ARTICLE IN PRESS

Journal of Analytical and Applied Pyrolysis xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

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

Formation of synthetic sludge as a representative tool for thermochemical conversion modelling and performance analysis of sewage sludge – Based on a TG-FTIR study

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

Keywords:
Composition
Model compounds
Pyrolysis
Synthetic sludge
Kinetics

ABSTRACT

Feasibility of thermochemical conversion processes to convert sewage sludge into valuable products such as pyrolytic oil, synthetic gases and biochar is attracting great research interests. However, uncertainty in kinetics analysis and conversion modelling of sludge is considered as a significant barrier for accurate determination and understanding of its conversion pathways, kinetic parameters, and process optimisation. This is caused by the heterogeneity and complexity in composition of sludge since multiple thermal degradation reactions of different components occurred concurrently. Therefore synthetic sludge study is carried out to establish a component-based methodology to produce a representative tool for sludge conversion modelling and to address these issues. Synthetic sludge is formed based on an analytical survey on sludge samples collected from Water Reclamation Plants (WRPs) in Singapore and selective screening of model compounds. Dried sludge (CsY) collected from Changi Water Reclamation Plant (WRP) is used as a reference waste sample in this study. Thermochemical properties, multiple heating rates thermogravimetric analysis (TG-DTG), kinetics study, products evolution analysis, Fourier-Transform Infrared Spectroscopy (FTIR) spectra obtained from synthetic sludge and collected real sludge samples were analysed and compared. Acceptable representation with improved consistency was achieved with discrepancy identified for further improvement on composition analysis and model compounds selection. With this modifiable tool, synthetic sludge of controllable composition could then be applied in complex thermochemical process analysis as a representative compound to improve consistency of the results. Composition of sludge could also be manipulated as a control parameter to develop study on impacts of feedstock properties to the performance and optimisation of thermochemical conversion processes.

1. Introduction

Rising demand of wastewater treatment and water reclamation causes increasing concerns on management of sewage sludge as a by-product generated by these treatment facilities. Global sludge production continuously increases because of population growth, industrialisation and urbanisation with approximately 20 million tons of dry matter is produced annually [1]. Sludge is considered as a complex waste mixture with heterogeneous composition. Different sources of wastewater and application of varying treatment technologies resulted in significant variations on characteristics of sludge produced [2,3]. Significant amount of heavy metals, toxic organic compounds, ash residues, high moisture contents, presence of nitrogen- and sulphur-containing compounds in sludge caused the handling of sludge regarded as a challenging issue [4–6]. No general consensus is achieved on the most suitable method for sludge treatment and final disposal but thermochemical conversion processes such as pyrolysis, gasification and incineration were considered as potential solutions in near future [3,7]. Compared to heat recovery by incineration plants, advanced thermochemical conversion processes included pyrolysis, gasification and hydrothermal are capable to convert solid wastes into valuable products. Therefore great research interests are focusing on feasibility of thermochemical conversion processes to convert municipal solid waste and sewage sludge into oil through pyrolysis, into synthetic gas

Abbreviations: WRP, Water Reclamation Plant; CsY, dried sludge from Changi WRP; EER, ethanol extracted residue; EFR, extractives free residue; EE, ethanol extractives; WE, water extractives; AHR, alkaline hydrolysed residue; ADR, acid digested residue; OOM, other organic matters; db, dry basis; icf, total inorganic contents free basis; wt%, weight%

* Corresponding author at: Residues and Resource Reclamation Centre, Nanyang Environment and Water Research Institute, Nanyang Technological University, 1 Cleantech Loop, CleanTechOne, Singapore 637141, Singapore.

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

https://doi.org/10.1016/j.jaap.2018.04.015
Received 22 December 2017; Received in revised form 25 March 2018; Accepted 22 April 2018

through gasification, and into biochar through hydrothermal processes [3,8,9]. Reaction mechanisms, kinetics modelling, and performance analysis of thermally induced degradations or pyrolysis reactions are further identified as important fields of research. This is because thermal degradations are considered as primary reactions generally occurred in all thermochemical conversion processes therefore important to feedstock characterisation, reactor design and process modelling [2,10].

