

1 Development of a partial heating system to enhance bio-ammonia
2 production and recovery by anaerobic digestion of nitrogen-rich
3 wastewater: effect of partial heating modules

4 Jingwen Lu^a, Yutaka Kitamura^{b,*}, Kenji Takisawa^a, Weizhong Jiang^c

5 ^a Graduate School of Life and Environmental Sciences, University of Tsukuba,
6 Japan 305-8572

7 ^b Faculty of Life and Environmental Sciences, University of Tsukuba, Tsukuba,
8 Japan 305-8572

9 ^c Key Laboratory of Agricultural Engineering in Structure and Environment,
10 Ministry of Agriculture, China Agricultural University, Qinghua Donglu 17,
11 Beijing 100083, China

12 *Corresponding Author. Tel.: +81 298 53 4655; Fax: +81 298 53 4655

13 E-mail address: kitamura.yutaka.fm@u.tsukuba.ac.jp (Dr. Kitamura).

14

1 **Abstract**

2 The treatment of nitrogen-rich wastewater has drawn increasing attention
3 recently. In this work, a partial heating system has been developed to treat the
4 wastewater with low C/N ratio by anaerobic digestion and simultaneously recover
5 ammonia as a biomass resource. Effects of various heating modules on bio-ammonia
6 production and organic degradation were investigated. The system with single
7 partial heating modules prevailed over the control (without partial heating module).
8 The highest ammonia volatilization rate and total carbon removal ratio obtained in
9 single partial heating modules were elevated by 5.0-folds and 57.9 % compared to
10 the control, respectively. Anaerobic digestion system with the dual partial heating
11 module showed similar performance as single partial heating modules with respects
12 to ammonia production and volatilization and the organic degradation. Results
13 demonstrated anaerobic digestion system with partial heating modules considerably
14 enhanced organics removal and simultaneously recovered potential valuable
15 by-products from the wastewater at extremely low C/N ratio.

16 **Keywords:**

17 Ammonia bioproduction, anaerobic digestion, wastewater, partial heating,

1 heating module; low C/N ratio

2

1 **1. Introduction**

2 Wastewater containing high strength nitrogenous concentration from the
3 industry and agriculture production has received increasingly attentions because its
4 pollution to the environment. The excessive introduction of nitrogen compounds into
5 the water body is one of the critical causes of eutrophication. Current treatment of
6 the nitrogen-rich waste/wastewater including compost, CANON, SHARON and
7 ANAMMOX (Claros et al., 2012; Kabore et al., 2010; Tang et al., 2010;
8 Vazquez-Padin et al., 2009) are all based on the nitrification and the denitrification
9 of the nitrogen compounds. The nitrogen compounds are converted to ammonium by
10 an anaerobic process, followed by an aerobic process to produce nitrite and nitrate.
11 The ammonium reacts with the produced nitrite/nitrate to remove nitrogen in the
12 form of N_2 (Kim et al., 2006a). However, the greenhouse gas N_2O is prone to
13 emission during the nitrification and the denitrification process especially at a low
14 C/N ratio (Okabe et al., 2011; Sun et al., 2013), which would intensify the global
15 warming. In addition, bioenergy contained in the N-rich biomass has been wasted.

16 In fact, ammonium largely produced from wastewater treatment process
17 mentioned above is a kind of potential biomass energy because it is the precursory
18 of ammonia. Ammonia is always known as a toxic compound because ammonia

1 could permeate the membrane of microbes used in the waste biological treatment.
2 That would hinder the microbes' metabolism and then result in a low treatment
3 efficiency or even a failure. On the contrary, ammonia is widely used in both
4 agriculture and industry. It is the second most used commercial chemical in the
5 world (Jensen et al., 2007) as the raw material for fertilizer and cryogen., ammonia
6 is also a carbon neutral storage medium of hydrogen with the advantages of easy
7 liquefaction and high energy density (Vitse et al., 2005). Besides, ammonia is a
8 carbon neutral biofuel alternative with high energy density comparable with the
9 petroleum energy (Klerke et al., 2008). Many studies dedicated to facilitate the
10 ammonia manufacture by Haber-Bosch process, electrochemical process and urea
11 decomposition by hydrolysis (Lan et al., 2012). The ammonia manufacture by
12 Haber-Bosch process requires high temperature (748 K) and pressure (20 MPa),
13 which means a great deal of energy input and CO₂ emission. The electrochemical
14 process was forecasted to save 20% energy compared to the conventional
15 Haber-Bosch process, however, it has a high risk of alkali contamination (Giddey et
16 al., 2013). The urea is able to decompose to ammonia by hydrolysis process,
17 however, the decomposition efficiency and cost should be well considered from the
18 perspective of life cycle assessment.

19 Recently ammonia recovery from an environmental-friendly way has been

1 focused on. The recovery of ammonia from the waste/wastewater not only could
2 avoid the eutrophication, but also would reduce the excessive use of fossil fuel and
3 alleviate the consequent global warming and energy challenge. The recovery of
4 ammonia from the anaerobic digestion broth is mainly determined by three factors,
5 *i.e.* ammonium concentration, pH and temperature in the broth. Ammonium
6 production in anaerobic digestion is dependent on the C/N ratio of substrate and the
7 inocula. Low C/N ratio of the substrate means the abundant nitrogen in raw
8 materials and enhances the ammonium production to some extent ([Jiang et al., 2013](#);
9 [Zeshan et al., 2012](#)). However, the extreme C/N ratio affects the sustainable
10 anaerobic process and lead to the bio-reaction suspend. It is a challenge to
11 successfully dispose the nitrogen rich stream with an extremely low C/N ratio. The
12 inocula which have been gradually acclimated before inoculating are easy to adapt
13 to the nitrogen-rich substrate and more tolerant to high ammonium production
14 ([Rajagopal et al., 2013](#)). The adjustment of pH by alkali has been widely used to
15 avoid the overly acidic condition and promote free ammonia stripping from the
16 anaerobic system. Although pH adjustment can maintain the anaerobic digestion of
17 high strength nitrogenous substrate to some extent, overly alkali addition hinders the
18 sustainable ammonium production and protein degradation Chen et al has witnessed
19 that the protein degradation and conversion declined by approximately 24.6 % at the

