CURRENT TECHNICAL DEVELOPMENT IN CONTINUOUS H$_2$ AND CH$_4$ PRODUCTION FROM ORGANIC WASTE

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ABSTRACT

Current development on continuous hydrogen and methane production at Korea Advanced Institute of Science and Technology was summarized in this manuscript. Long-term operation of H$_2$-producing processes fed with non-sterile food waste exhibited successful results. Adjusting dilution rate in a sequence (from 4.5 to 2.5 d^{-1}) was optimized for H$_2$ production in leaching beds system. The wastewater from the leaching beds was converted to CH$_4$ in a upflow anaerobic sludge blanket reactor. Meanwhile, H$_2$ production in an anaerobic sequencing batch reactor (ASBR) was enhanced by maintaining solid retention time independent from hydraulic retention time and the decrease of H$_2$ partial pressure by CO$_2$ sparging. Co-digestion was another main research objective. A temperature-phased ASBR system showed effective CH$_4$ production due to fast hydrolysis and acidogenesis in the thermophilic first-stage. These stable and effective results could provide various options in biogas production from organic waste.

INTRODUCTION

Growing environmental awareness and public health concerns have led to the implementation of more stringent environmental regulations in the world. Such regulations limit conventional disposal options for organic waste such as direct landfill. Therefore, organic waste generators are compelled to adopt efficient and reliable waste treatment system that meets the regulatory compliance. If the waste treatment could be linked to byproduct recovery, it may provide an incentive for waste generators to set-up the waste treatment facility. Anaerobic digestion can convert the waste into valuable byproducts including methane. Besides, acidogenic fermentation of organic waste is recently considered as an economic route to generate H$_2$, which is the promising alternative to fossil fuels [1].

The most abundant and problematic organic wastes in Korea are food waste and sewage sludge. The generation of food waste reaches about 11,398

tons per day, accounting for 22.5% of municipal solid wastes [2]. It had been the major source of odor emanation, vermin attraction, toxic gas emission and groundwater contamination in collection, transportation and landfill of solid waste due to the high organic concentration (volatile solids (VS)/total solids (TS): 0.8-0.9) and moisture content (80-85%). In 2005, as the direct landfill of food waste is prohibited by government, 97% of food waste is collected separately and 91% of the collected food waste is recycled to animal feed or aerobic compost. However, the recycle products are not popular in agricultural market as animal feed and aerobic compost need perfect stabilization and high operational cost, respectively. As food waste has high energy content and biodegradability, anaerobic digestion seems ideal to achieve dual benefits of energy production and waste stabilization. Especially, H$_2$ production from food waste has considerable potential to enhance the economic feasibility of waste treatment. Approximately 5,700 tons of sewage sludge cakes are generated daily from 201 domestic

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wastewater treatment plants in Korea [3]. Due to high moisture content (75-80%), direct landfill of sewage sludge from wastewater treatment plants larger than 100,000 m^3 has been prohibited since July in 2003. Now, 72% of sludge cake is disposed by ocean dumping. However, it would be also banned according to the London Convention in a near future. The enhancement of anaerobic digester is, therefore, urgent to reduce the amount of the sludge cakes and to improve the quality for reuse. Co-digestion of sludge with carbon-rich wastes is known as an economic and feasible approach to retrofit conventional digesters [4,5]. If hydrogen can be produced by anaerobic fermentation of food waste with sewage sludge, they would be the important source for hydrogen production due to the amount.

Korea Advanced Jnstitute of Science and Tcehnology (KAIST) has conducted a National Research Laboratory Project, named "Development of Biocell Plant: Integrated Anaerobic Technology for Biogas Production" since 2002 [6-14]. In this paper, we will introduce current research on continuous H$_2$ and CH$_4$ production from food waste and sewage sludge.

