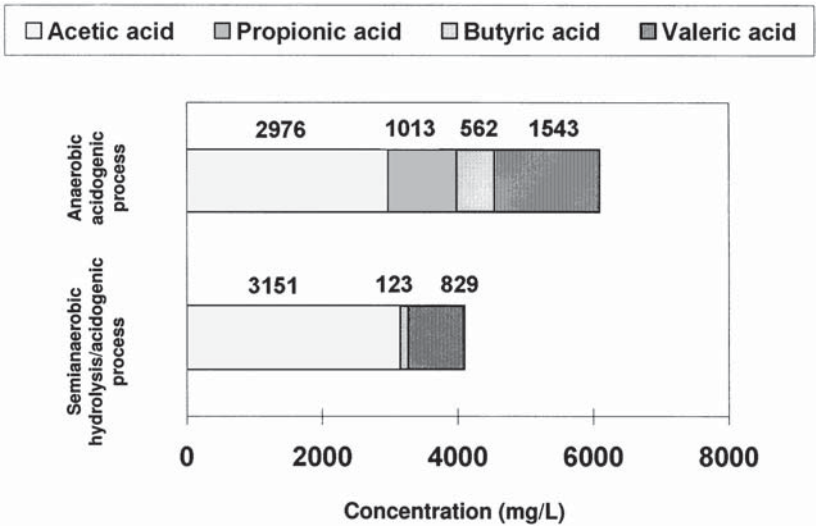

Fig. 2. VFA production from a semianaerobic hydrolysis/acidogenic process and an anaerobic acidogenic process.

serial culture, they were mixed and inoculated into the digester. During the digestion, small amounts of glucose, cellobiose, rhamnose, and several unidentified sugars were detected (data not shown). At the same time, large amounts of lactic, acetic, and propionic acids were continuously monitored in the fermentation process (Fig. 2). Although the initial pH was adjusted to 6.0, it decreased to 4.0 as the acid was produced (Fig. 3). Consequently, it seemed that the easily degradable polymers were hydrolyzed rapidly to oligomers or monomers by the aerobic bacteria, and that they were simultaneously further converted to the acids by anaerobic bacteria. Acids were fermented by the anaerobic microorganisms contaminated from food wastes. It was postulated that 2 d of HRT was enough to digest the waste in the primary digester. The tCOD and sCOD of the hydrolysate were 45,000 and 32,000 mg/L, respectively (Fig. 4). However, the BOD (51,000 mg/L) was higher than the tCOD, because the mixture contained a lot of particles, and therefore it was difficult to measure precise values of tCOD and BOD. In addition, removal of nondegradable materials was a very important step for pretreatment of food wastes. As the wastes were digested, heavy materials sedimented to the bottom and were easily removed from the reactor through a hole in the bottom of the digester.

The hydrolysate from the primary digester was added to the secondary acid digester using a gear pump. *C. butyricum*, cultured in the *C. acetobutyricum* medium, was inoculated and acclimated to the food extracts by serial cultures as described previously. The cell mixture was applied to the secondary digester, and acid fermentation was carried out for 2 d. The products still showed high values of tCOD and sCOD; however, BOD decreased to 60%, indicating that a significant amount of the biodegradable

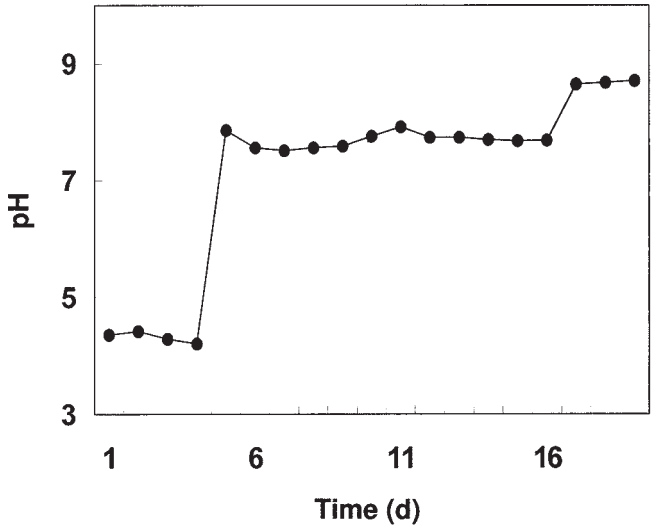

Fig. 3. pH changes through the full processes of a modified three-stage system.