1 pH of 8-10 compared to that at pH of 5-8 (Chen et al., 2012). High pH may destroy
 2 the origin microbial community structures and damage the cell activity (Hidaka et
 3 al., 2013). Besides, alkali addition increases the operation cost of the anaerobic
 4 fermentation in practical engineering. Temperature is another crucial factor for
 5 ammonium production. Numerous researches proved that thermophilic process is
 6 preferred rather than the mesophilic one due to its achievement of higher loading
 7 rates of digestion and greater conversion of proteins (Yenigun & Demirel, 2013).
 8 Luo et al (2010) found that total ammonium nitrogen (TAN) production was
 9 increased by 30.1 % and 77.7 % at 60 and 70 °C, respectively, compared to that at
 10 35 °C. Not only ammonium production is promoted by the thermophilic process, but
 11 also the ammonia volatilization is expected to be enhanced. Free ammonia
 12 concentration can be determined by in equation (1) (Bonmati & Flotats, 2003) and
 13 (2) (Turner, 1991).

$$14 \quad [NH_3] = \frac{[NH_3 + NH_4^+]}{1 + \frac{[H^+]}{Ka}} = \frac{[NH_3 + NH_4^+]}{1 + 10^{pKa-pH}} \quad (1)$$

$$15 \quad pKa = 4 * 10^{-8} * t^3 + 9 * 10^{-5} * t^2 - 0.0356 * t + 10.072 \quad (2)$$

16 According to the equations above, higher temperature could facilitate free ammonia
 17 recovery. The recovery of ammonia from the anaerobic digestion further helps the
 18 ammonium production and conversion due to the chemical equilibrium in the
 19 reaction system. However, the application of anaerobic digestion at thermophilic

1 temperature has been limited in practical engineering due to its high operation cost.

2 In this work, a partial heating system was developed to produce ammonium by
3 anaerobic digestion of nitrogen-rich wastewater and recover bio-ammonia at the
4 same time. The objectives of this work are to (1) establish a partial heating system
5 for the bio-ammonia production and recovery by anaerobic digestion; (2) investigate
6 the effect of partial heating modules on the ammonium production and ammonia
7 recovery.

8 **2. Materials and methods**

9 *2.1. Substrate and seeding sludge*

10 The soluble protein powder (ORIHIO, Tokyo, Japan) was used to prepare the
11 synthetic wastewater as the substrate. The powder is derived from soy protein. The
12 protein powder are made by protein (81.2 %), lipid (1-5 %), carbohydrate (2-12 %).
13 Besides, Na (0.43-1.2 %), K (0.25 %), Ca (0.80 %), Mg (0.04-0.11 %), Fe,
14 (0.005-0.015 %), Vitamin B1 (0.016‰), Vitamin B2 (0.018‰), Co (0.05 mg/L) and
15 Ni (0.5 mg/L) are included in the synthetic wastewater as well. The total nitrogen
16 (TN) of the substrate is 1009 mg-N/L. The C/N ratio for the synthetic wastewater is
17 3.9.

18 The seeding sludge was collected from a sewage treatment center in Ibaraki,

1 Japan. The seeding sludge was acclimated by the synthetic wastewater mentioned
2 above under HRT of 3 d at 35 °C. The pH, total suspended solids (TSS) and volatile
3 suspended solids (VSS) for the acclimated sludge were 6.8, 1 % and 0.71 %,
4 respectively.

5 2.2. *Experiment apparatus*

6 **Fig. 1 Schematic of ammonia production and recovery system under various** 7 **partial heating modules**

8 The fixed bed reactor was employed in this work. The working volume of the
9 fixed bed reactor was 2.6 L with $D_{in}=10$ cm and $H=50$ cm. Pall rings, which are
10 made of plastic and have diameters of 25 mm, were packed into the reactor. A ribbon
11 heater (Heater Engineer, Tokyo, Japan) was used for the partial heating in this work.
12 The ribbon heater wrapped the fixed bed reactor. The height of the wrapped part of
13 the fixed bed reactor is 6 cm. the ribbon heater and the thermal sensor (Sheathed
14 thermocouple, Toyonetsukagaku Co.,Ltd, Japan) were connected to a temperature
15 controller (TC-3000, AS ONE Corporation, Japan). The temperature sensor was
16 inserted into the gap between the ribbon heater and the wall of the fixed bed reactor
17 to respond to the temperature of the partial heating. The temperature of the partial
18 heating was set at 60 °C.

1 2.3. Experiment procedure

2 2.3.1. Effects of single partial heating modules on the ammonia volatilization

3 Four fixed bed reactors were used to research the effect of varied single partial
4 heating modules on ammonia production and recovery in this experiment. The one
5 with partial heating was set as the control (marked as SR). The other three reactors
6 whose ribbon heater was set at the top, middle and bottom of the reactor were
7 marked as THSR, MHSR and BHSR, respectively. As shown in Fig. 1, the sample
8 was taken from the middle sample port. Then the substrate was fed from the bottom
9 of the reactor. The mixing gas emitted from the fixed bed reactor contained the free
10 ammonia and biogas. The free ammonia was continuously stripped from the broth
11 and captured when the mixed gas went through the ammonia trap (4M H₂SO₄),
12 while the biogas was collected in a gas bag. The biogas was used to agitate the broth
13 in this work. The biogas was recycled into the reactor before sampling and after
14 feeding, and mixed for 5 min at each phase at the rate of 2 L L⁻¹ min⁻¹. Biogas
15 agitation was performed for 60 min in total for one day.

16 The continuous operation was performed with HRT of 0.9 d at 37°C. Data was
17 obtained after at least 2.5 HRTs to reach the steady state.