LEACHING BEDS-UASB SYSTEM FOR H$_2$ AND CH$_4$ PRODUCTION FROM FOOD WASTE

1. Process Description

This process was invented to produce H$_2$ and CH$_4$ from food waste. It comprises two main parts: leaching-bed reactors for hydrogen recovery, and an upflow anaerobic sludge blanket (UASB) reactor for methane recovery. The leaching-bed reactors were fed with food waste periodically, and produce hydrogen and soluble fermentation products. A UASB reactor converts soluble fermentation products from the leaching-bed reactors to methane continuously. Effluent from the UASB reactor recirculates to the leaching-bed reactors as dilution water. All the reactors were operated at a temperature of 37 °C.

2. Results

2.1. Optimization of H$_2$ production

Figure 1 illustrates the effect of initial dilution rate (D) on pH, cumulative H$_2$ production. The R1 system showed low pH values (3.9-4.1) in the first two d. Since simple organic matters were rapidly acidified in initial stage, low D of 2.0 d^{-1} resulted in pH drop. On the other hand, R4 indicated high pH (6.1-7.2) during the operating period. At high D of 5.5 d^{-1}, microbial washout might be greater than microbial growth, so the low concentration of biomass in the reactor led to the decrease of volatile fatty acid (VFA) production and the increase of pH. The maximum H$_2$-
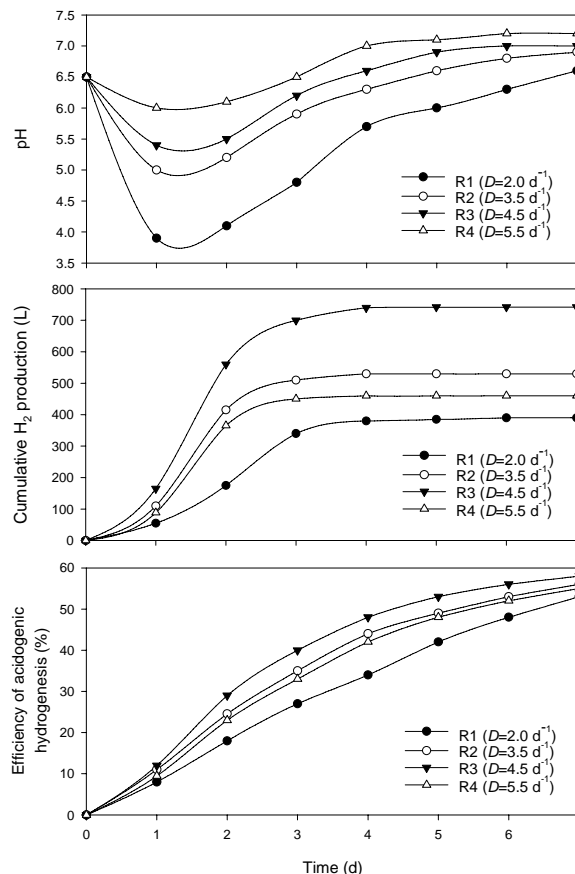

Fig. 1. Effect of initial D on pilot-scale acidogenic hydrogenesis.

production was observed in R3. In summary, initial D of 4.5 d^{-1} was appropriate to avoid pH drop and the washout of H$_2$-producing bacteria in the initial stage of acidogenic hydrogenesis.

