Waste Management xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Waste Management

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

Characterisation of sludge for pyrolysis conversion process based on biomass composition analysis and simulation of pyrolytic properties

Wei Ping Chan [a,b,*], Jing-Yuan Wang [a]

[a] School of Civil and Environmental Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore
[b] Residues and Resource Reclamation Centre, Nanyang Environment and Water Research Institute, Nanyang Technological University, 1 Cleantech Loop, CleanTechOne, Singapore 637141, Singapore

ARTICLE INFO

Article history:
Received 27 April 2017
Revised 6 November 2017
Accepted 12 November 2017
Available online xxxx

Keywords:
Sludge
Pyrolysis
Biomass composition
Model compounds
Simulation

ABSTRACT

Pyrolytic behaviour of sludge is highly complex and obscure because of its heterogeneous and diverse composition. Therefore, an analytical procedure is proposed to categorise and quantify the main constituents in sludge. In addition, a simulation study of sludge characteristics is carried out to complement the composition analysis and to improve our understanding on the relationship between composition of sludge and its corresponding properties. Different types of sludge samples were collected at different treatment stages from four Water Reclamation Plants in Singapore in two separate batches. Model compounds are selected to represent components identified and are used in simulation of pyrolytic properties of sludge. Constituents of sludge are adequately categorised, quantified and characterised in this study. Qualitative similarities and quantitative variations on characteristics of different sludge samples were identified. Comparison among the samples collected with the simulation provided insights on how differences in organic composition of sludge affected its properties.

1. Introduction

Sewage sludge is a complex waste mixture generated in wastewater treatment facilities as a by-product. Main constituents in sludge are bacterial components such as nucleic acids, lipids, protein and carbohydrates, the corresponding decay products, undigested lignocellulosic materials, coagulation-flocculation aids added and inorganic content (Manara and Zabaniotou, 2012). In addition to the complex nature, composition and properties of sludge were also found to be varying for samples collected at various stages of treatment from multiple different plants (Chan and Wang, 2016a,b). Complexity and heterogeneity of sludge cause significant difficulties in understanding the pyrolysis pathways since multiple components react concurrently and/or consecutively (Bengoa et al., 2011; Thipkhunthod et al., 2006). The various organic sludge components have different energy content, reactivity, degradation behaviours and products released during the conversion due to variations in molecular structures, bond energy levels and physical structures of char formed (Channiwala and Parikh, 2002; Lv et al., 2010). Existing research classifies sewage sludge into three main fractions according to their corresponding pyrolytic degradation temperature regions. These regions have previously been identified as i) degradation of biodegradable materials at 200–300 °C, ii) degradation of microorganisms at 300–400 °C, and iii) degradation of non-biodegradable polymers at 400–600 °C (Conesa et al., 1997; Font et al., 2005). However, thermal stability of sludge may not correlate directly to the degree of biodegradability, and in previous studies a high thermal stability was observed for biodegradable materials such as protein and lipids which thermally decompose at 300–400 °C (Kristensen, 1990; Thipkhunthod et al., 2007). Another study on sludge pyrolysis kinetics has showed that high values of reaction order in the three suggested fractions (biodegradable materials, microorganisms and non-biodegradable polymers) indicating simultaneous degradation of multiple compounds (Font et al., 2005). In addition, fractional decomposition analysis based on comparisons to lignocellulosic biomass components further showed that sludge can be more complex than most biomass and degrade differently in pyrolysis (Thipkhunthod et al., 2007). These findings suggest that the main components of sludge and corresponding characteristics related to thermochemical conversion processes should be analysed and quantified to facilitate new developments within pyrolysis and gasification of sewage sludge.

This idea is supported by thermal degradation studies of individual components in biomass. Reactions between protein

* Corresponding author at: School of Civil and Environmental Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore.

E-mail address: chan0671@e.ntu.edu.sg (W.P. Chan).

https://doi.org/10.1016/j.wasman.2017.11.026
0956-053X/

Nomenclature

List of symbols and abbreviations

AD	anaerobic digestion
ADR	acid digested residues
AHR	alkaline hydrolysed residues
Ash_{950}	ash residues remained after combustion at 950 °C
$CHNSO_{Inorganic}$	CHNSO content of Ash_{550}
$CHNSO_{Organic}$	CHNSO content of organic matters in sludge
$CHNSO_{Total}$	total CHNSO content in sludge
C_p	heat capacity at constant pressure
db	dry basis
ε_{Abs}	absolute error
ε_{Bias}	Bias error
EER	ethanol extracted residues
EFR	extractives free residues
Ex-EtOH	ethanol extractives
Ex-H_2O	water extractives
FR	fixed residues
icf	total inorganic content free basis
IM	inorganic matters
OOM	other organic matters
SD	standard deviations
TI	total inorganic content
WRP	water reclamation plant
wt%	weight percentage (weight %)
U-R	raw sludge from Ulu Pandan WRP (Batch 1)
U-D	dewatered sludge from Ulu Pandan WRP (Batch 1)
C-P	primary sludge from Changi WRP (Batch 1)
C-S	secondary sludge from Changi WRP (Batch 1)
C-Y	dried sludge from Changi WRP (Batch 1)
J-R	raw sludge from Jurong WRP
J-D	dewatered sludge from Jurong WRP
K-R	raw sludge from Kranji WRP
K-D	dewatered sludge from Kranji WRP
Us-R	raw sludge from Ulu Pandan WRP (Batch 2)
Us-D	dewatered sludge from Ulu Pandan WRP (Batch 2)
Cs-P	primary sludge from Changi WRP (Batch 2)
Cs-S	secondary sludge from Changi WRP (Batch 2)
Cs-Y	dried sludge from Changi WRP (Batch 2)