18 2.3.2. Effects of dual partial heating module on the ammonia volatilization

19 The dual partial heating module was developed to enhance the production and

1 volatilization of ammonia from anaerobic digestion. The reactor performed with
2 dual partial heating module is marked as DSR in this work. According to the results
3 of single partial heating modules, the combination of THSR and BHSR was adopted
4 in this work.

5 The operation conditions were the same as mentioned in 2.3.1.

6 *2.4. Analytical methods*

7 pH and TAN were monitored daily. TSS, VSS, total volatile acid concentration
8 (TVA) and TN were measured during the steady state.

9 The pH was tested by a pH meter (TRX-90, TOKO, Japan), and TAN was
10 tested by ammonia electrode (Ti-9000, TOKO, Japan). TSS and VSS test followed
11 the standard method (APHA, 2005). TVA and VA(volatile acid) composition (VA
12 spectrum) was tested by a gas chromatography (Shimadzu GC-14B, Japan) with an
13 column (Unisole F-200) at the carrier gas (N₂) 40 mL/min. TN is detected by a
14 TOC/TN analyzer (TOC-VCPH Shimadzu, Japan) with a nitrogen analyzer unit
15 (TNM-1) with the carrier gas of pure air.

16 *2.5. Parameter calculations*

17 *2.5.1. Undegraded nitrogen (UN)*

18 UN represents the nitrogen amount which has not been degraded.

19 UN (mg/L) can be expressed by the following equation:

1
$$UN = TN - TNO_x - TAN \quad (3)$$

2 where TN (mg/L) is the total nitrogen in the broth; TNO_x (mg/L) is the nitrite and
3 nitrate nitrogen in the broth; TAN is the NH₃/NH₄⁺-N in the broth.

4 TNO_x in this work was so little that can be ignored. Thus, UN in this work can
5 be calculated as follow:

6
$$UN = TN - TAN \quad (4)$$

7 *2.5.2. Ammonia volatilization ratio (AVR)*

8 Ammonia volatilization ratio can be calculated by the equation as follows:

9
$$AVR = \frac{TN_i - TN_f}{TN_i} \cdot 100\% \quad (5)$$

10 where TN_i is the total nitrogen (mg/L) of the synthetic wastewater at the initial
11 period and TN_f is the total nitrogen (mg/L) of the broth at the steady state.

12 *2.5.3. Ammonia recovery potential (ARP)*

13 Only free ammonia in the aqueous can be recovered from the broth by chemical
14 and physical methods. Thus, the ammonia recovery potential (ARP) can be
15 calculated by equation(5) :

16
$$ARP = \frac{NH_3 - N}{TAN} \cdot 100\% \quad (5)$$

17 where NH₃-N (mg/L) and TAN (mg/L) are the free ammonia nitrogen concentration
18 and total ammonia concentration in the broth, respectively.

1 2.5.4. Unionized VA concentration (UVA)

2 UVA content can be determined by equation (4):

3
$$UVA = TVA \frac{10^{(pKa-pH)}}{1+10^{(pKa-pH)}} \quad (6)$$

4 where TVA (g/L) is the total VA concentration of the broth, pKa is the acid
5 dissociation constant in water; the pKa of acetic acid at 37 °C is 4.762.

6 **3. Results and discussion**

7 *3.1. Effects of single partial heating modules on the NH_3/NH_4^+ bioproduction and*
8 *the anaerobic process*

9 *3.1.1 Effects of single partial heating modules on NH_3/NH_4^+ bioproduction and*
10 *nitrogen conversion*

11 **Fig. 2 Time course of TAN for the control and runs with single partial heating**

12 **Table 1 Characteristics of the continuous operations at steady state**

13 Time course of TAN was shown in Fig. 2. TAN rapidly increased during the
14 first day and gradually reached the steady state after 2.5 HRTs. The average TAN at
15 the steady state was shown in Table 1. The average TAN for SR, THSR, MHSR and
16 BHSR were 743.7, 777.6, 834.1 and 751.1 mg/L, respectively. The lowest TAN was
17 obtained in SR as expected. The TN in the supernatant of broth for SR, THSR,
18 MHSR and BHSR were 969.1, 804, 949.0 and 836.0 mg/L, respectively. TN in the

1 supernatant of broth included the degradable dissolved protein (or amino group),
2 TAN and nitrogenous compounds in other forms. The reduction of TN in the liquid
3 part of the broth was mainly caused by the volatilization of free ammonia.
4 According to the equation (1) and (2), free $\text{NH}_3\text{-N}$ in the broth for SR, THSR,
5 MHSR and BHSR should be 8.9, 7.2, 4.9 and 7.1 mg/L. In other words, the
6 theoretical ARP in certain pH and temperature for this work ranged from 0.6% to
7 1.2%. However, the volatilized $\text{NH}_3\text{-N}$ obtained in all experiments reached 39.9,
8 205.0, 60.0 and 173.0 mg/L in SR, THSR, MHSR and BHSR, respectively, meaning
9 the AVR_s in the four runs were promoted to the range of 3.3-19.8%. The high AVR_s
10 obtained in experiments were resulted from the continuous release of free ammonia,
11 leading to the continuous chemical equilibrium transfer and protein degradation.

12 The enhancement of protein degradation can be proved by the results of UN
13 (shown in Table 1). The lowest UN was attained in THSR, followed by BHSR and
14 MHSR. UN in the control (SR) was highest in the four runs, taking 22.3% of the TN
15 at the initial period. These results demonstrated anaerobic process with partial
16 heating modules improved the ammonia transfer in the broth. In addition, the partial
17 heating module of THSR and BHSR sharply enhanced ammonia volatilization.

