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A new torrefaction system employing spontaneous self-heating of livestock manure under elevated pressure

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ABSTRACT

This report describes a new oxidative torrefaction method employing spontaneous self-heating of feedstock as a means of overcoming practical difficulties in converting livestock manure to biochar. We examined the initiating temperature required to induce self-heating of wet dairy cattle manure under 1.0 MPa pressure and conducted elemental and calorific analyses of the solid products prepared at 200, 250, and 300 °C. Self-heating was initiated with oxidation below 100 °C, and the lower limit of the initiation temperature was between 85 and 90 °C. Comparing processes performed at 0.1 and 1.0 MPa, the higher pressure promoted self-heating by both preventing heat loss due to moisture evaporation occurring at approximately 100 °C and supplying oxygen to the high-moisture feedstock. In addition, as drying occurred at 160–170 °C during the process, the system did not require pre- or post-drying. Although the heating values of the solid products decreased due to high ash content, the elemental composition of the products was altered to that of peat-like (200 °C) and lignite-like (250 and 300 °C) materials. Cessation of self-heating of the manure is recommended at approximately 250 °C to avoid severe decomposition at higher temperatures. Overall, these results demonstrated the utility of the proposed method for converting wet manure into dried biochar through self-heating as well as potential applications in manure management systems.

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1. Introduction

A sustainable management system for livestock manure is needed in the agricultural sector. Manure is a primary source of environmental methane, nitrous oxide, and ammonia emissions, and improper management of manure not only accelerates global warming but also causes eutrophication and acidification (Amon et al., 2006). In addition, the growth of intensive agriculture has generated concerns over groundwater pollution resulting from nitrate leaching from applied manure and manure-derived fertilizers (Basso and Ritchie, 2005; Goldberg, 1989; Maeda et al., 2003). Although manure not treated appropriately can threaten human health and environmental quality, the conversion of manure into biochar represents a potentially desirable alternative for manure management. Because biochar can help retain nutrients such as nitrogen and phosphorus in the soil (Lehmann, 2007), its application to farmland would reduce the risk of pollution while simultaneously increasing crop productivity. Biochar can also be used as a feedstock for gasification and co-firing at electric power generation plants (Phanphanich and Mani, 2011; Prins et al., 2006; Recari et al., 2017; Xue et al., 2014). The development of methods for the production of manure-derived biochar would not only help reduce risks of water pollution associated with manure use but also provide marked economic benefits.

Despite the benefits of biochar utilization, the high moisture content of livestock manure has thus far prevented economical production of biochar. Although both dry and wet torrefaction processes are suitable for producing biochar or hydrochar, their usefulness is limited due to problems related to biomass moisture. The removal of moisture prior to the decomposition (torrefaction) step in dry torrefaction by heating to 200–300 °C represents the most energy-intensive step of the process (Basu, 2013; Bergman et al., 2005). Thus, based on energy consumption considerations, dry torrefaction would appear to be unsuitable for use with high-moisture feedstocks. By contrast, wet torrefaction utilizing pressurized hot water at 180–260 °C is an appealing alternative because it does not require pre-drying of the feedstock (Bach et al., 2017; Wang et al., 2018). However, the process liquid in wet torrefaction contains a variety of organic compounds (e.g.,
furfural and its derivatives, organic acids, and phenol and phenolic derivatives (Reza et al., 2014), thus necessitating chemical or biological treatment before discharge into the environment (Toufiq Reza et al., 2016; Wirth and Mumme, 2014; Wirth and Reza, 2016).

To overcome the abovementioned limitations, we developed a new torrefaction system incorporating spontaneous self-heating of biomass induced by low-temperature oxidation (LTO). Oxidation occurring at a temperature below 100 °C was shown to generate sufficient heat to induce self-heating and spontaneous combustion of coal (Wang et al., 2003), suggesting that LTO would be capable of generating heat sufficient for drying and decomposition of biomass feedstock. The proposed system is expected to be applicable to treatment of high-moisture biomass and enable the conversion of such biomass into biochar with less environmental impact than current technologies.