Based on the results of the preceding experiment, initial D was kept at 4.5 d^{-1} in all the reactors in the first 2 d. Figure 2 illustrates the effect of D control on pH, cumulative H$_2$ production and the efficiency of pilot-scale acidogenic hydrogenesis of food waste. During the first 2 d, pH was maintained in the range of 5.3-5.6. Although simple organic matters were rapidly degraded, pH drop did not occur at initial D of 4.5 d^{-1}. After 2 d, in R1 and R2, the reduction of simple organic matters caused the decrease of VFA production and the increase of pH. Cumulative H$_2$ production also slightly increased, as microbial proliferation was less than microbial loss by washout. However, the performance of R3 was dramatically improved by reducing D from 4.5 to 2.5 d^{-1}. The pH was maintained below 6.2 on d 3-7. Cumulative H$_2$ production was the highest among the reactors, indicating that D control (4.5-2.5 d^{-1}) resulted in the enhanced degradation of slowly degradable matters. The COD removed in R3 was converted to H$_2$ (19%), VFA (37%), and ethanol (15%).
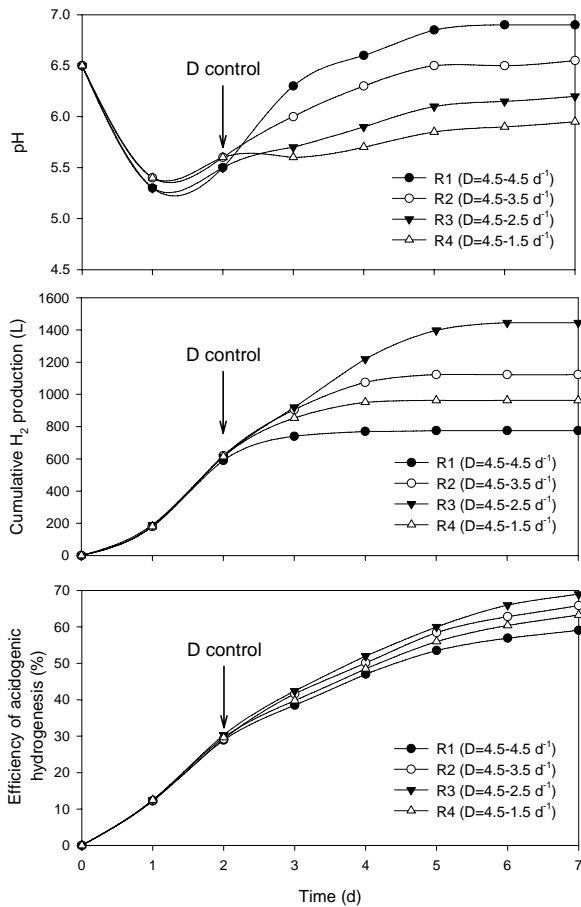
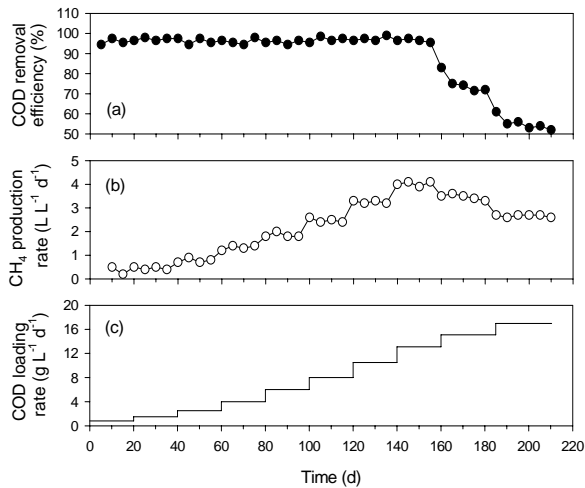Fig. 2. Effect of D control on pilot-scale acidogenic hydrogenesis.

Fig. 3. Performance of pilot-scale UASB reactor: (a) COD removal efficiency; (b) CH$_4$ production rate; (c) COD loading rate.

2.2. Optimization of CH4 production

Figure 3 illustrates the performance of the pilot-scale UASB reactor treating wastewater generated from acidogenic hydrogenesis of food waste. In the
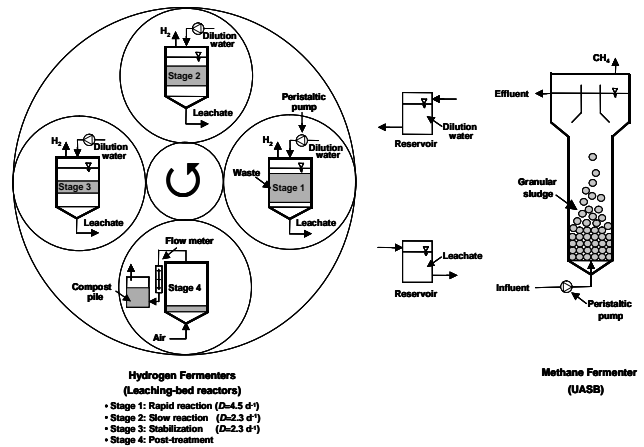