1 *3.1.2. Effects of partial heating module on the acidogenesis*

2 **Fig. 3 Time course of pH for the control and runs with single partial heating**

3 The acidogenesis of the nitrogen-rich substrate was evaluated by pH, TVA and
4 VA compositions (present in Table 1). Fermentation progress can be indirectly
5 understood by the observation of acidogenesis because a sound acidogenic process
6 suggested the sustainable CH₄ production. The pH in the four runs varied in the
7 range of 6.7-7.0. Lower pH with partial heating modules may be caused by the free
8 ammonia release when H⁺ was accumulated in the broth.

9 TVA in the four runs varied in the range of 1.4 -2.8 g/L. The highest TVA was
10 obtained in SR, followed by THSR and MHSR. The lowest TVA was achieved in
11 BHSR. TVA of THSR, MHSR and BHSR were lower by 28.6%, 46.4% and 50.0%
12 than that of SR, respectively. It seems that TVA has not reached the critical
13 concentration of inhibition to the anaerobic process.

14 **Fig. 4 VA content for the control and varied single partial heating modules**

15 For the VA compositions, acetic acid dominated in each run. Acetic acid
16 contents in runs with partial heating were higher than that of the control (SR).
17 Propionic acid is believed to be the retardative VA in anaerobic digestion, whereas it
18 changed in the range of 1.3-9.9% in this experiment. Propionic acid concentration
19 trended oppositely to acetic acid, which was consistent with previous findings that

1 the propionic acid degradation rate increased in the case of low acetic acid content
2 (Mawson, 1986; Mawson et al., 1991). The long chain VA (including the butyric
3 acid and valeric acid) ratio in THSR was slightly lower than that of the control (SR),
4 while the ones in MHSR and BHSR were lower by 29.6% and 21.4% compare to
5 that of the control. The reduction of long chain VA in system with single partial
6 heating modules suggested the enhanced conversion to acetic acid from the organic
7 substrate. The high ratios of acetic acid in MHSR and BHSR provide evidence for
8 the phenomena.

9 *3.1.3. Effects of single partial heating modules on the organic degradation*

10 The total carbon (TC) removal ratio was present in Table 1. The carbon in SR,
11 THSR, MHSR and BHSR reduced to 2402, 1511, 1706 and 1719 mg/L from the
12 initial 3936 mg/L, respectively. The carbon removal ratio of THSR, MHSR and
13 BHSR grew by 57.9%, 45.4% and 44.4% than that of SR, respectively, indicating
14 that partial heating modules obviously enhanced the carbon degradation. Similar
15 researches also demonstrated that the organic degradation was enhanced at the
16 thermophilic condition compared to the mesophilic condition (Kim et al., 2006b;
17 Lee et al., 2009). Kim et al (2006b) found that there is a function relationship
18 between temperature and the soluble chemical oxygen demand. Kim et al also
19 (2012) witnessed that the enzymes' activities of protein, lipid and amylum starch

1 have been improved at the thermophilic environment.

2 In addition, the organic removal with single partial heating modules can be
3 compared to other researches even though it is restricted by the low C/N ratio. The
4 total organic carbon utilization of 83.9 % at C/N ratio of 6.5 has been reported
5 (Wang et al., 2013) in previous research. Zhong et al (2013) has found that the
6 organic removal ratio reached 42.2% in case of C/N ratio of 6. These results
7 emphasized that C/N ratio of the substrate is a crucial controlling factor in the
8 anaerobic digestion.

9 *3.2. Effects of dual heating module on NH_3/NH_4^+ bioproduction and the anaerobic*
10 *process*

11 *3.2.1. Effects of DSR on the NH_3/NH_4^+ production and recovery*

12 **Table 2 Characteristics of ammonia production in case of the dual partial**
13 **heating module under the steady state**

14 According to the results of single heating modules, THSR and BHSR presented
15 better performance. The idea of a dual heating module by combining THSR and
16 BHSR emerged after these observations. Therefore, based on the investigation of
17 effects of single heating modules on ammonium production and recovery, the dual
18 heating module was developed. The performance of the dual partial heating module
19 at the steady state was shown in Table 2.

1 TAN for DSR was 736.8 mg/L. Although TAN for DSR seems no higher than
2 that of the SR, the AVR for DSR prevailed. The AVR for DSR was 18.4%.
3 Compared to its theoretical ARP of mere 0.5% at the certain pH and TAN
4 concentration, the ammonia volatilization has been considerably promoted by the
5 dual partial heating. Besides, the ARP for DSR was 5.6-folds of that of the SR,
6 which also illustrated the enhancement of ammonia volatilization by dual partial
7 heating considering the lower pH and TAN concentration in DSR.

8 UN in DSR was 92.7 mg/L, which was lower by 59.2% compared to that of the
9 SR. UN in DSR was even higher than those of THSR and BHSR, although their
10 AVRs were similar. The phenomena suggested that the dual partial heating provided
11 high ammonia volatilization efficiency in spite of the low pH in the liquid. Higher
12 UN in DSR can be illustrated by the change of the heating module. Dual partial
13 heating module may affect the temperature through the fixed bed reactor in
14 comparison with the single partial heating modules. Organic degradation and
15 acidogenesis can be improved at thermophilic conditions (Kim et al., 2012; Kim et
16 al., 2006b), which led to the decrease of pH and the subsequent retard of ammonia
17 volatilization. The existence of ammonium and ammonia in the broth would be
18 adverse to the conversion of protein in the anaerobic digestion. Therefore, the UN in
19 DSR did not prevail over the THSR or BHSR. On the other hand, this result

1 suggests that higher organic loading rate (including both the carbon and nitrogen) is
2 possibly degraded by the system with the help of DSR module. In the future, higher
3 feedstock concentration and shorter HRT at the module of DSR should be further
4 considered.