The proposed system enables efficient biochar production by employing LTO to induce subsequent self-heating at a lower temperature. The rate of heat production is generally low in the low-temperature range, and loss of heat due to the latent heat of evaporation can significantly affect the heat balance, making it difficult to maintain stable self-heating. Additionally, although ventilation is utilized for oxidation and drying in the proposed system, transporting oxygen to the biomass surface becomes more difficult with increasing moisture content. To overcome these drawbacks, our preliminary study focused on using an elevated-pressure environment and confirmed that higher pressure accelerates the LTO of manure (unpublished data). Based on those findings, the current study examined the hypothesis that introducing an elevated-pressure environment would promote LTO and subsequent self-heating by increasing the dissolved oxygen concentration in the biomass moisture while avoiding the loss of heat at low temperature (around 100 °C at 0.1 MPa) by elevating the boiling point of the biomass moisture.

To date, no peer-reviewed reports describing a torrefaction system employing spontaneous self-heating of biomass have been published. Therefore, the objective of the present study was to determine the optimal temperature required to induce self-heating of wet dairy cattle manure under elevated pressure. Elemental and caloric analyses of the resulting solid products were carried out to verify the feasibility of the proposed methodology.

2. Materials and methods

2.1. Materials

Dairy cattle manure was used as the feedstock. Prior to each experiment, the moisture and ash content were determined by drying wet samples at 105 °C for 24 h, followed by incineration at 600 °C for 3 h. The total amount of organic matter (volatile matter and fixed carbon) was expressed as ash-free solid (AFS) and determined by subtracting the amount of ash from the amount of dry solid. A total of 200 ± 1 g of wet mass of manure (63 ± 3% wet basis [wb] moisture content) was placed in the reactor for each experiment.

2.2. Experimental system

A schematic of the experimental system is shown in Fig. 1. A 1-L stainless-steel reactor with a double wall separated by an air-space to provide thermal insulation was used. The reactor was placed in an oven and connected to an air cylinder, a mass flow controller (F-201CV Series, Bronkhorst), and a back-pressure regulator (BP-3 series, Go Regulator). Ventilation (0.83 ± 0.02 L/min kg-AFS⁻¹), corresponding to an oxygen supply rate of 13.9 ± 0.4 g-O₂ h⁻¹ kg-AFS⁻¹, was employed to promote oxidation and drying. The pressure was maintained at 1.0 MPa during the process. The outlet concentrations of O₂, CO, and CO₂ were determined using an oxygen sensor and gas chromatograph (GC-4000, GL Science, Inc.) equipped with an activated carbon column (60/80 mesh), a methanizer, and hydrogen flame ionization detector. The concentration of each gas was converted to the corresponding consumption or production rate according to a previously reported procedure (Saludes et al., 2007).

2.3. Evaluation of optimal self-heating initiation temperature

We investigated the range of initiation temperatures required to induce optimal LTO and sample self-heating using pre-heating temperatures of 80, 85, 90, and 100 °C. These temperatures were selected based on our previous study indicating that LTO of cattle manure proceeds at 90 °C (Itoh et al., 2018). Once the sample temperature exceeded the pre-heating temperature due to self-heating, the oven temperature was controlled to follow the sample temperature to within 1.5 °C. The criterion for successful self-heating of the sample was defined as the sample temperature reaching 300 °C, which is the maximum temperature in general dry torrefaction (Basu, 2013). To evaluate the necessity of using elevated pressure, an experiment was also conducted at a pre-heating temperature of 100 °C and atmospheric pressure (0.1 MPa). Self-heating experiments were conducted at least twice to maximize experimental accuracy.

2.4. Biochar preparation

Following determination of the optimal initiation temperature range, biochar was prepared from manure at 200, 250, and 300 °C to investigate the effects on product physiochemical properties. Because self-heating of the sample continues throughout the process in the proposed system, the reaction was stopped by supplying nitrogen gas after depressurization when the sample reached the desired temperature. Approximately 20 min was required to decrease the temperature from 300 to ≤200 °C. Based on the result obtained in the prior experiment described in Section 2.3, a pre-heating temperature of 100 °C was used to induce self-heating of the samples. Biochar preparation at each temperature was conducted twice, and solid and energy yields are expressed as the average values of two replicates. The relative error between the average and measured values was <5.5%.
2.5. Analyses

Elemental analyses were carried out using both an elemental analyzer (CE-440, Exeter Analytical, Inc.) for carbon, hydrogen, and nitrogen and an ion chromatograph ( Dionex ICS-1600, Thermo Fisher Scientific Inc.) for sulfur, and the oxygen content was calculated by subtraction (O = 100 – C – H – N – S). The rate of decrease in the concentration of each element was determined according to the ash tracer method (Chen et al., 2012a). An energy analysis was also carried out in order to evaluate the potential for using the resulting biochar for bioenergy production. The higher heating value (HHV) was determined using an OSK 200 bomb calorimeter (Ogawa Sampling Co. Ltd.), and the data are expressed on both a dry basis (HHV[dB]) and dry/ash-free basis (HHV[daf]). The energy yield of the solid product and HHV were calculated according to the equation developed by Lu et al. (2012).