Fig. 4. Pilot-scale leaching beds-UASB system producing H$_2$ as well as CH$_4$ from food waste.

first 155 d, the COD removal efficiency was consistently over 95% up to the loading rate of 13.1 g COD L^{-1} d^{-1}, which corresponded to HRT of 0.25 d. The pH of the effluent was within 7.7-7.9, as compared to pH 6.6-6.9 in the wastewater. The CH$_4$ production rate increased with COD loading rates and reached the maximum of 3.4 L L^{-1} d^{-1} at 13.1 g COD L^{-1} d^{-1}. Over this loading rate, the efficiency decreased as the loading rate increased. The COD removal efficiency was drastically reduced to about 75% at 15.1 g COD L^{-1} d^{-1}, and to about 55% at 17.0 g COD L^{-1} d^{-1}. The specific methane production rate increased linearly with the specific substrate utilization rate with a slope of 0.94, until reaching the maximum of 0.56 g CH$_4$ COD g^{-1} VSS d^{-1} at the specific substrate utilization rate of 0.60 g COD g^{-1} VSS d^{-1} (VSS: volatile suspended solids). The slope indicated that, of all the COD removed, 94% was converted to CH$_4$ and the rest 6% was presumably converted to biomass.

3. Pilot-scale Operation

A pilot-scale leaching beds-UASB system was devised based on the preceding experiments (acidogenic hydrogenesis and methanogenesis). Figure 4 illustrates that the pilot-scale system consists of four leaching-bed reactors (50 L each) a UASB reactor (219.4 L).

Over 120 d, it demonstrated that it could remove 71% of VS at the high loading rate of 12.5 VS kg m^{-3} d^{-1} and convert VS$_{added}$ to H$_2$ (19%) and CH$_4$ (52%) on COD basis in 8 d as shown in Table 1. H$_2$ gas production rate was 3.05 L L^{-1} d^{-1}, while CH$_4$ gas production rate was 1.57 L L^{-1} d^{-1}. The yields of H$_2$ and CH$_4$ were 249 and 209 L kg^{-1} VS$_{added}$, respectively.

ANAEROBIC SEQUENCING BED REACTOR FOR H$_2$ PRODUCTION

1. Process Description

Table 1. COD balance in a pilot-scale leaching beds-UASB system

Item	Acidogenic hydrogenesis	Methanogenesis	Overall (100)
H_2 production (%)	19	-	19
VFA production (%)*	(39)	-	-
Alcohol production (%)*	(15)	-	-
CH_4 production (%)	-	52	52
COD remaining (%)	27	2	29

* VFA and alcohol were converted to CH_4 in methanogenesis
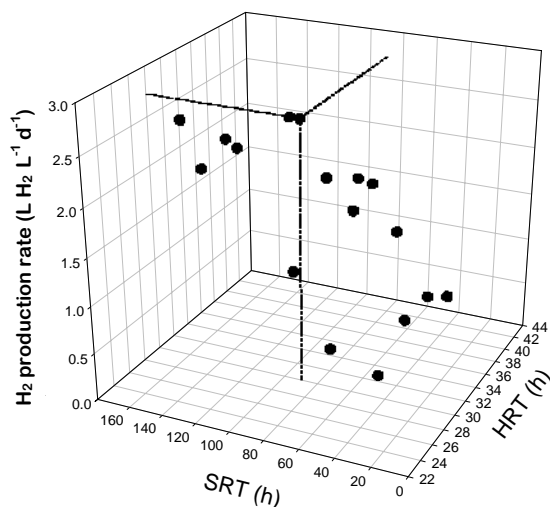