5 *3.2.2. Effects of DSR on the acidogenesis and organic degradation of nitrogen-rich*
6 *wastewater*

7 The average pH for the DSR was 6.6, much lower than the control of 7.0. As
8 shown in equation(1), NH_3 emission greatly depends on pH. Even small variance of
9 pH would result in great difference of NH_3 volatilization. The reason for pH
10 decrease in DSR should be ascribed to the increase of TVA. TVA for the DSR was
11 3.6 g/L, which was 28.6 % higher than that of the control. TVA exists in the
12 anaerobic digestion mainly in two forms, i.e. UVA and ionized volatile acid (IVA).
13 pH was affected by IVA because of the VA ionization. On the contrary, microbes
14 were mainly impacted by the UVA. UVA could pass through the cell membrane and
15 cause the imbalance of intracellular and extracellular. The UVA concentration
16 imbalance would lead to the microbes' activity decline and even to the fractures. The
17 UVA in DSR took only 5 % according to equation(6) , which was much lower than
18 the threshold documented in previous studies. This result demonstrated that the
19 disorder in the low C/N wastewater treatment for this work was not caused by the

1 excessive UVA. In fact, higher temperature caused by dual partial heating favored
2 the organics conversion and the acidogenesis rather than the methanogenesis (Kim et
3 al., 2006b; Lee et al., 2009). The methanogenesis was more stable at mesophilic
4 condition (Bayr et al., 2012). The methanogenesis seems not to match the rapid acid
5 production led by the higher temperature. In addition, the temperature control for the
6 dual partial heating module should be improved in order to avoid the temperature
7 increases through the fixed bed reactor in the future.

8 VA spectrum for DSR was also present in Table 2. Although acetic acid
9 dominated in DSR, its content was lower than that of the control. Acetic acid is the
10 precursor of methane for the acetate-consumed methanogens. Lower content of
11 acetic acid in DSR suggested the conversion of VA to methane. Long chain volatile
12 acids are produced from the degradation of complicated compounds. The long chain
13 volatile acid concentration in DSR was higher by 73.8% and 152.7% than those of
14 the SR and THSR, respectively. It indicated an effective acidogenesis of organics,
15 but at the same time meant an imbalance between the rapid acidogenesis and slow
16 acid consumption. Interestingly, the n-valeric concentration was much lower than
17 that of i-valeric acid. Wang et al has found that the n-valeric acid was prone to
18 degradation rather than i-valeric acid in anaerobic digestion (Wang et al., 1999). The
19 lower n-valeric acid content in DSR agreed with these findings as well.

1 TC removal ratio in DSR was 65.2 %. Taken into the short HRT in this work,
2 the TC removal efficiency is 2850.7 mg/(L⁻¹•d). The TC removal ratio was higher by
3 67.4% than that of the SR, while slightly higher than those of THSR. The results
4 also evidenced that the accumulation of acidogenic products, caused by the rapid
5 acid production rate and the relatively slow consumption rate decelerated the
6 degradation of organics.

7 **4. Conclusion**

8 In this work, an anaerobic digestion system with a partial heating system for the
9 bio-ammonia production and recovery has been developed. The effect of various
10 heating modules on bio-ammonia production and organic degradation were
11 investigated. For the single partial heating module, THSR and BHSR considerably
12 prevailed over the control (without the partial heating). The ammonia volatilization
13 ratio in THSR and BHSR were elevated by 5.0 and 4.0-folds compared to the
14 control. The TC removal ratio in THSR in and BHSR were increased by 57.9% and
15 44.3%, respectively. Dual partial heating system showed similar performance as the
16 single partial heating with respects to ammonia production and volatilization and the
17 organic degradation. Results in this work demonstrated that the partial heating
18 system considerably enhanced the organics removal and simultaneously recovered

1 the potential valuable by-products from the wastewater at extremely low C/N ratio.

2 **Acknowledgements**

3 We sincerely appreciate the support of Chikusei sewage treatment centre in

4 Ibaraki, Japan.

1 **Abbreviation List**

ARP	ammonia recovery potential
AVR	ammonia volatilization rate
HRT	hydraulic retention time
IVA	ionized volatile acid
TAN	total ammonium nitrogen
TC	total carbon
TN	total nitrogen
TS	total solids
TSS	total suspended solids
TVA	total volatile acid
UN	Undegraded nitrogen
UVA	Unionized volatile acid
VA	volatile acid
VS	volatile solids
VSS	volatile suspended solids
WRS	wheat-rice-stone (andesite porphyry)

2

3

1 Reference

2 APHA. 2005. *Standard methods for the examination of water and*
3 *wastewater. 21st ed.* APHA, Washington, D.C.

4 Bayr, S., Rantanen, M., Kaparaju, P., Rintala, J. 2012. Mesophilic and
5 thermophilic anaerobic co-digestion of rendering plant and slaughterhouse
6 wastes. *Bioresource Technology* **104**, 28-36.

7 Bonmati, A., Flotats, X. 2003. Air stripping of ammonia from pig
8 slurry: characterisation and feasibility as a pre- or post-treatment to
9 mesophilic anaerobic digestion. *Waste Management* **23**, 261-272.

10 Chen, Y.G., Xiao, N.D., Zhao, Y.X., Mu, H. 2012. Enhancement of
11 hydrogen production during waste activated sludge anaerobic fermentation
12 by carbohydrate substrate addition and pH control. *Bioresource Technology*
13 **114**, 349-356.

14 Claros, J., Serralta, J., Seco, A., Ferrer, J., Aguado, D. 2012. Real-time
15 control strategy for nitrogen removal via nitrite in a SHARON reactor using
16 pH and ORP sensors. *Process Biochemistry* **47**, 1510-1515.

17 Giddey, S., Badwal, S.P.S., Kulkarni, A. 2013. Review of
18 electrochemical ammonia production technologies and materials.
19 *International Journal of Hydrogen Energy* **38**, 14576-14594.

20 Hidaka, T., Wang, F., Togari, T., Uchida, T., Suzuki, Y. 2013.
21 Comparative performance of mesophilic and thermophilic anaerobic
22 digestion for high-solid sewage sludge. *Bioresource Technology* **149**,
23 177-183.

