Water Science & Technology

IWA PUBLISHING

Water Science & Technology Vol 87 No 3, 614 doi: 10.2166/wst.2023.015

Study on ammonia generation from digested sludge by subcritical water treatment

Takahiro Kato*, K. Kojima, M. Sumikura and Y. Kuroiwa
Shimizu Corporation, 3-4-17, Etchujima, Koto-ku, Tokyo 135-8530, Japan
*Corresponding author. E-mail: t.kato@shimz.co.jp

TK, 0000-0002-4806-6717

ABSTRACT

Organic sludge has recently attracted attention as a renewable energy source. While the organic matter contained in sludge can be utilized as various renewable energy sources, its nitrogen component has limited use. In this study, subcritical water treatment was conducted to recover ammonia from digested sludge. While ammonia recovered via stripping is limited to soluble components, subcritical water treatment can convert solid components and dissolved organic nitrogen sludge into ammonia. Digested sludge was treated at several reaction temperatures, reaction pressures, treatment times, and oxygen ratios to determine the ammonia generation rate. Among the conditions tested in this study, an ammonium generation rate of 84.0% was obtained at 400 °C, 10 MPa, a treatment time of 5 min, and at an oxygen ratio of 1.2.

Key words: ammonification, high temperature and pressure treatment, oxidation treatment, pyrolysis treatment, sewage sludge, sludge decomposition

HIGHLIGHTS

- Subcritical water treatment efficiently converts nitrogen in digested sludge into ammonia.
- Under 400 °C, 10 MPa, 5 min, and an oxygen ratio of 1.2, ammonia was produced for 84.0% of total nitrogen.
- Subcritical water treatment can recover more nitrogen components as ammonia compared to ammonia stripping. This is because solid nitrogen and dissolved organic nitrogen can also be converted into ammonia by this method.

INTRODUCTION

Sewage sludge and livestock manure have attracted attention as new renewable energy sources for the formation of a circular economy (Kirchher *et al.* 2017; Oladejo *et al.* 2019), and technology to recover energy from these sources is currently being developed (Almås & Singh 2017; Kacprzak *et al.* 2019). This technology mainly utilizes the organic matter contained in sludge to generate biogas, biomethane, crude oil, and biochar, which are then used as energy sources. On the other hand, the use of nitrogen components in sludge is limited to fertilizers for agriculture. Because the agricultural use of sludge is not widespread in Japan, nitrogen is mostly disposed of. Ammonia, a nitrogenous component found in large amounts in sewage sludge, is not only available as a fuel (Kurata *et al.* 2017), but it has attracted attention as a storage and carrier of hydrogen (Lamb *et al.* 2019). According to Japanese sewage statistics, sewage treatment plants overall receive about 484,000 t-N/year of nitrogen components, and they release about 174,000 t-N/year as effluent and about 134,000 t-N/year as sludge (Kojima *et al.* 2021). The difference, about 176,000 t-N/year, is released into the atmosphere by denitrification, which consumes a large amount of energy. If all of the approximately 134,000 t-N released as sludge from sewage treatment plants in a year were converted into ammonia, the energy potential would be about 1.02 billion kWh, which is about 15.8% of the annual electricity consumption of all sewage treatment plants in Japan, based on an estimate of 382.6 kJ/mol for the calorie of ammonia combustion. Thus, the recovery of nitrogen components from sewage sludge via replacement with ammonia is considered a new and effective utilization technology for sewage sludge.

The ammonia stripping method is one way to release ammonia from sewage sludge (Kinidi *et al.* 2018). However, this method can only recover soluble ammonia. The nitrogen component in sewage sludge can be divided into solids and dissolved nitrogen. Even in digested sludge, where the amount of nitrogen dissolved in the water in the sludge is considered

---

high, the amount of nitrogen derived from solids is crucial because it accounts for about 51.3% of the total (Kojima *et al.* 2021). Therefore, to recover nitrogen components from sewage sludge and use them as energy, nitrogen derived from solids must also be recovered, and pretreatment (e.g., through solubilization) is necessary. Solubilization methods include hydrothermal treatment and microbial degradation (Park *et al.* 2019), but most are aimed at increasing methane recovery in anaerobic fermentation, and few at recovering nitrogen components.