Fig. 5. Hydrogen production rate (L H_2 L^{-1} d^{-1}) at various HRTs and SRTs; dashed line indicates the optimum condition.
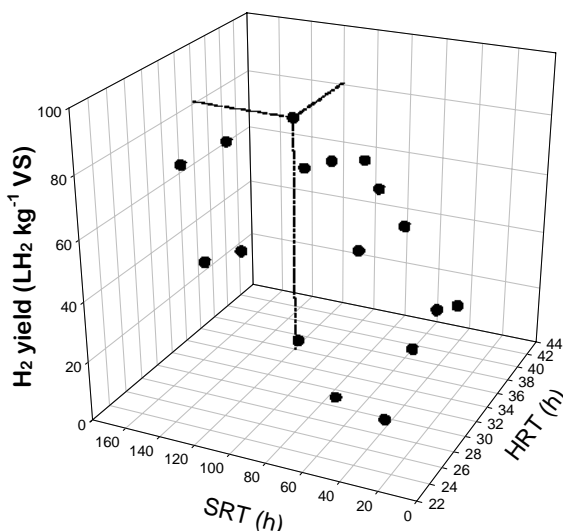

Fig. 6. Hydrogen production yield (L H_2 kg^{-1} VS) at various HRTs and SRTs; dashed line indicates the optimum condition.

This process was designed to produce H_2 from not only porous waste, but also non-porous waste. The
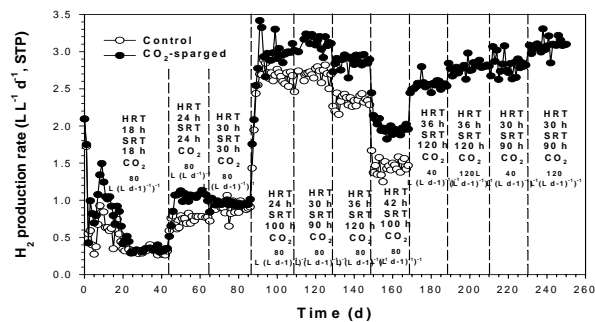

Fig. 7. Daily variation of hydrogen production rate at control and CO_2-sparged reactors.

anaerobic sequencing batch reactor was operated three times per day, providing one batch time of 8 h. The reactor has steps of filling, reacting, and decanting phases. In filling and reacting phases, the pH of the mixed liquor was maintained over 5.3±0.1 by feeding 3 M KOH. Settling phase was introduced for liquid/solid separation. As, there was no international sludge wasting, solids retention time (SRT) was determined by ratio of mixed-liquor volatile suspended solids (MLVSS) to effluent VSS.

As a first step, an alkali-treated (pH 12.5 during 1 d) and diluted (VS 4.6%) food waste was used as a feedstock. Effects of hydraulic retention time (HRT), SRT, and CO_2 sparging were examined. In each condition, operation period was longer than 20 d, and steady hydrogen production (±10%) was maintained longer than twice of SRT.

2. Results

2.1. Optimum HRT and SRT

HRT and SRT were varied from 18 to 42 h and 18 to 160 h, respectively. Maintaining sufficient SRT independent of HRT improved hydrogen production. The maximum hydrogen production rate (2.72 L H_2 L^{-1} d^{-1}) was found at 30 h HRT and 90 h SRT. The maximum hydrogen production yield (80.5 L H_2 kg^{-1} VS and 1.11 mol H_2 mol^{-1} hexose$_{added}$) was found at 36 h HRT and 120 h SRT. The yield at HRT 36 h was slightly higher than that at 30 h, because yield is the multiple of the flow rate and HRT and reciprocal of concentration.