24 Jensen, J.O., Vestbo, A.P., Li, Q., Bjerrum, N.J. 2007. The energy
25 efficiency of onboard hydrogen storage. *Journal of Alloys and Compounds*
26 **446**, 723-728.

27 Jiang, X., Hayashi, J., Sun, Z.Y., Yang, L., Tang, Y.Q., Oshibe, H.,
28 Osaka, N., Kida, K. 2013. Improving biogas production from protein-rich
29 distillery wastewater by decreasing ammonia inhibition. *Process*
30 *Biochemistry* **48**, 1778-1784.

31 Kabore, T.W.T., Houot, S., Hien, E., Zombre, P., Hien, V., Masse, D.
32 2010. Effect of the raw materials and mixing ratio of composted wastes on
33 the dynamic of organic matter stabilization and nitrogen availability in
34 composts of Sub-Saharan Africa. *Bioresource Technology* **101**, 1002-1013.

35 Kim, D.-J., Lee, D.-I., Keller, J. 2006a. Effect of temperature and free

1 ammonia on nitrification and nitrite accumulation in landfill leachate and
2 analysis of its nitrifying bacterial community by FISH. *Bioresource*
3 *Technology* **97**, 459-468.

4 Kim, H.W., Nam, J.Y., Kang, S.T., Kim, D.H., Jung, K.W., Shin, H.S.
5 2012. Hydrolytic activities of extracellular enzymes in thermophilic and
6 mesophilic anaerobic sequencing-batch reactors treating organic fractions of
7 municipal solid wastes. *Bioresource Technology* **110**, 130-134.

8 Kim, J.K., Oh, B.R., Chun, Y.N., Kim, S.W. 2006b. Effects of
9 temperature and hydraulic retention time on anaerobic digestion of food
10 waste. *Journal of Bioscience and Bioengineering* **102**, 328-332.

11 Klerke, A., Christensen, C.H., Norskov, J.K., Vegge, T. 2008. Ammonia
12 for hydrogen storage: challenges and opportunities. *Journal of Materials*
13 *Chemistry* **18**, 2304-2310.

14 Lan, R., Irvine, J.T.S., Tao, S.W. 2012. Ammonia and related chemicals
15 as potential indirect hydrogen storage materials. *International Journal of*
16 *Hydrogen Energy* **37**, 1482-1494.

17 Lee, M., Hidaka, T., Hagiwara, W., Tsuno, H. 2009. Comparative
18 performance and microbial diversity of hyperthermophilic and thermophilic
19 co-digestion of kitchen garbage and excess sludge. *Bioresource Technology*
20 **100**, 578-585.

21 Luo, G., Xie, L., Zou, Z.H., Zhou, Q., Wang, J.Y. 2010. Fermentative
22 hydrogen production from cassava stillage by mixed anaerobic microflora:
23 Effects of temperature and pH. *Applied Energy* **87**, 3710-3717.

24 Mawson, A.J. 1986. Factors affecting the rate and stability of the
25 anaerobic digestion process., Vol. Ph. D, Massey University. Palmerston
26 North New Zealand.

27 Mawson, A.J., Earle, R.L., Larsen, V.F. 1991. Degradation of Acetic and
28 Propionic Acids in the Methane Fermentation. *Water Research* **25**,
29 1549-1554.

30 Okabe, S., Oshiki, M., Takahashi, Y., Satoh, H. 2011. N₂O emission
31 from a partial nitrification-anammox process and identification of a key
32 biological process of N₂O emission from anammox granules. *Water*
33 *Research* **45**, 6461-6470.

34 Rajagopal, R., Masse, D.I., Singh, G. 2013. A critical review on
35 inhibition of anaerobic digestion process by excess ammonia. *Bioresource*
36 *Technology* **143**, 632-641.

37 Sun, S.C., Cheng, X., Li, S., Qi, F., Liu, Y., Sun, D.Z. 2013. N₂O
38 emission from full-scale urban wastewater treatment plants: a comparison

1 between A(2)O and SBR. *Water Science and Technology* **67**, 1887-1893.

2 Tang, C.J., Zheng, P., Mahmood, Q., Chen, J.W. 2010. Effect of
3 substrate concentration on stability of anammox biofilm reactors. *Journal of*
4 *Central South University of Technology* **17**, 79-84.

5 Turner, G.L.E. 1991. Crc Handbook of Chemistry and Physics:a
6 Ready-Reference Book of Chemical and Physical Data, 70th
7 Edition-Weast,Rc, Lide,Dr. *Annals of Science* **48**, 496-497.

8 Vazquez-Padin, J.R., Pozo, M.J., Jarpa, M., Figueroa, M., Franco, A.,
9 Mosquera-Corral, A., Campos, J.L., Mendez, R. 2009. Treatment of
10 anaerobic sludge digester effluents by the CANON process in an air pulsing
11 SBR. *Journal of Hazardous Materials* **166**, 336-341.

12 Vitse, F., Cooper, M., Botte, G.G. 2005. On the use of ammonia
13 electrolysis for hydrogen production. *Journal of Power Sources* **142**, 18-26.

14 Wang, Q.F., Peng, L.Y., Su, H.J. 2013. The effect of a buffer function on
15 the semi-continuous anaerobic digestion. *Bioresource Technology* **139**,
16 43-49.

17 Wang, Q.H., Kuninobu, M., Ogawa, H.I., Kato, Y. 1999. Degradation of
18 volatile fatty acids in highly efficient anaerobic digestion. *Biomass &*
19 *Bioenergy* **16**, 407-416.

20 Yenigun, O., Demirel, B. 2013. Ammonia inhibition in anaerobic
21 digestion: A review. *Process Biochemistry* **48**, 901-911.

22 Zeshan, Karthikeyan, O.P., Visvanathan, C. 2012. Effect of C/N ratio
23 and ammonia-N accumulation in a pilot-scale thermophilic dry anaerobic
24 digester. *Bioresource Technology* **113**, 294-302.