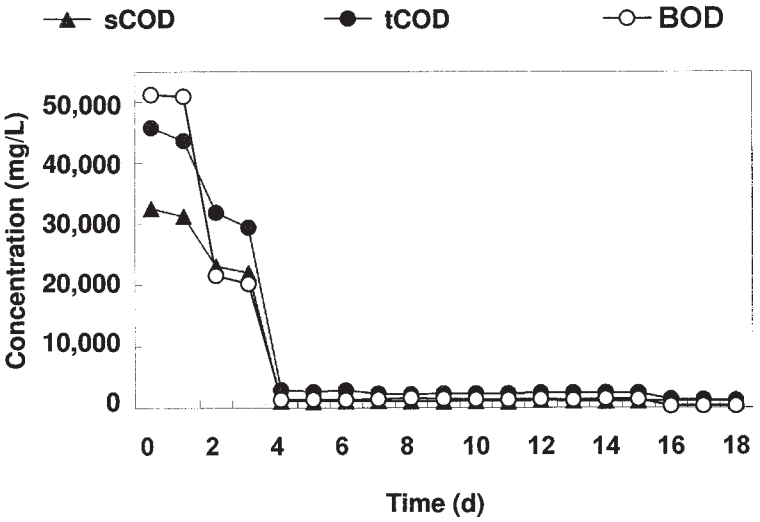

Fig. 4. Reduction of tCOD, sCOD, and BOD during the full digestion processes.

materials from food wastes is digested sufficiently and converted to VFAs and carbon dioxide. As shown in Table 3, the gas produced from the acidogenic digester was mainly carbon dioxide. During the fermentation, the pH range was maintained at 5.0–5.5 to prevent the retardation of acid production. Generally, syntrophic and acetoclastic methanogenic activities are severely inhibited under sour digestion conditions *(7,8)*. Therefore, it was necessary to mix the acid effluent and the alkalic effluent (pH 7.6–8.0) from the methane digester to neutralize it; then more acid could be produced continuously.

Table 3
Operational Conditions and Performance of Three-Stage System

Parameter	First process	Second process	Third process	Biological filter
HRT (d)	2	2	12	9
Loading (kg VS/[m^3·d])	20–22.8	25–27.4	12–18.8	1–1.2
pH	5.0–5.5	5.0–5.5	7.6–7.9	8.3–8.7
Temperature (°C)	30	35	41	30
T-N (mg/L)	4287	3216	2624	166
NH_3-N (mg/L)	117	172	1205	66
COD (mg/L)				
tCOD	44,948	30,582	2382	1145
sCOD	32,223	20,632	1071	1104
BOD (mg/L)	51,081	20,876	1356	287
Gas yield (m^3/kg VS)	—	—	0.65–0.70	—
Gas composition (%)				
CH_4	—	8.9	72	—
CO_2	—	91.1	28	—
Methane yield (m^3/kg VS)	—	—	0.45–0.50	—
Volatile acids (mg/L)				
Acetic	3151	2976	313	—
Propionic	0	1013	0	—
Butyric	123	562	0	—
Valeric	829	1543	0	—
Caproic	0	0	0	—
Total	4103	6094	313	—

As soon as the acid effluent was injected into the methane digester, the pH was adjusted to the optimal condition with 5 *N* NaOH to relieve acid impact on the methanogenic bacteria. This was done because the methane fermentation virtually stopped under extreme sour-digestion conditions. The acid effluents were retained for 12 d in the methane digester. Under this condition, tCOD, sCOD, and BOD values of the effluent were reduced dramatically. The reduction rates of tCOD, sCOD, and BOD in the complete process were 95, 96, and 97%, respectively. This indicates that the modified three-stage digestion system is an effective and time-saving process for the disposal of high TS content food wastes compared with the data of Park et al. *(15)*. At the same time, T-N was reduced from 4287 to 2624 mg/L through the processes. However, NH_3-N increased slowly in the anaerobic acidogenic process and accumulated to 1200 mg/L in the methanogenic process (Fig. 5). Because these nitrogen concentrations were too high for environmentally sound disposal, additional treatment was required. To solve this problem, oxic and anoxic biological filter systems were used. The biological filters contained immobilized nitrifying and denitrifying bacteria, together with heterotrophic bacteria to degrade residual organic wastes in the wastewater. As a result, T-N and NH_3-N concentrations decreased to 166 and 66 mg/L, respectively, and BOD reduced to 287 mg/L. T-N and BOD