In this paper, we examined a technology for converting solid nitrogen components in sewage sludge into ammonia under subcritical conditions. Water at higher temperatures and pressures than the critical point (374.2 °C, 22.1 MPa) is known as supercritical water, which has excellent hydrolytic resolution. Subcritical conditions are not clearly defined. However, they are generally understood to refer to lower temperatures and pressures near the critical point. For example, Qian *et al.* showed that adding an excess of oxidants to supercritical water can remove and completely degrade more than 99% of chemical organic demand (COD), total organic carbon (TOC), and NH_3 in municipal sewage sludge (Qian *et al.* 2016). Ammonia produced by heat treatment was considered a waste product that had to be removed. Therefore, ammonia was either decomposed and treated as nitrogen using a catalyst that decomposes ammonia, treated at even higher temperatures, or treated for longer periods of time (Sumikura *et al.* 2006; Li *et al.* 2020). In Sumikura's work, the ammonia generation rate from the methane fermentation residue was the highest under 450 °C, 15 MPa, 20 min. Under higher temperature and pressure conditions, ammonia was decomposed into nitrogen. Therefore, equivalent or lower temperature and pressure conditions are considered suitable for ammonia recovery. The objective of this research is to identify the superior conditions for generating ammonia from digested sludge by subcritical water treatment. Through this research, we will confirm that subcritical water treatment is a superior method compared to the existing method of ammonia stripping. If it can be confirmed that a greater amount of ammonia is produced than that contained in the original digested sludge, it suggests that more ammonia can be generated from the sludge than with ammonia stripping. The amount of ammonia generated was investigated for the combustion condition, in which hydrogen peroxide was added to oxidize nitrogen-containing organic matter, and the pyrolysis condition, in which less energy input is required and the organic matter after treatment is expected to be utilized.

MATERIALS AND METHODS

The digested sludge used in the experiment was provided by the Northern Sludge Materialization Center of Yokohama City in 2017. Table 1 shows the properties of the sludge. In the digested sludge used in this study, the nitrogen component in the solids was 1,728 mg/kg and that in the water was 1,362 mg/kg. Water content was determined from the decrease in weight when heated at 105 °C. Among the elemental contents, C, H, N, and S were determined by an elemental analyzer (Analytik Jena, 2400 II). Cl was measured according to the Wastewater Examination Method (Yamaguchi 2012) published by the Japan Sewage Works Association, and ash by intense thermal loss at 600 °C. In addition, the content of O elements was calculated by subtracting the C, H, N, S, Cl, and ash values from 100%. The total N in filtered solution was determined by

Table 1 | Property of digested sludge

Water content	(%)	97.3
Elemental composition[a]		
C	(%)	37.10
H	(%)	6.00
N	(%)	6.40
O	(%)	25.56
S	(%)	2.30
Cl	(%)	0.24
Ash	(%)	22.40
dissolved nitrogen		
Total N	(mg/L)	1,400
NH_4-N	(mg/L)	1,200

[a] per dry weight.

a combustion catalyst-based elemental analyzer (Shimadzu, TOC-L), and NH_4^+-N by ion chromatography (ThermoFisher, ICS-1600). Small batch-type experimentals were conducted. Digested sludge and H_2O_2 as combustion agents were placed in the reaction vessel (10 mL, SUS316) and sealed. The amount of each input was determined from the pressure, volume, and temperature (P–V–T) relationship to achieve the target pressure under the target temperature. All the gases inside each reaction vessel were replaced with argon gas. Reaction vessels with samples were put in a sand bath (TECHNE) preheated at reaction temperature. The reaction time refers to the time in which the vessel was put into the sand bath, and the reaction temperature was assumed to be the same as the set temperature of the sand bath. The reaction pressure was calculated from the total water content in the digested sludge and H_2O_2 in the reaction vessel, the gas volume in the reaction vessel, the internal volume of the reaction vessel, and the reaction temperature using the P–V–T relationship for water. After a predetermined reaction time, the reaction was stopped by removing the vessel from the sand bath and cooling it in running water. After cooling, the decomposition products in the reaction vessel were filtered by a 0.45 μm cellulose acetate filter (ADVANTEC, 25CS045AN), and NH_4^+ was determined by ion chromatography. The ammonia generation rate was calculated by comparing the total nitrogen content in the digested sludge and NH_4^+-N after treatment. Each experiment was repeated in triplicate.