25 Zhong, W.Z., Chi, L.N., Luo, Y.J., Zhang, Z.Z., Zhang, Z.J., Wu, W.M.
26 2013. Enhanced methane production from Taihu Lake blue algae by
27 anaerobic co-digestion with corn straw in continuous feed digesters.
28 *Bioresource Technology* **134**, 264-270.

29
30
31

1 **Figure captions**

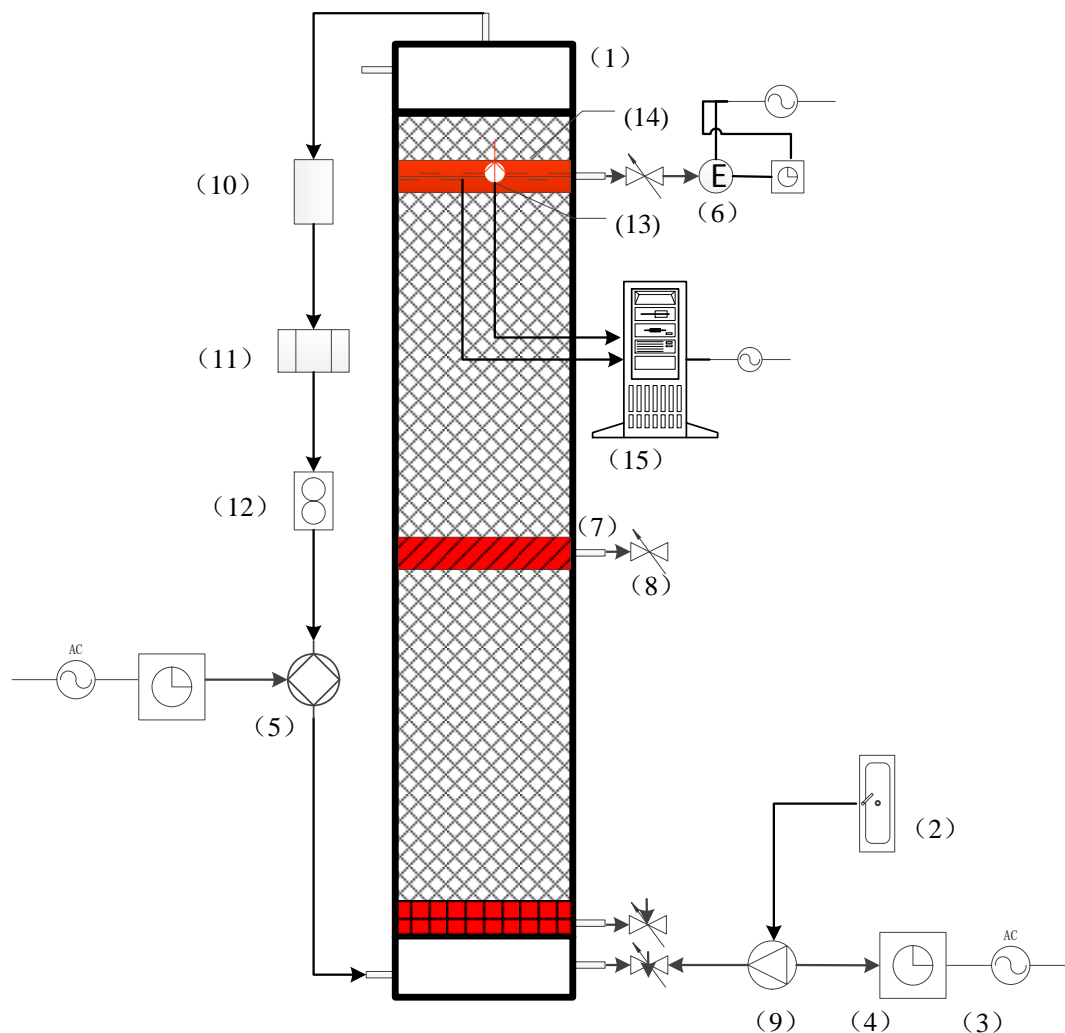
2 Fig. 1 Schematic of ammonia production and recovery system under various
3 partial heating modules

4 Fig. 2 Time course of TAN for the control and runs with single partial heating




5 Fig. 3 Time course of pH for the control and runs with single partial heating

6 Fig. 4 VA content for the control and varied single partial heating modules

1 **Fig. 1**



2
3

- | | | | |
|---|---------------------------|----|---|
|  | Ribbon heater for THSR; | 8 | DSR means the double heating module, which is |
|  | Ribbon heater for MHSR; | 9 | the combination of THSR and BHSR according |
|  | 6 Ribbon heater for BHSR; | 10 | to the results |

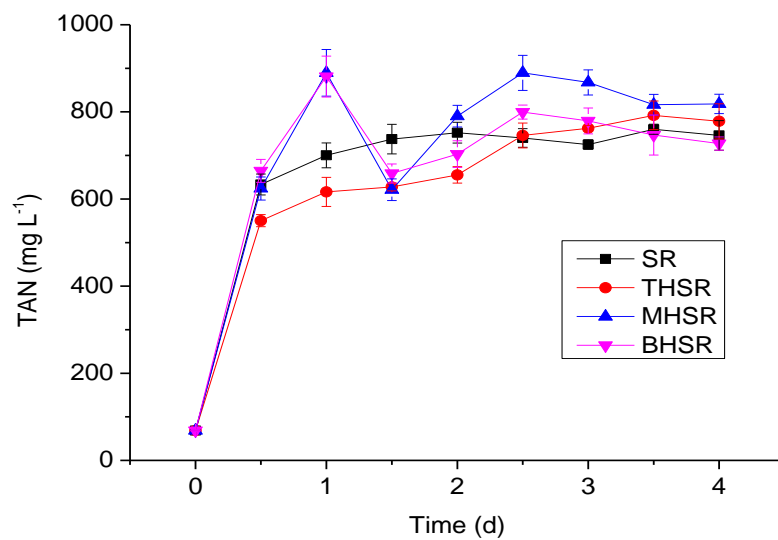
7

- 11 (1)Fixed bed (2) Wastewater (3) Power (4) Time (5) Air pump
 12 (6) Magnetic valve (7) Sample port (8) Valve (9) Peristaltic pump (10) Gas bag
 13 (11) Flow meter (12) NH₃ trap (13) Temperature sensor (14) Ribbon heater (15) Temperature controller

