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# Low-temperature hydrothermal pretreatment followed by dry anaerobic digestion: A sustainable strategy for manure waste management regarding energy recovery and nutrients availability

Weiwei Huang [a,b], Ziwen Zhao [a], Tian Yuan [a], Wenli Huang [c], Zhongfang Lei [a,*], Zhenya Zhang [a,*]

[a] Graduate School of Life and Environmental Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8572, Japan
[b] Key Laboratory of Coal Gasification and Energy Chemical Engineering of Ministry of Education, East China University of Science and Technology, No. 130 Meilong Road, Xuhui District, Shanghai 200237, China
[c] MOE Key Laboratory of Pollution Process and Environmental Criteria, College of Environmental Science and Engineering, Nankai University, No. 94 Weijin Road, Nankai District, Tianjin 300071, China

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ABSTRACT

This study evaluated the feasibility of low-temperature hydrothermal (HT) pretreatment for improving dry anaerobic digestion (AD) of swine manure (SM) and nutrient elements reclamation, with specific goals to minimize the drawbacks of conventional HT process including high energy consumption, inhibitory compounds formation and unfavorable pH/alkalinity decrease. Pretreatment at 110–130 °C for holding 30 min increased the soluble organic carbon (SOC) concentration in SM by 13–26%. After being mixed with inocula, the pretreated SM was applied for dry AD tests successfully without initial pH adjustment, achieving a $CH_4$ yield of 280.18–328.93 ml/g-$VS_{fed}$ (14–34% increase compared to that from raw SM). Energy assessment indicated a positive net gain of 0.95 kJ/g-VS by adopting HT pretreatment at 130 °C. Except for increment in $CH_4$ yield, low-temperature HT pretreatment also promoted organic-N mineralization, increasing N fractions in the digestate available for plants. After 70 days' dry AD, a high ammonia-N to total nitrogen (TN) ratio of 71% was obtained for the SM sample pretreated at 130 °C, in sharp contrast to that of 38% in raw SM. P bioavailability in the final digestate was not greatly affected by the HT pretreatment since the labile organics were mostly degraded after AD, in which P existing forms were influenced by the multivalent metals content in SM. Overall, 23–27% of the total P was potentially bioavailable in all digestates.



## 1. Introduction

Anaerobic digestion (AD) is a promising technology for converting organic manures into profitable $CH_4$ and producing digestates with high agronomic values. In particular, dry AD at total solids (TS) content ≥ 15% is an attractive option over wet AD (TS < 10%) owing to its high volumetric loading capacity and easy handling of the digestate. Despite of these advantages, dry AD process has some limitations like long retention time, restrictive hydrolysis of the particulate organics (e.g. fibers, undigested food) and consequently low overall degradation efficiency of volatile solids (VS) in animal manure (< 30% in mesophilic dry AD) (Menardo et al., 2011).

Pretreatment is usually applied to improve $CH_4$ production from animal manure. Methods to promote organic matters hydrolysis and disintegration mainly include hydrothermal (HT) technology, chemical or ultrasonic treatment, extrusion and microwave processes (Carlsson et al., 2012; Carrere et al., 2016). Among them, HT technology is an advantageous choice due to its efficacy, simplicity, no chemical addition and sanitation effects. The process can effectively break up the crystalline complexes of lignocellulose in manure, causing the biomass to swell and thus become more accessible to the bacteria (Rodriguez et al., 2017). On the other hand, HT pretreatment reduces the substrate viscosity, which facilitates the feeding process (Rodriguez et al., 2015). Deactivation of the pathogens is a further advantage of this process. Although HT technology has been successfully implemented at full-scale for improving AD of animal byproducts, lignocellulosic materials, food wastes and sewage sludge (Carrere et al., 2016), little information is available for its pilot- or full-scale application in animal manure treatment, especially under high TS conditions.

* Corresponding authors.
*E-mail addresses:* lei.zhongfang.gu@u.tsukuba.ac.jp (Z. Lei), zhang.zhenya.fu@u.tsukuba.ac.jp (Z. Zhang).

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Most studies on HT pretreatment for improving AD process claimed an optimal HT temperature range of 170–190 °C (Bougrier et al., 2008; Wilson and Novak, 2009). However, pretreatments under such high temperatures lead to high energy consumption and strict requirements for the facilities. Another possible disadvantage is the undesirable decrease in system pH/alkalinity (Yin et al., 2014), and pH adjustment is often necessary to achieve neutral that is suitable for methanogenesis (Chen et al., 2007), which also needs extra cost. What's more, a high ammonia release during HT process could exert inhibition to the methanogens during start-up of an AD reactor, which is considered the most critical step in the operation of a digester (Griffin et al., 1998). Thus the application of low-temperature HT pretreatment might be more beneficial. For instance, Wilson and Novak (2009) suggested temperatures < 150 °C in order to marginally reduce ammonia release from activated sludge. On the other hand, Dwyer et al. (2008) noticed insignificant changes in sludge biodegradability and degradation rate when decreasing the HT temperature from 165 to 140 °C. After HT pretreatment of solid manure (TS = 12–28%) at 120 °C for holding 30 min, Menardo et al. (2011) obtained increased $CH_4$ yield from the pretreated biomass by 35–171%. Despite these efforts, more details regarding energy balance, microbial dynamics and possible reclamation of nutritional elements are necessary to fully evaluate the stability, reliability and economic feasibility of low-temperature HT pretreatment for improving dry AD of manure waste. Particularly, fertilizer potential of the digestate related with existing forms of N and P, the two most important nutrient components in commercial fertilizers, is also important for assessing the economic performance of a biogas plant.

