Journal of Environmental Management 198 (2017) 308–318

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Research article

Changes imposed by pyrolysis, thermal gasification and incineration on composition and phosphorus fertilizer quality of municipal sewage sludge

Tobias Pape Thomsen [a, *], Zsuzsa Sárossy [a], Jesper Ahrenfeldt [a], Ulrik B. Henriksen [a], Flemming J. Frandsen [a], Dorette Sophie Müller-Stöver [b]

[a] Technical University of Denmark, Department of Chemical Engineering, DTU Risø Campus, Technical University of Denmark Building 313, Frederiksborgvej 399, 4000 Roskilde, Denmark

[b] University of Copenhagen, Department of Plant and Environmental Sciences, Plant and Soil Science, Thorvaldsensvej 40, Frederiksberg, Denmark

A R T I C L E I N F O

Article history:
Received 29 November 2016
Received in revised form
18 April 2017
Accepted 23 April 2017

Keywords:
Sewage sludge
Pyrolysis
Gasification
Incineration
Incubation study
Phosphorous fertilizer

A B S T R A C T

Fertilizer quality of ash and char from incineration, gasification and pyrolysis of a single municipal sewage sludge sample were investigated by comparing composition and phosphorus (P) plant availability. A process for post oxidation of gasification ash and pyrolysis char was developed and the oxidized materials were investigated as well. Sequential extraction with full elemental balances of the extracted pools as well as scanning electron microscopy with energy dispersive X-ray spectroscopy were used to investigate the mechanisms driving the observed differences in composition and P plant availability in a short-term soil incubation study. The compositional changes related mainly to differences in the proximate composition as well as to the release of especially nitrogen, sulfur, cadmium and to some extent, phosphorus (P). The cadmium load per unit of P was reduced with 75–85% in gasification processes and 10–15% in pyrolysis whereas no reduction was observed in incineration processes. The influence on other heavy metals was less pronounced. The plant availability of P in the substrates varied from almost zero to almost 100% of the plant availability of P in the untreated sludge. Post-oxidized slow pyrolysis char was found to be the substrate with the highest P fertilizer value while ash from commercial fluid bed sludge incineration had the lowest P fertilizer quality. The high P fertilizer value in the best substrate is suggested to be a function of several different mechanisms including structural surface changes and improvements in the association of P to especially magnesium, calcium and aluminum.

1. Introduction

Municipal sewage sludge (MSS) is a byproduct from municipal wastewater treatment which can be considered valuable or problematic, depending on local politics, available handling options, and the quality of the MSS (Hukari et al., 2016; Kelessidis and Stasinakis, 2012). Usually, MSS contains significant amounts of nitrogen (N), phosphorus (P), organic matter and various micro nutrients. These valuable constituents make MSS in many regards a cheap fertilizer and soil enhancer (Linderholm et al., 2012). For this reason, composting or direct application of MSS on farm soil or in landscaping has been practiced intensively in the past (Fytili and Zabaniotou, 2008).

However, MSS can also contain significant amounts of emerging organic pollutants and xenobiotics (e.g. antibiotics, fragrances, UV-filters, antiseptics, micro plastics, phthalates, hormones etc.) as well as heavy metals and pathogens (Igos et al., 2012; Krüger et al., 2014; Michael et al., 2013). In recent years, concerns related to the use of MSS on land used for food production or water procurement has increased (Fytili and Zabaniotou, 2008; Krüger et al., 2014). As a result hereof, incineration of MSS has been growing into conventional practice in many countries (Krüger et al., 2014), and several EU member countries now have harder restrictions on MSS application than the current EU-directive (Inglezakis et al., 2014; Kelessidis and Stasinakis, 2012).

The dilemma between recovery of MSS nutrients and the risks related to direct application in food production systems is further complicated by a growing political demand for increased P-recycling on the one hand, and the increased concentration of heavy

* Corresponding author.
E-mail address: ttho@kt.dtu.dk (T.P. Thomsen).

http://dx.doi.org/10.1016/j.jenvman.2017.04.072
0301-4797/

metals and loss of P plant availability often associated with incineration on the other hand (Jakobsen and Willett, 1986; Krüger et al., 2014; Ottosen et al., 2013). To meet this challenge, new ways to upgrade ash from MSS incineration or recirculate MSS-P directly are under development (Atienza-Martínez et al., 2014; Parés Viader et al., 2015; Vogel et al., 2013; Xu et al., 2012). To increase society's benefit from thermal MSS management, optimized systems for simultaneous energy utilization and safe recycling of nutrients are required. This study therefore aims towards identifying relevant differences and similarities between various thermal MSS conversion processes, thereby adding knowledge that is required for such an optimization process.

MSS can be thermally converted in processes involving pyrolysis, thermal gasification, incineration and various hydrothermal processes as well as combinations hereof (Mulchandani and Westerhoff, 2016; Nakakubo et al., 2012; Qian et al., 2016; Samolada and Zabaniotou, 2014). In the present study, the focus is on pyrolysis, thermal gasification and incineration of dewatered or dry MSS.

A Cross Platform Sludge Experiment (CPSE) has been designed and executed in collaboration between two Danish universities and four Danish companies. The purpose of the CPSE study was to compare key fertilizer characteristics of ashes and chars produced by thermal conversion of sub-samples from a single large MSS sample on multiple thermal platforms and determine how the plant design and operation parameters affect these properties. One of the main focal points was to characterize and analyze changes in P chemistry induced by the thermal conversion and relate these to changes in the P-fertilizer quality of the ash or char. Furthermore, the study aimed at acquiring new knowledge about the behavior of selected heavy metals during thermal conversion of MSS. To the best of our knowledge, the study is the first of its kind, and the proposed method and results are expected to increase the odds of developing more optimal thermal MSS management platforms.