14

15 Fig. 1 Schematic of ammonia production and recovery system under various partial heating modules

1 **Fig. 2**



2

3

4 Fig. 2 Time course of TAN for the control and runs with single partial heating modules

5

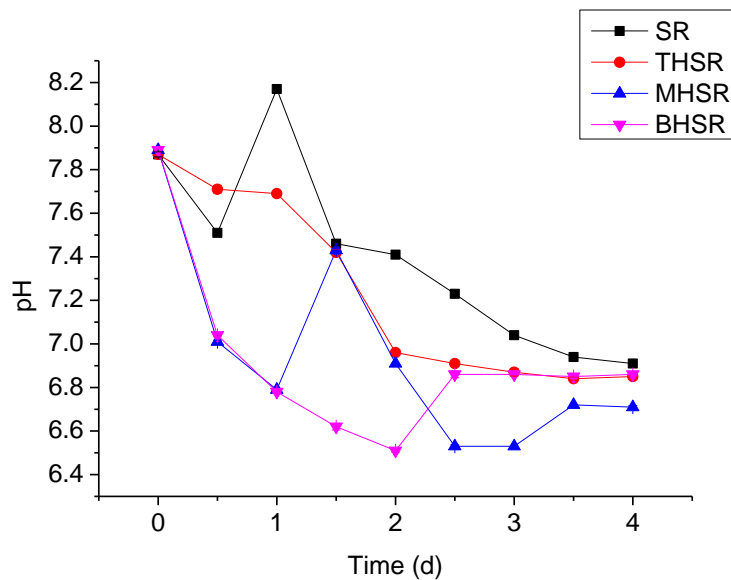
Operation conditions are as follows:

6

HRT: 0.9 d, Temperature 35 °C; Partial heating temperature: 60 °C.

7

1 **Fig. 3**



2
3
4
5
6
7

Fig. 3 Time course of pH for the control and runs with single partial heating modules

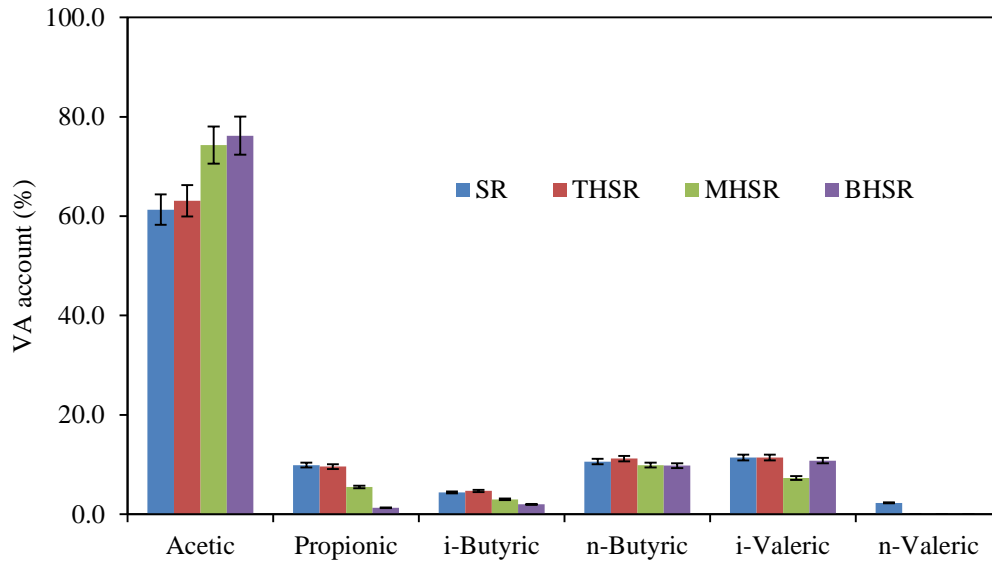
Operation conditions are as follows:

HRT: 0.9 d, Temperature 35 °C; Partial heating temperature: 60 °C.

1 **Fig. 4**

2

3



4

5

Fig. 4 VA content for the control and varied single partial heating modules

6

Operation conditions are as follows:

7

HRT: 0.9 d, Temperature 35 °C; Partial heating temperature: 60 °C.

8

9

1 **Table 1**

2

3

Table 1 Characteristics of the continuous operations at steady state

	SR	THSR	MHSR	BHSR
pH	7.0±0.1	6.9±0.1	6.7±0.0	6.9±0.1
TAN(mg/L)	743.7±17.6	777.6±14.8	834.1±29.0	751.1±26.3
TN(mg/L)	969.1±40.9	804.0±24.3	949.0±5.1	836.0±4.5
UN (mg/L)	225.4	26.4	114.9	84.9
AVR (%)	3.3	19.8	5.3	16.6
TC removal ratio (%)	39.0	61.6	56.7	56.3
TVA (g/L)	2.8	2.0	1.5	1.4

4

5

1 **Table 2**

2

3

Table 2 Characteristics of ammonia production in case of the dual partial heating module under the steady state

pH	TC removal					VA composition (%)					
	TAN (mg/L)	ratio (%)	TN (mg/L)	AVR (%)	TVA (g/L)	Acetic	Propionic	i-Butyric	n-Butyric	i-Valeric	n-Valeric
6.6±0.1	736.8±31.8	65.2±0.5	829.5±17.7	18.4±0.9	3.6±0.3	52.1±1.6	9.7±0.9	6.9±0.6	11.7±0.7	19.6±2.4	N.D.

4