2.2. Enhancement by CO_2 sparging

Figure 7 illustrates that CO_2 sparging increased H_2 production by 5-36% at all the examined conditions. It implied that the decrease of H_2 partial pressure by CO_2 sparging had a beneficial effect on H_2 fermentation of food waste. The effect of CO_2 sparging rate was investigated at two HRT/SRT conditions. Within the examined conditions, 80 L L^{-1} d^{-1} of CO_2 sparging rate showed the highest hydrogen

Table 2. Maximum hydrogen production in continuous process fed with organic waste

Feedstock	Condition	Maximum H_2 production*		References
		Rate (L H_2 L^{-1} d^{-1})	Yield (L kg^{-1} VS_{added})	
Food waste	ASBR, CO_2 sparging	3.18	97.3	This study
Food waste	ASBR	2.72	80.5	This study
Food waste	Leaching bed	3.13	249	This study
Food waste juice	CSTR with recirculation	1.55	22.6	[15]
Brewery waste	CSTR	2.68	37.9	[16]
Jackfruit waste	Contact filter	0.42	189.5	[17]

*All date was corrected to standard temperature (0 °C) and pressure (760 mmHg).

production. At the CO_2 sparging rate, H_2 contents at HRT 30 h (SRT 90 h) and HRT 36 h (SRT 120 h) were 3.7%, 3.4%, respectively. The H_2 contents and at same HRT/SRT in the control reactor were 49% and 52%, respectively. The maximum H_2 production rate of 3.18 L H_2 L^{-1} d^{-1} was found at 80 L L^{-1} d^{-1} of CO_2 sparging rate, 30 h HRT and 90 h SRT. As shown in Table 2, it was higher than most of reported maximum H_2 production rates (0.42-3.13 L H_2 L^{-1} d^{-1}) in continuous processes fed with organic waste [15-17]. The maximum H_2 yield of 97.3 L H_2 kg^{-1} VS_{added} was observed at 80 L L^{-1} d^{-1} of CO_2 sparging rate, 36 h HRT, and 120 h SRT. The yield was also comparable to the reported maximum H_2 production yields (25.0-249.2 L H_2 kg^{-1} VS_{added}). The H_2 yield based on $hexose_{added}$ was 1.36 mol H_2 mol^{-1} $hexose_{added}$.

TEMPERATURE-PHASED CH_4 PRODUCTION FROM CO-DIGESTION OF FOOD WASTE AND SEWAGE

1. Process Description

If two or more unique technologies were combined properly, better solid waste management could be possible. Accordingly, this research was performed to overcome the low efficiency of each anaerobic digestion of sewage sludge and food waste by the optimized combination of temperature-phased digestion, sequencing batch operation, and co-digestion technology.

A unified high-rate anaerobic digestion (UHAD) system and the control system of mesophilic two-stage anaerobic digestion were operated continuously to compare their performances with organic loading rate (OLR). The UHAD system was two cylindrical type reactors of working volume of 4 L with electrical agitator at the head. The first-stage thermophilic reactor was directly connected to the second stage mesophilic reactor. The control system had the same configuration except temperature of the first-stage (35 °C). In sequencing batch operation, one cycle of each reactor consisted of 4 sequences such as fill (1 h), react (17 h), settle (5 h), and draw (1 h). The sequence was possible by controlling peristaltic pumps with solenoid
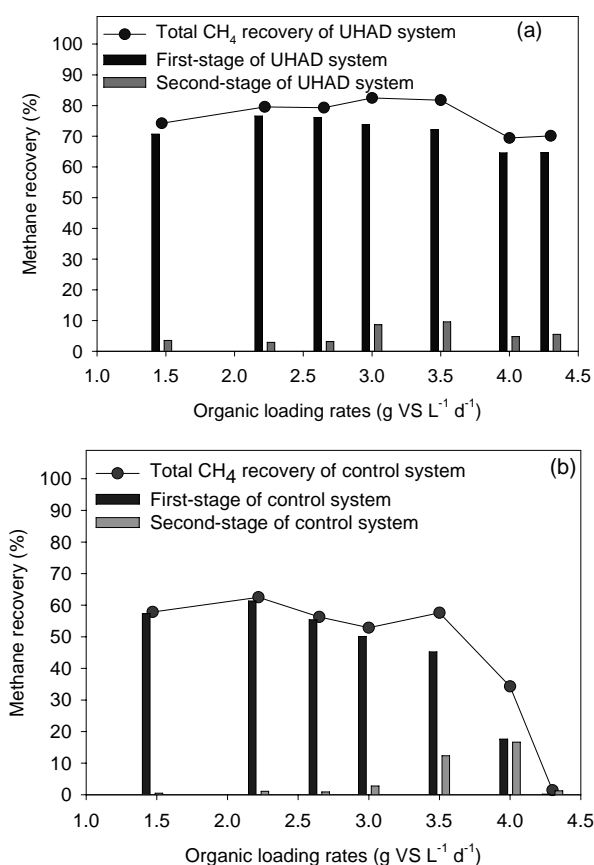