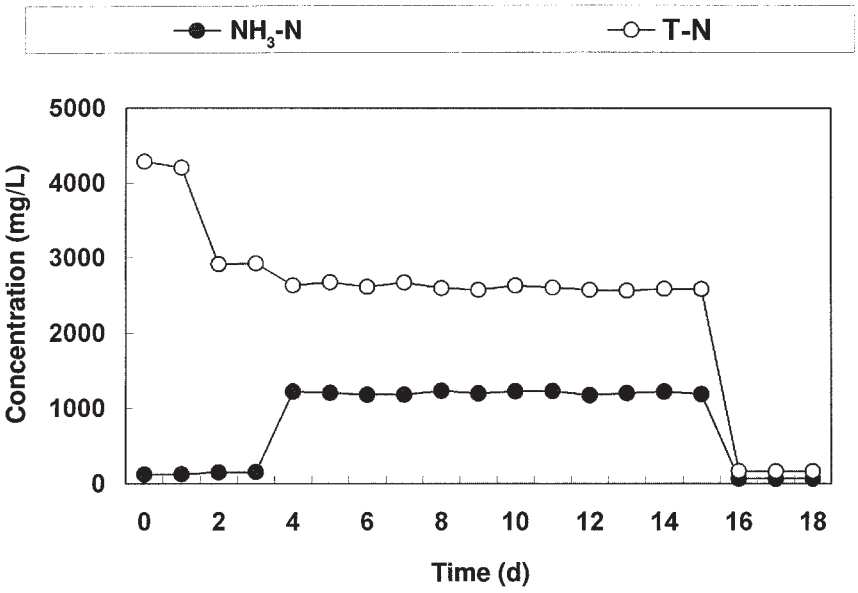

Fig. 5. Removal of T-N and NH_3-N from food wastewater during the full digestion processes.

decreased to 96 and 99.9%, respectively. Less than 10 mg/L of T-P was detected in the final effluent. Consequently, the final effluent was treated appropriately for disposal.

Production of VFAs and Methane

Although 4100 mg/L of tVFA was produced in the primary digestion process, acetic acid was the favored product (77%) (Fig. 2). Interestingly, the concentration of lactic acid was ninefold higher than that of acetic acid in this step. However, the lactic acid was further converted to acetic acid (data not shown). In the secondary acidogenic process, the concentration of tVFA increased from 6100 to 9100 mg/L, and several types of VFA were produced (Fig. 2). Because 6100 mg/L of tVFA was produced, the major VFAs were acetic (3000 mg/L), valeric (1540 mg/L), and propionic acids (1000 mg/L). Although small amounts of VFA (310 mg/L) remained in the effluent from the methane digester, most of the organic carbon was converted to methane and carbon dioxide (Table 3). The most important parameters for the normal operation of the digestion systems were pH, the organic loading rate, and the volume rate between the acid and the methane fermenter.

The total gas yield was 0.65–0.70 m^3/kg of VS. The main gas components were methane, carbon dioxide, ammonia, and hydrogen sulfide. Seventy-two percent of the total gas volume produced was methane, and the methane yield was 0.45–0.50 m^3/kg of VS (Table 3). The methane conversion rate and the yield showed similar values compared with those of

Table 4
Comparison of Performance of Three-Stage System with Conventional Anaerobic Digestion System at Mesophilic Temperature

	Three-stage system (food wastes)[a]			Two-phase (food wastes)[b]		Pilot two-phase (activated sludge)[c]	
Parameter	Hydrolysis	Acid	Methane	Acid	Methane	Acid	Methane
HRT (d)	2	2	12	5	15	3.1	9.1
Loading (kg VS/[m^3·d])	20–22.8	25–27.4	12–18.8	25–35	10–15	18.9	6.2
pH	5.0–5.5	5.0–5.5	7.6–7.9	5.5–6.5	7.4–7.8	5.6	7.7
TS in feed (%)	17.53	7.4	6.5	25.8	5–6	7.5	4.3
tVFA	4100	6100–9100	313	9000–13,000	4000–7000	9445	172
Methane yield (m^3/kg VS added)	—	—	0.45–0.50	—	0.44	—	0.29
VS reduction (%)[d]	8.2	9.5	38	—	—	25.0	41.8

[a]Data from this work.
[b]Data from Park et al. *(15)*.
[c]Data from Ghosh *(17)*.
[d]These VS reductions were calculated by the Water Pollution Control Federation (WPCF) formula in order for them to be compared with reductions reported by others.

other works *(8,15–17)*. A high NH_3-N concentration of 1200 mg/L generated from the methane fermentor did not inhibit methane production. Table 3 summarizes the data obtained from the full processes.

Conclusion

The modified three-stage system developed by this study was an effective methane-producing system, compared with those by other works (Table 4). When food wastes were used as substrate, 16 d of HRT was enough to produce methane at a yield of 0.50 m^3/kg of VS. During these periods, more than 95% of tCOD, sCOD, and BOD was removed, and 96% of T-N was also eliminated successfully.

Acknowledgment

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