To investigate better ammonia creation conditions, temperature (350–450 °C), pressure (1–25 MPa), time (0–15 min), and oxygen ratio (0–2.0) were utilized as parameters. The composition formula of digested sludge shown in Equation (1) was determined from the properties of the digested sludge, and the amount of oxygen required to burn all carbon components in the digested sludge to CO_2 was estimated as the minimum amount of oxygen required:

$$C_{6.8}H_{13.1}NO_{3.5} + 7.6O_2 \rightarrow 6.8CO_2 + 5.1H_2O + NH_3 \tag{1}$$

The oxygen ratio in this paper refers to the ratio between the minimum stoichiometric amount of oxygen required for the complete combustion of C and H in organic sludge to produce 1 mol of ammonia and the quantity of oxygen contained in the material enclosed in the reaction vessel. The former was calculated from Equation (1), which shows that 7.6 mol of oxygen is required to obtain 1 mol of ammonia, or 46.1 mmol of oxygen per gram of sludge. The latter was calculated by the amount of oxygen contained in the digested sludge itself, water, and hydrogen peroxide. Note that this study did not analyze the composition of organic matter in detail, and the oxygen demand may differ from actual values. An oxygen ratio of 0 indicates pyrolysis under subcritical conditions, and the other ratio (0.3–2.0) indicates combustion conditions. Similar tests were conducted using ammonia water to confirm the transformation of ammonium into other nitrogen forms under subcritical treatment conditions.

RESULTS AND DISCUSSION

Figure 1 shows the ammonium generation ratio with each temperature, pressure, treatment time, and oxygen ratio. No significant differences were found in the combustion process under combustion treatment in subcritical conditions from 350 to 450 °C. Ammonia nitrogen generation ranged from 77.8 to 84.0%, and it was highest at 400 °C. When the pressure was varied, the generation rate of ammonium nitrogen ranged from 61.7 to 84.0%, with no significant difference in *p*-values above 5 MPa ($p > 0.05$). When time was varied, the generation rate of ammonium nitrogen ranged from 45.3 to 84.2%, with no significant difference observed for reaction times longer than 5 min ($p > 0.05$). When the oxygen rate was varied, the generation rate of ammonium nitrogen was 78.5–84.0% at oxygen rates of 1.0 or higher.

Under pyrolysis treatment in subcritical conditions, when the temperature was increased, ammonium nitrogen generation experiences a decreasing trend from 69.9 to 62.7%. When the pressure was varied, no significant differences were found; however, conditions under 1 MPa had the lowest mean value of 54.9%. When the reaction time was increased until 5 min, the rate of ammonium nitrogen generation increased from 40.2 to 64.6%. For reaction times longer than 5 min, the rate was 64.2–64.7%.

Figure 2 shows the rate of ammonia generation under the best results found in this research. Under combustion conditions, ammonia was produced for 84.0% of the total nitrogen. Ammonia was produced for 64.6% of the total nitrogen under pyrolysis conditions. Focusing on the nitrogen in the solid content and the nitrogen that was present in forms other than ammonia, 74.3% of the nitrogen was converted into ammonia in the combustion condition and 43.2% in the pyrolysis condition. The fact that ammonia is not degraded under these conditions is confirmed by testing with reagent ammonia water instead of digested sludge. Table 1 shows that the digested sludge used in this study contained 3,106 mg/kg of total nitrogen, while