This study aimed to investigate the feasibility of dry AD of animal manure after HT pretreatment at low temperatures of 110 and 130 °C. Swine manure (SM) was selected as a typical example of manure waste in this work. Restated, $CH_4$ production from dry AD of the pretreated SM and the changes in N and P availability were studied. Energy assessment was also conducted to compare the energy input for pretreatment (heating and stirring) and the net increase in energy output (improvement in $CH_4$ yield). Finally, the whole process performance of low-temperature HT pretreatment followed by dry AD was evaluated by comparing the net energy gain, C capture efficiency and fertilizer potentials of the digestate.

## 2. Materials and methods

### 2.1. Raw materials

Fresh raw swine manure (RSM) containing no bedding materials was sampled from concrete floor of a pig finishing unit near Tsukuba campus, where the fattening pigs were fed with soybean, corn, bran, etc. The collected RSM was mixed thoroughly and refrigerated at 4 °C before use. Mature digestate from a semi-batch dry AD reactor treating SM (taken from the same farm) was used as inocula. The semi-batch reactor was successfully operated at 35 °C for about 5 months in the lab after acclimation. Characteristics of the RSM and the inocula are listed in Table 1.

**Table 1**
Main characteristics of raw swine manure and inocula used in this study.

| Parameter | Raw swine manure (RSM) | Inocula |
|---|---|---|
| Total solids (TS, %) | 25.02 ± 0.11 | 19.10 ± 0.21 |
| Volatile solids (VS, %) | 20.06 ± 0.12 | 11.74 ± 0.15 |
| Total alkalinity (TA, mg/g as $CaCO_3$) | 18.34 ± 0.53 | 26.66 ± 0.64 |
| Total ammonia nitrogen (TAN, mg/g) | 0.62 ± 0.02 | 2.59 ± 0.10 |
| Total nitrogen (TN, mg/g) | 4.67 ± 0.15 | 3.54 ± 0.14 |
| Organic phosphorus (OP, mg/g) | 1.12 ± 0.09 | 0.70 ± 0.04 |
| Apatite phosphorus (AP, mg/g) | 3.80 ± 0.21 | 5.36 ± 0.31 |
| Non-apatite inorganic phosphorus (NAIP, mg/g) | 2.13 ± 0.14 | 1.47 ± 0.08 |
| C/N | 16.76 ± 0.20 | 13.10 ± 0.17 |
| pH | 6.91 ± 0.08 | 7.54 ± 0.08 |

The results are presented as mean values of five determination ± standard deviation.
All concentrations presented in the table were calculated based on fresh mass.

### 2.2. Hydrothermal treatment

An enclosed stainless steel reactor (cylindrical shape with inner diameter of 4.0 cm, height of 19.0 cm, wall thickness of 0.25 cm, and working volume of 200 ml) equipped with a cylindrical electric heating jacket and an internal temperature sensor (OM Lab-tech MMJ-200, Japan) was employed for the HT experiments. The operation temperatures were maintained within ±4 °C of the set conditions. Agitation was achieved with a motor-driven propeller. In each HT experiment, the reactor was loaded with 140 g RSM (TS 25% without dilution) and sealed. Under constantly stirring at 100 rpm, the reactor was heated at an average rate of 14.4 °C/min up to a designated temperature (110 or 130 °C) and maintained at this temperature for 30 min. The corresponding pressures at 110 and 130 °C were about 0.05 and 0.18 MPa, respectively. Then the reactor was cooled down with a fan to ambient temperature (around 25 °C) before opened for sampling. All HT experiments were conducted in triplicate, and the analysis of each parameter was repeated twice. After sample analysis, 100 g manure sample was collected from each HT run (totally 300 g for each temperature condition) and used for the subsequent dry AD test.

### 2.3. Dry anaerobic digestion

For $CH_4$ fermentation, 300 g RSM or pretreated SM at 110 and 130 °C respectively were mixed thoroughly with 150 g inocula, then the mixtures were loaded into a series of 500 ml fermentation bottles (with diameter of 6.5 cm and height of 15.1 cm) labeled as R-RSM, R-110 and R-130, respectively. Meanwhile, a fermentation bottle loaded with inocula only was prepared as the control. The bottles were then flushed with $N_2$, sealed with silicone stoppers and incubated at 35 (± 1) °C for 70 days without agitation. To simplify the process for its possible application in practice and to avoid changes in the microenvironment brought about by acid/alkali addition, no further pH adjustment was performed. The initial AD conditions are listed in Table 2. All analyses of the SM characteristics were performed three times. The biogas ($H_2$ + $CH_4$ + $CO_2$, ml/g-VS) was collected and quantified, and the gas composition ($H_2$, $CH_4$ and $CO_2$) was determined with a gas chromatograph (Shimadzu, Japan) equipped with thermal conductivity detector. Net $CH_4$ yield (in ml/g-$VS_{fed}$) of the SM was obtained by subtracting the amount produced from the inocula.

### 2.4. Sample analysis

Sample preparation and analysis of TS, VS, manure pH, total nitrogen (TN), organic C and N contents, total ammonia nitrogen (TAN), soluble proteins, soluble carbohydrates, soluble organic carbon (SOC) and volatile fatty acids (VFAs) were performed according to the literature (Huang et al., 2016a). Total alkalinity (TA) was determined with titration method to an endpoint of pH 4.3. Amino acids and urea were assayed on an amino acid analyzer (JEOL JLC-500/V2, Japan).

For P fractionation, the solid samples were subjected to the Standards, Measurements and Testing (SMT) extraction procedure