Fig. 8. Methane recovery of UHAD system (a) and control system (b).

valves. Also, batch experiments were conducted in duplicate using sewage sludge and food waste to verify the effects of major components in the food waste on the methane yields in a UHAD system.

2. Results

2.1. Methane production rate

Figure 8 illustrates the methane production rate (MPR) of the unit volume at OLR from 1.5 to 4.3 g VS L^{-1} d^{-1}. In the first-stage, methane contents of UHAD and control systems under the steady state were 53-64% and 51-64%, respectively. The average
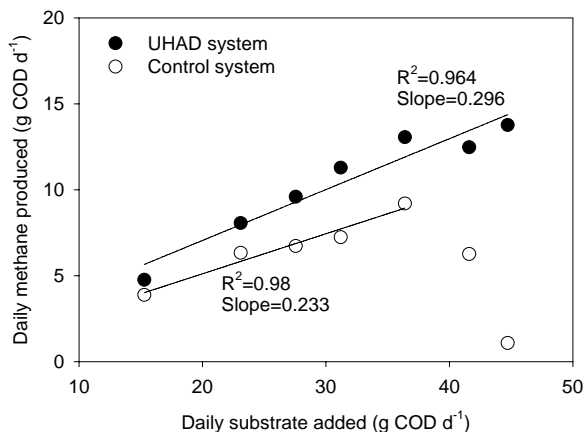
Fig. 9. Methane production rate at various substrate utilization rates.

Fig. 10. Methane yields in the BMP tests using major components of food waste.

MPR of UHAD system linearly increased from 0.21 to 0.60 L CH_4 L^{-1} d^{-1} depending on the OLR. The UHAD system always showed higher MPR than the control. Although the difference of the MPR increased at OLR of 4.3g VS L^{-1} d^{-1}, high-rate operation of UHAD system was maintained and decrease of MPR was rapidly recovered. The methane recovery of UHAD system was 69% to 82% depending on OLR. That of control ranged from 53% to 63% and sharply decreased when OLR exceeded 3.5 g VS L^{-1} d^{-1}. As demonstrated in vertical bar, most methane was recovered at the first stage of UHAD system. At OLR of over 3.0 g VS L^{-1} d^{-1}, methane recovery of first stage in UHAD system decreased by about 10% and remained methane potential was recovered in the second stage mesophilic reactor as a post treatment. It indicated that the following mesophilic second stage successively polished the thermophilic effluent to remove the remaining or slowly biodegradable substances, such as VFAs and suspended solids as pointed out by Welper et al. [18]. Similar trends were observed in the control as well. When the OLR was increased from 3.5 to 4.0 g VS L^{-1} d^{-1}, methane recovery of the second stage increased from 12 to 17%. However, at OLR of 4.3 g VS L^{-1} d^{-1}, pH of the second stage also decreased because hydrolyzed and acidified substrates were transferred to second stage. Thus, second stage of control system should have coped with high organic loading due to the ceased methanogenesis of first stage. That led to the failure of the control as no methane recovery was observed.