and lignin compounds with oxygen were observed at higher temperature compared to the oxidation of carbohydrates (Francisca Gómez-Rico et al., 2005; Kristensen, 1990). During pyrolysis, cellulose and hemicellulose decomposed in overlapping temperature regions at 300–350 °C and at 250–320 °C respectively while lignin decomposed in a wide temperature region from 150 °C to 900 °C (Biagini et al., 2006; Orfão et al., 1999; Thipkhunthod et al., 2006). In addition, hemicellulose produced higher yield of CO_2, cellulose produced more CO while lignin produced more H_2 and CH_4 when pyrolyzed (Yang et al., 2007). Another gasification study showed that the composition of syngas (H_2, CO, CO_2 and CH_4) from different types of woody biomass were correlated to their respective content of cellulose, hemicellulose and lignin (Hanaoka et al., 2005). However, only limited literature is available regarding the relationship between the components in sludge with its corresponding pyrolytic properties. In addition, the existing studies extensively focus on anaerobic digested sludge (Fonts et al., 2012; Thipkhunthod et al., 2007).

Therefore, a comparison study of sludge composition was carried out for sludge generated at various stages of wastewater treatment processes from different plants since characteristics and composition of sludge varied significantly according to differences in sources of wastewater and treatment processes applied (Jimenez et al., 2013; Ruggieri et al., 2008; Vriens et al., 1989). Biomass composition analysis was performed to determine the distribution of organic components in sludge. Analytical procedure proposed in this study was established with reference to the suggested methods found in published literature and standards (Ruiz et al., 2005; Sluiter et al., 2010; Sun et al., 2004). This procedure focused on quantification of main organic components such as lipids, protein, sugars, polysaccharides, hemicellulose, cellulose, and lignin. Simulation study was conducted for pyrolytic properties of sludge which include heat capacity, heating values, heat of pyrolysis, distribution of volatile matters and char solids, elemental content. Heat capacity and heat of pyrolysis can be used to calculate the energy requirement for heating the feedstock from initial to operating temperature and pyrolytic reactions respectively while heating value is used for energy audit and modelling in thermochemical conversion processes (Dogru et al., 2002). Volatile matters, char solids and elemental content are used to estimate the products distribution and yield during pyrolysis. Model compounds were selected with reference to the main compounds found in sludge (Fytili and Zabaniotou, 2008; Jardé et al., 2005; Manara and Zabaniotou, 2012; Réveillé et al., 2003; Siddiquee and Rohani, 2011; Sud et al., 2007). Superposition principle (direct summative calculation) was applied since thermochemical characteristics for biomass materials and wastes could be generally estimated as summation of individual components in the mixture (Biagini et al., 2006; Heikkinen et al., 2004; Orfão et al., 1999). Interaction and synergism between these constituents can alter the properties of sludge. However, these effects were hypothesized as secondary phenomenon and were difficult to be quantified before contributions of individual components were clearly determined. Therefore, no quantification of interaction effects was attempted in this study. Characteristics of sludge were simulated based on properties of model compounds and with reference to the constituents of sludge. Characteristics of individual components and their impacts on properties of sludge were then estimated based on the results of simulation study.

2. Material and methods

2.1. Sludge samples collection and pre-treatment

There are four existing Water Reclamation Plants (WRP) in Singapore namely Ulu Pandan (U), Changi (C), Jurong (J) and Kranji (K). Residential and industrial (after treated on-site) wastewater are discharged into sewer system and directed to these four plants. Five different types of sludge were collected namely primary (P), secondary (S), raw (R), dewatered (D) and dried sludge (Y). P and S sludge samples were collected from primary (coagulation, flocculation, sedimentation of sludge and removal of floating grease from wastewater) and secondary (activated sludge process) treatment respectively. R sludge was the mixture of P and S before transferred to anaerobic digestion (AD). P:S mixing ratio varies based on daily generation rates of primary and secondary sludge, generally at around 1.4–1.6:1.0. D and Y sludge samples were mechanically dewatered or thermally dried respectively, after AD digestion. 25 L of liquid samples (P, S and R) and 20 kg of solid samples (D and Y) were collected respectively. First batch of samples was collected in Year 2012. Additional second batch of sludge samples were col-