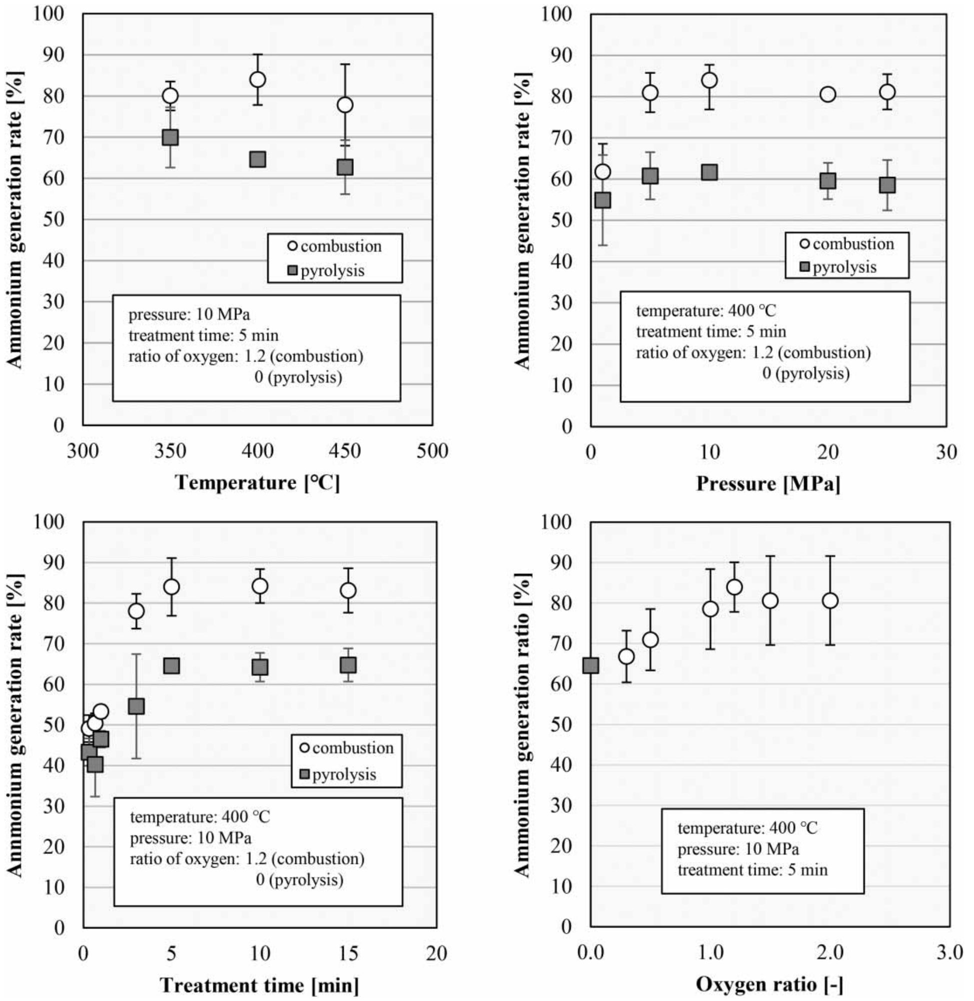

Figure 1 | Ammonium generation rate with each temperature, pressure, treatment time, and oxygen ratio. The white circle shows the result under combustion conditions. The black squares show the result under pyrolysis. The error bars indicate the standard deviations of at least three experiments.

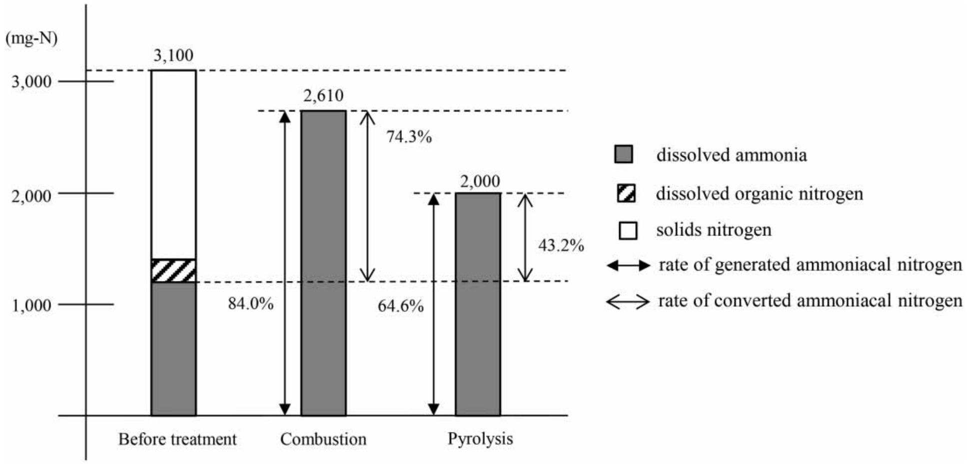

Figure 2 | Amount of nitrogen before and after treatment in combustion or pyrolysis at 400 °C, 10 MPa, 5 min, and a ratio of generated ammonium nitrogen from whole nitrogen in digested sludge and converted ammonium nitrogen from solid nitrogen and dissolved organic nitrogen in digested sludge.