3. Results and discussion

3.1. Determination of optimal self-heating initiation temperature range

The results of self-heating of manure at 1.0 MPa at various pre-heating temperatures are shown in Fig. 2. Self-heating to 300 °C was observed with pre-heating temperatures of 85 °C or higher. In the case of pre-heating at 85 °C, a marked increase in temperature was observed in only one of the three trials. By contrast, no self-heating of manure was observed at a pre-heating temperature of 80 °C, although a slight temperature increase was detected. These results demonstrated that self-heating of manure is induced with a pre-heating temperature of 85 °C or higher at 1.0 MPa, with an ultimate increase in sample temperature to 300 °C. Self-heating of manure did not always occur with a pre-heating temperature of 85 °C, indicating that the lower limit of the initiation temperature is between 85 and 90 °C. It is known that the entire LTO process consists of a slow oxidation stage at temperatures below 65 °C, a transition stage at 65–80 °C, and a rapid oxidation stage at temperatures above 80 °C (Qi et al., 2015; Su et al., 2017). Hence, the rapid oxidation occurring at temperatures above 80 °C plays an important role in the self-heating of manure.

During self-heating to 300 °C, substantial evaporation and a temporary delay in temperature increase were observed in the range 160–170 °C for 24 h (Fig. 2). Considering that the boiling point of water is approximately 180 °C at 1.0 MPa, we concluded that this stagnation period corresponds to the drying process. Indeed, the moisture content of the solid products was <2.0% (Table 1), indicating that the system provides adequate drying.

As drying is thus integrated into the process, the proposed system does not require pre- or post-drying steps.

3.2. Gas analyses

To investigate the mechanism of the self-heating process, the rates of oxygen consumption and CO and CO2 production were determined, and the results are shown in Fig. 3. At temperatures >140 °C, the O2 consumption rate increased with increasing temperature and remained constant at 13.6 g-O2 h−1 kg-AFS−1, almost equal to the supply rate. The CO2 production rate exhibited a trend similar to that of oxygen consumption, increasing sharply between 100 and 140 °C and then remaining constant at approximately 15.0 g-CO2 h−1 kg-AFS−1 at temperatures >140 °C. Both the O2 consumption and CO2 production rates exhibited a small peak at approximately 90 °C, probably due to microbial respiration during the pre-heating stage. In composting processes, microbial activity is intensive at mesophilic (about 40 °C) and thermophilic temperatures (about 60 °C) and shows distinct O2 consumption at those temperatures (Miyatake and Iwabuchi, 2006). Although the current study found that the specific rate peaks at 90 °C due to the pre-heating operation and the time delay of detecting the gas behavior inside the reactor, those peaks were associated with microbial activity during the pre-heating stage. The CO production rate increased exponentially, reaching a maximum of 0.8 g-CO h−1 kg-AFS−1 at 300 °C, suggesting that O2 deficiency occurs at high temperatures.

The gas analyses revealed that self-heating is induced by oxidation at temperatures <100 °C. The consumption and production rates above 140 °C were indicative of incomplete oxidation. However, this did not prevent self-heating to 300 °C, indicating that the O2 supply rate was sufficient to support the increase in temperature.

3.3. Effects of pre-heating temperature

The pre-heating temperature affected the duration of the entire process. At a pre-heating temperature of 100 °C, the time required to reach 300 °C was more than 20 h shorter than at pre-heating temperatures of 85 or 90 °C. The time difference can be explained by the reaction rate at low temperatures (<120 °C). As the reaction rate is comparatively slower at low temperatures, more time is required to produce a marked temperature increase. Shortening the duration of the entire process is thus a key consideration in the proposed process: reduced space and period of storage requirements and smaller volumes of operation units (Cantrell et al., 2007; Hanifzadeh et al., 2017). Hence, it would be preferable to use a pre-heating temperature of ≥100 °C in order to complete the process in the least possible amount of time.