2.2. Enhanced methane production

Calculated average methane yield of UHAD system was 300 L CH_4 g^{-1} VS_{added} and that of the control was 230 L CH_4 g^{-1} VS_{added} when OLR was less than 3.5 g VS L^{-1} d^{-1}. From the results mentioned above, it was clear that the enhanced performance of 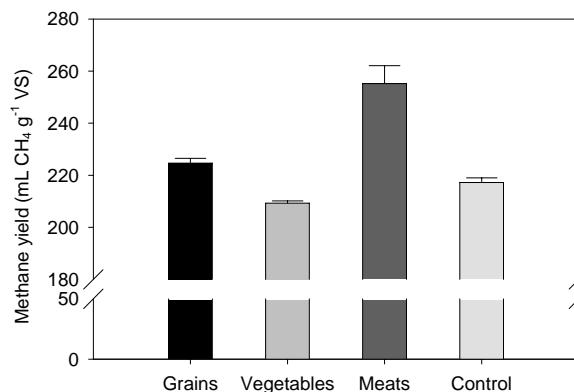UHAD system owed to the application of thermophilic reactor in the first-stage. Increased reaction rates in hydrolysis, acidogenesis, and methanogenesis resulted in increased methane yield by 30% in UHAD system. Figure 9 shows methane production rate at various substrate utilization rates. MPR of each system was converted to the COD basis. Substrate utilization rate was calculated based on the average unit COD equivalent (1.3 g COD g^{-1} VS) of co-substrate. The slope indicated that of all the substrate utilized as COD, 30% and 23% were converted to methane in UHAD and control systems, respectively. The rest was presumably converted to other by-products in effluent and used for the microbial growth.

The co-substrate, food waste, and sewage sludge consisted of complex compounds. Among them, food waste was abundant in readily biodegradable substances resulting in the enhancement of rate-limiting hydrolysis under thermophilic condition. To investigate the reasons of enhanced methane yield, a batch test on thermophilic co-digestion was designed in duplicate to verify the contributions of major components in food waste. As shown in Fig. 10, when meats were added as a sole co-substrate, it generated higher methane yield in the thermophilic co-digestion than grains and vegetables. It indicates that protein-the major component-degradation under thermophilic was more preferable. Harris and Dague [19] and Orlygsson et al. [20] reported that a higher degree of protein destruction in thermophilic condition and higher levels of alkalinity in the thermophilic reactors due to protein degradation at increased OLR. That means that higher degradation of meats in thermophilic condition can prevent pH drop effectively and contribute to stable operation of UHAD system at high OLR.

SUMMARY

Researches on continuous H_2 and CH_4 production from organic waste, conducted at Korea Advanced Institute of Science and Technology were reviewed. Continuous H_2 production fed with nonsterile complex feedstock was successful with two

types of process configuration. Firstly, the optimization of H$_2$-producing leaching beds system by dilution rate control (from 4.5 to 2.5 d^{-1}) resulted in H$_2$ production rate of 3.05 L L^{-1} d^{-1} and H$_2$ yield of 249 L kg^{-1} VS$_{added}$. Furthermore, the leaching beds were followed by a UASB reactor, which showed CH$_4$ production rate of 1.57 L L^{-1} d^{-1} and CH$_4$ yield of 209 L kg^{-1} VS$_{added}$. Secondly, a H$_2$-producing ASBR was optimized by maintaining SRT independent from HRT and the decrease of H$_2$ partial pressure by CO$_2$ sparging. The maximum H$_2$ production rate and yield from food waste in the process was 3.18 L L^{-1} d^{-1} and 97.3 L kg^{-1} VS$_{added}$. Meanwhile, the co-digestion of food waste and sewage sludge was conducted at a temperature-phased ASBR system. The temperature-phased system showed the highest CH$_4$ recovery (> 70%), CH$_4$ yield (300 L CH$_4$ kg^{-1} VS$_{added}$) and CH$_4$ production rate (0.6 L CH$_4$ L^{-1} d^{-1}) owing to the fast hydrolysis and acidogenesis in the thermophilic first-stage. These processes could be stable, reliable and effective in the treatment and biogas production of various organic wastes.

ACKNOWLEDGMENTS

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