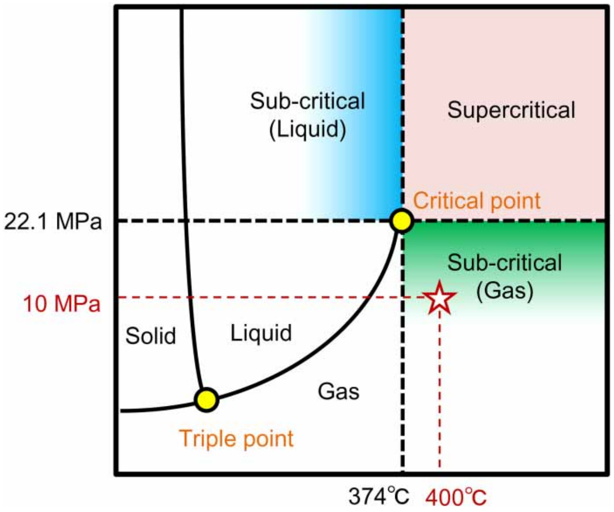

Figure 3 | Three-state diagram of water and optimal point (star mark) in this research for ammonia generation from digested sludge.

1,167 mg/kg was dissolved ammonia. Therefore, the recovery rate obtained by ammonia stripping, which only recovers soluble ammonia, is 37.6% at maximum. Compared to this, the subcritical water oxidation process can recover nitrogen components other than soluble ammonia as nitrogen components, indicating that more nitrogen components can be recovered as ammonia.

Under the conditions of this research, the highest ammonium nitrogen generation rate of 84.0% was obtained at a temperature of 400 °C, a pressure of 10 MPa, a treatment time of 5 min, and an oxygen ratio of 1.2. At 400 °C and 10 MPa, the water in the reaction vessel was considered to be in a gas state (Figure 3). Although no compound analysis of nitrogen components was conducted in this study, proteins – and their degradation products, amino acids – were identified as the main nitrogen-containing substances in sludge. These are the major sources of ammonia. Amino acids have various properties depending on their side chains, and they produce ammonia and carbon dioxide through deamination reactions. Among amino acids, glycine and alanine, which have simple structures, are decomposed at 350 °C, 34 MPa, and in 5–15 s (Toor *et al.* 2011). Temperature at which the highest average ammonia generation was obtained in our study (400 °C) is close to these conditions. The lower pressure conditions (10 MPa) would have required higher temperatures and longer processing times than the reference.

The rate of ammonium nitrogen generation will vary depending on the material compositions. Previous studies have shown that in the treatment of food residues with subcritical water, the products after treatment vary depending on the constituents, and amino acids are the main source of ammonia (Posmanik *et al.* 2017). Sewage sludge with a high nitrogen content, such as amino acids, would be more desirable to increase the amount of ammonia created by this method.

The rate of ammonia nitrogen generation was higher in the combustion condition than in the pyrolysis condition for all the conditions in this study. As to the supercritical treatment of sewage sludge (450 °C, 25 MPa, 2 min), the solid content decreased, and the NH_3 removal rate increased as the amount of hydrogen peroxide added was increased (Xu *et al.* 2013). Our conditions (400 °C, 10 MPa, 5 min) were milder than these because no ammonia decomposition occurred, we believe that the higher the amount of H_2O_2 added, the higher the rate of ammonium nitrogen generation. Another approach, focusing on energy recovery, involves the effective use of the organic matter contained in sludge by utilizing the residue after methane fermentation or by suppressing the decomposition of organic carbon under pyrolysis. Furthermore, we find that a more detailed study of the composition of the sludge would lead to further efficiency improvements.

CONCLUSIONS

This study investigated the superior conditions for the creation of ammonia from nitrogen components in digested sludge by subcritical treatment. The conditions under which this paper was conducted were as follows: the ammonia generation rate was 84.0% at 400 °C, 10 MPa, 5 min, and an oxygen ratio of 1.2. This result suggested that 74.3% of the nitrogen component and soluble organic nitrogen contained in the solid content of digested sludge could be converted into ammonia, presenting the possibility of recovering more nitrogen components as ammonia compared to ammonia stripping, which can only recover soluble ammonia.