2. Methods

2.1. The MSS sample

MSS from the municipal wastewater treatment plant (WWTP) Bjergmarken Renseanlæg in Roskilde, Denmark, was used as fuel for all experiments. The WWTP is a Mechanical-Biological (active sludge loop)-Nitrification-Denitrification-Chemical cleaning facility dimensioned for 125.000 person equivalents (PE), and usually treating wastewater corresponding to 92.000 PE. Iron chloride sulfate ($ClFeO_4S$) is used for chemical P removal and added before the active sludge cycle, while aluminum chloride ($AlCl_3$) is added in the clarifiers and used mainly to precipitate floating sludge and prevent filamentous bacteria in the cold season. All sludge goes through the active sludge cycle before it is digested anaerobically for three weeks in a thermophilic process. After digestion, the sludge is mechanically dewatered and the majority of it is dried. Sludge can thus be produced as de-watered MSS or dry MSS (in granules or pellets). The drying is conducted in a BioCon drying and granulating unit (Krüger A/S, Denmark) using hot air at temperatures ranging from 100 to 175 °C (Krüger, 2009). The complete MSS sample used for the CPSE study (28 ton mixed sludge fractions containing a total of 9.9 ton dry matter) was produced during 6 consecutive days in March 2015.

2.2. The thermal conversion processes

The thermal conversion processes of the CPSE study include 2 incineration processes, 1 pyrolysis process and 2 gasification processes. All ashes, chars and MSS samples that were collected in the study are collectively referred to as the CPSE substrates. An overview is provided in Table 1. Sample reproducibility decreases with increasing plant scale due to potential pollution from imperfectly clean equipment as well as increased influence from process parameter variations. To mitigate these influences, fuel and ash samples were increased beyond proportionality in larger scale processes.

2.2.1. Fluid-bed incineration at 850 °C

The experiment was conducted at Spildevandscenter Avedøre, Denmark in March 2015, in a mono-incineration process on a fluid-bed oven, with a maximum capacity around 6.5 tons of de-watered MSS per hour (at 77% moisture). Pure quartz sand without additives is used as bed material. Pre-heated air is used for fluidization of the bed and char oxidation (primary air) and gas combustion in the free board (secondary air). Total system Air Equivalence Ratio (AER) is slightly above 1. The incineration occurs at bed temperatures around 840–850 °C and freeboard temperatures around 890 °C. The average particle retention time in the oven is around 5 s (Prisum, 1999). Ash particles are captured and cooled in an electrostatic filter (98 wt% of ash removed at 180–220 °C) and a bag house filter (2% of ash removed at 160 °C). The two ash fractions are transported to a storage silo and mixed. Three ash sub-samples of around 200 kg each were collected from the ash silo.

2.2.2. Fixed bed incineration at 750 °C and 850 °C

The experiment was conducted in the laboratories of the Biomass Gasification Group (BGG) at DTU, Risø Campus near Roskilde, Denmark, in April and May 2015. Samples were pre-dried for 24 h in hot air at 104 °C. Two batches with around 0.5 kg dry MSS distributed in multiple thin layers of 1–2 cm were incinerated in an electrically heated stainless steel reactor of 4 L, supplied with 25 L air per minute. Maximum temperatures were 750 and 850 °C, maintained for 30 min, with heating and cooling rates of 10 °C/min. Around 200 g of ash was produced at each temperature.

2.2.3. Two-Stage down draft gasification

The experiment was carried out in April and May 2015 at BGG, Risø DTU, converting MSS pellets in a pilot scale TwoStage downdraft gasifier with a thermal capacity of 50 kW. The plant structure follow the VIKING gasifier design which has been described several times in published literature (Ahrenfeldt et al., 2013a, 2006; Henriksen et al., 2006). Main differences relate to scale and the absence of internal heat integration in the 50 kW unit. MSS gasification in the 50 kW unit was conducted with a regulation strategy to avoid maximum temperatures above 1000 °C which is not usually applied when gasifying wood chips in the VIKING gasifier. The process uses air (AER around 0.4 during MSS experiment) and steam (around 0.25 kg/kg MSS during MSS experiment). The high-end temperature in the char bed was up to 850 °C during the CPSE experiment. Around 20 kg of ashes were collected for analysis.

2.2.4. Low Temperature Circulating Fluidized Bed gasification

This experiment was carried out in April 2015 at BGG, Risø DTU, converting MSS granules on a pilot-scale Low Temperature Circulating Fluidized Bed gasifier (LT-CFB gasifier) (Ahrenfeldt et al., 2013b; Narayan et al., 2016; Nielsen, 2007; Stoholm et al., 2007; Thomsen et al., 2015), with a thermal capacity of 100 kW. Quartz sand without additives was used as bed material (DanSand.dk, 2013). Temperatures during operation varied between 630 and 680 °C in the pyrolysis reactor and 700 and 730 °C in the char conversion reactor. Air and water was supplied for char conversion and fluidization of the char reactor and a small amount of air was supplied for fluidization of the pyrolysis reactor. During operation, the average A for the whole system was around 0.3. Ash for the