On the other hand, it is also of interest to minimize the temperature required to induce efficient self-heating of the manure. In the current study, a pre-heating temperature of 80 °C appeared to induce some LTO, but no significant temperature change was observed because the heat production rate was lower than the rate of heat loss (e.g., due to ventilation). Accordingly, it would be expected that self-heating could be initiated at lower temperatures if thermal insulation effects were increased, such as by reducing the ventilation rate. Moreover, a recent study reported that heat loss decreases as biomass volume increases (García-Torrent et al., 2012), suggesting that preparation of biochar from a larger biomass volume would induce self-heating at lower temperatures.

3.4. Effect of elevated pressure

Elevating the pressure greatly enhanced the induction of self-heating by minimizing heat loss due to moisture evaporation at
temperatures near 100°C. For example, self-heating of the manure was not observed at a pressure of 0.1 MPa (Fig. 2), indicating that the rate of heat loss exceeded that of heat production at approximately 100°C. Furthermore, at 0.1 MPa, self-heating of manure was not induced after moisture evaporation ceased, because a certain amount of moisture is essential for oxidation at low temperatures (Itoh et al., 2018). In order for LTO to progress, oxygen molecules must be chemically adsorbed to the surface of biomass particles, and this adsorption is significantly inhibited when the biomass is dry (Wang et al., 2003; Yu et al., 2013). Therefore, stable self-heating of manure could be achieved by retaining an amount of moisture necessary for oxidation at approximately 100°C by conducting the reaction in an elevated-pressure environment.

A potential concern is that excessive moisture could retard LTO. Indeed, the maximum LTO reaction rate occurs at a critical moisture content of 7–17%db at atmospheric pressure (Chen and Stott, 1993), indicating that the reaction would be inhibited at a high moisture level. Nevertheless, in our experiments, LTO and subsequent self-heating of 63%wb (≈170%db) manure occurred under elevated pressure (Figs. 2 and 3). This observation strongly suggests that elevated pressure facilitates the reaction between oxygen molecules and manure, inducing both LTO and self-heating of the manure even at a high moisture level.

As discussed above, an elevated-pressure environment promotes LTO and stable self-heating of wet biomass by both ensuring a continuous supply of oxygen and retaining a moderate level of moisture in the sample. However, more energy is required to maintain an elevated pressure throughout the process. Therefore, after stable self-heating of the feedstock is induced, it is preferable to depressurize and allow the rest of the reaction to proceed at atmospheric pressure to reduce energy consumption.

### 3.5. Elemental composition

The physicochemical properties of feedstock and biochar prepared at different temperatures are summarized in Table 1. Elemental and ash analyses confirmed that the relative contents of carbon, nitrogen, and ash increased from 50.8 to 66.1%daf for carbon, 2.5–7.2%daf for nitrogen, and 18.5–40.2%daf for ash, whereas those of hydrogen and oxygen decreased from 6.2 to 3.2%daf for hydrogen and 40.5–24.0%daf for oxygen. Particularly, the changes in carbon and oxygen content clearly indicate that the manure is altered into a char-like material by the proposed system. In comparison with standard coals, the elemental composition of the biochar was similar to that of peat or lignite (Table 1). The analyses also showed that the elemental composition of the biochar is affected by the process temperature. Although the carbon content increased at temperatures up to 250°C, no further increase was observed at 300°C, most likely because carbon consumption due to oxidation increases at temperatures over 250°C. For this reason,
self-heating of the manure should be terminated before significant destructive effects associated with high temperatures occur.

The optimal temperature range for the production of manure-derived biochar was determined from a plot of elemental decrease rates (Fig. 4) and a van Krevelen diagram (Fig. 5). The rates of decrease in hydrogen and oxygen were greater than that of carbon, demonstrating that more carbon remained compared with the other two elements, even in the oxidative environment. It should be noted that the rates of decrease in carbon and hydrogen increased proportionally as the process temperature increased, whereas that of oxygen did not significantly increase at temperatures between 250 and 300 °C (Fig. 4). This means that marked elimination of oxygen occurs in the process up to 250 °C but does not proceed considerably above that temperature. Similarly, the van Krevelen diagram indicated that the composition of biochar is affected by the process temperature, particularly below 250 °C (Fig. 5). The diagram shows that the raw manure located in the biomass region shifted to the peat (the process at 200 °C) and lignite (the processes at 250 and 300 °C) regions, and the atomic oxygen to carbon ratio decreased only minimally at a temperature of 250 °C or higher (Fig. 5). Thus, the proposed system converts manure into lignite-like material if the self-heating is terminated at approximately 250 °C.