ACKNOWLEDGEMENTS

The digested sludge used in this study was provided by the Northern Sludge Materialization Center of Yokohama City. We would like to take this opportunity to express our gratitude to the Center.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

REFERENCES

Almås, A. & Singh, B. R. 2017 Sewage sludge disposal strategies for sustainable development. *Environ. Res.* **156**, 39–46.

Kacprzak, M., Neczaj, E., Fijałkowski, K., Grobelak, A., Grosser, A., Worwag, M., Rorat, A., Brattebo, H., Park, M., Kim, N., Lee, S., Yeon, S., Seo, J. H. & Park, D. 2019 A study of solubilization of sewage sludge by hydrothermal treatment. *J. Environ. Manage.* **250**, 109490.

Kinidi, L., Tan, I., Wahab, N., Tamrin, K., Hipolito, C. & Salleh, S. 2018 Recent development in ammonia stripping process for industrial wastewater treatment. *Int. J. Chem. Eng.* **2018**, 3181087.

Kirchherr, J., Reike, D. & Hekkert, M. 2017 Conceptualizing the circular economy: an analysis of 114 definitions. *Resour. Conserv. Recycl.* **127**, 221–232.

Kojima, K., Kato, T., Sumikura, M. & Kawamoto, T. 2021 Estimation of nitrogen-derived energy potential in sewage treatment plants and its use. *Sewage Assoc. Mag.* **58** (708), 78–87.

Kurata, K., Iki, N., Matsunuma, T., Inoue, T., Tsujimura, T., Furutani, H., Kobayashi, H. & Hayakawa, A. 2017 Performances and emission characteristics of NH_3-air and NH_3-CH_4-air combustion gas-turbine power generations. *Proc. Combust. Inst.* **36**, 3351–3359.

Lamb, K. E., Dolan, M. D. & Kennedy, D. F. 2019 Ammonia for hydrogen storage; a review of catalytic ammonia decomposition and hydrogen separation and purification. *Int. J. Hydrogen Energy* **44** (7), 3580–3593.

Li, J., Wang, S., Li, Y., Jiang, Z., Xu, T. & Zhang, Y. 2020 Supercritical water oxidation and process enhancement of nitrogen-containing organics and ammonia. *Water Res.* **185**, 116222.

Oladejo, J., Shi, K., Luo, X., Yang, G. & Wu, T. 2019 A review of sludge-to-energy recovery methods. *Energies* **12** (60). doi:10.3390/en12010060.

Park, M., Kim, N., Lee, S., Yeon, S., Seo, J. H. & Park, D. 2019 A study of sewage sludge by hydrothermal treatment. *J. Environ. Manage.* **250**, 109490.

Posmanik, R., Cantero, D. A., Malkani, A., Sills, D. L. & Tester, J. W. 2017 Biomass conversion to bio-oil using sub-critical water: study of model compounds for food processing waste. *J. Supercrit. Fluids* **119**, 26–35.

Qian, L., Wang, S., Xu, D., Guo, Y., Tang, X. & Wang, L. 2016 Treatment of municipal sewage sludge in supercritical water: a review. *Water Res.* **89**, 118–131.

Sumikura, M., Shibuya, K., Noguchi, H., Okajima, I. & Sako, T. 2006 Advanced methane fermentation by hydrothermal liquefaction and wastewater treatment by supercritical water oxidation. In *Renewable Energy 2006 International Conference and Exhibition*, Chiba, Japan.

Toor, S., Rosendahl, L. & Rudolf, A. 2011 Hydrothermal liquefaction of biomass: a review of subcritical water technologies. *Energy* **36**, 2328–2342.

Xu, D., Wang, S., Tang, X., Gong, Y., Guo, Y., Zhang, J., Wang, Y., Ma, H. & Zhou, L. 2013 Influence of oxidation coefficient on product properties in sewage sludge treatment by supercritical water. *Int. J. Hydrogen Energy* **38**, 1850–1858.

Yamaguchi, M. 2012 *Wastewater Examination Method*. Japan Sewage Works Association, Tokyo, Japan.

First received 23 September 2022; accepted in revised form 9 January 2023. Available online 20 January 2023