3.6. Energy analysis

The potential for using the manure-derived biochar prepared using the proposed system as a solid biofuel was also considered. The HHVs of biochar shown in Fig. 6, representing the HHV(db) and HHV(daf), exhibited different trends. The HHV(db) of the biochar decreased compared with that of raw manure due to the high ash content, but an increase was observed in the HHV(daf). Both the solid and energy yields decreased with increasing process temperature: solid yield decreased from 64.0 to 49.3%db, and energy yield decreased from 60.9 to 42.1% as the temperature increased to 300 °C (Table 1).

The HHV(db) results differed from the general torrefaction results; the HHV(db) of the manure-derived biochar decreased with increasing temperature (Fig. 6). It is assumed that significant oxidative decomposition occurred during the process, resulting in the high ash content of the product. Indeed, the HHV(daf), which exhibited an upward trend, also consistently explains the decrease in HHV(db) caused by the high ash content. A similar trend can be observed in oxidative torrefaction of the same fibrous biomass as manure. For example, Chen et al. (2013) torrefied two different types of biomass (fibrous and ligneous) in an oxidative environment and investigated their decomposition behaviors. From their results, they concluded that fibrous biomass should be avoided in oxidative torrefaction because it decomposes more readily than ligneous biomass. Furthermore, another study confirmed that increases in HHV(db) rate tendency to be lower in sawdust (11.78 wt. % of ash) and rice husk (10.99 wt.% of ash) compared with coffee residue (1.76 wt.% of ash) (Chen et al., 2012b). These data suggest that it is more difficult to increase the HHV(db) of manure—a fibrous biomass with high ash content—in an oxidative environment. Therefore, it is expected that the manure-derived biochar produced by the proposed system would be more suitable for use as a soil amendment rather than solid biofuel.

3.7. Future works

This study showed a possible application of the proposed method for manure management. However, further research is necessary before applying this system on site. First, the ranges of operating parameters for inducing spontaneous self-heating should be determined. The proposed system involves several parameters that should be fully characterized,
such as pre-heating temperature, pressure, and ventilation rate. Particularly, the pre-heating temperature and pressure could substantially affect the self-heating of the feedstock and might pose a trade-off relationship (e.g., elevating the pressure lowers the pre-heating temperature whereas decreasing the pressure increases the pre-heating temperature). Elucidating the relationship between the operating parameters would also be helpful for optimizing the process.

Second, we should evaluate the overall energy balance, economic perspectives, and environmental impact of the system. The primary concern raised by the proposed system is the necessity for preparing superheated steam drying would reduce the risks of eutrophication, which has several problems when treating high-moisture biomass. Furthermore, it is reported that rapid drying of manure using superheated steam drying would reduce the risks of eutrophication and global warming compared to direct field application (Hanifzadeh et al., 2017). The present report suggests that the proposed system, in which manure is converted into dried biochar, would also be an environmentally friendly alternative.

Finally, we should analyze the characteristics of biochar produced for potential application as a soil amendment or bulking agent for composting. As described in the Introduction, biochar is believed to exhibit positive effects on plant growth and water management. Liang et al. (2006) reported that biochar enhances retention of nutrients in soils owing to its unique properties, such as a greater surface area, greater negative surface charge, and greater charge density, and it is suggested that manure-derived biochar would also exhibit these properties. Another potential use of manure-derived biochar is adding it as raw manure as a bulking agent for composting processes. Sanchez-Monedero et al. (2018) reviewed the benefits of the use of biochar in composting from the viewpoint of process performance, compost microbiology, organic matter degradation and humification, reduction of nitrogen losses and greenhouse gas emissions, and fate of heavy metals. If manure-derived biochar also shows such potential applications, a more advanced manure management system composed of composting and the proposed torrefaction systems will be addressed. Hence, it would be worthwhile to conduct comprehensive analyses of the physicochemical properties of biochar produced in order to establish the advanced system.

4. Conclusions

We presented a novel torrefaction system for drying and valorizing livestock manure by inducing self-heating of the feedstock, with the objective of minimizing the energy required for drying and torrefaction. We found that the lower limit temperature for inducing self-heating of wet dairy cattle manure is between 85 and 90 °C at a pressure of 1.0 MPa. The HHV(db) of the solid product was lower than that of the feedstock due to the high ash content; nevertheless, the proposed system converted the manure into lignite-like material without the need for pre- or post-drying steps. These results therefore indicate that the proposed methodology is applicable to high-moisture biomasses such as manure and provide insights into approaches for overcoming practical difficulties in manure management.

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