Thermal degradation behaviour of sludge is found to be distinctive and complex as compared to other traditional feedstock such as coal and lignocellulosic biomass [6,9,11]. Complexity in sludge composition causes significant difficulties on understanding conversion pathways since different thermal degradation reactions occurred concurrently and consecutively [12]. Uncertainty in kinetics analysis and modelling caused by heterogeneity and complexity of sludge is also an important barrier for accurate determination of kinetic parameters, models development and process optimisation [10,13–15]. Fundamental study on sludge as a potential feedstock for advanced thermochemical conversion processes is therefore necessary. However, only limited number of studies were carried out on the impacts of sludge composition to the performance of thermochemical processes as existing research focused extensively on the impacts of operating conditions such as temperature, pressure, heating rate and other engineering parameters [7,16–19]. Recently, comprehensive characterisation and comparison study of sludge was carried out [6,11,20]. These results indicated the presence of comparable components among sludge residues generated by all four currently operating Water Reclamation Plants (WRPs) in Singapore. Analytical procedure proposed for sludge biomass composition analysis suggested the potential of separating organic matters in sludge into different categories [20]. Impacts of composition on thermochemical properties and yield distributions during thermal degradation identified in previous studies further revealed the feasibility of modelling for thermochemical processes through components analysis [20–22].

Hence synthetic sludge study is carried out to address research issues of sludge thermochemical conversion on uncertainty in kinetics analysis and modelling caused by heterogeneity of sludge. In addition, impacts of sludge composition on thermal degradation behaviours and products evolution can also be further explored by using the of synthetic sludge formed. Sludge samples were collected from WRPs in Singapore [6,11]. Model compounds selection was carried out with reference to sludge composition analysis and characterisation study found in published literature [20,23–29]. TG-DTG profiles were used for synthetic sludge simulation by considering superposition principle suggested for biomass materials and solid wastes [30–32]. Synthetic sludge was formed based on the data from biomass composition analysis and by using dried sludge (CsY) collected from Changi WRP as a reference real waste sample. Model compounds selected were physically mixed to form the organic matters in synthetic sludge while ash residues of CsY (collected after combustion at 550 °C) were used to form the inorganic substances in synthetic sludge. Thermochemical characteristics, Fourier-Transform Infrared Spectroscopy (FTIR) spectra analysis, multiple heating rates TG-DTG, kinetics study and products evolution analysis based on TG-FTIR of synthetic sludge and CsY were analysed and compared. Results showed adequate representation of real waste sludge sample with the synthetic sludge formed. By using the proposed methodology, sample with controlled composition could be potentially prepared and applied in complex thermochemical process analysis and modelling with improved consistency. Composition of sludge could be further manipulated as one of the control parameters to develop comprehensive study on impacts of feedstock characteristics on performance parameters for thermochemical conversion processes.

2. Material and methods

2.1. Sludge samples collection and model compounds preparation

Details of sludge samples collection, categorisation, characterisation, biomass composition analytical procedure and model compounds selection with at least triplicated results were described in previous studies [6,11,20]. This detailed analytical survey was carried out based on five different types of sludge collected from four operating WRPs in Singapore which showed that comparable composition of sludge can be observed for all the 14 samples (primary, secondary, raw, dewatered and dried sludge) collected before and after anaerobic digestion. Furthermore, component-based simulation for thermochemical properties of sludge agreed well with the experimentally measured data for these samples suggested that this methodology can be generally applied for different types of sludge. To further demonstrate the potential of producing a representative tool for wider application of these findings, dried sludge, CsY (collected at thermal dryer after treated in anaerobic digestion process) from Changi WRP is selectively focused in this study. A sequential isolating procedure by applying ethanol & water extractions, nitrogen content quantification, alkaline hydrolysis, acid digestion and estimation by difference was developed to categorise and quantify components in sludge [20]. Isolated components from sludge were categorised as ethanol extracted residue (EER), extractives free residue (EFR), ethanol extractives (EE), water extractives (WE), alkaline hydrolysed residue (AHR), acid digested residue (ADR) and other organic matters (OOM) according to biomass composition analysis. Before analysis, all sludge samples and solid residues isolated (EER, EFR, AHR, and ADR) were dried at 105 °C for 24 h. Extractives (EE and WE) were placed on alumina crucible and dried at 60 °C until constant weight measured. Model compounds selected were whey isolates, asolectin, cholesterol, glyceryl tripalmitate, glycogen, starch, sucrose, cellulose, xylan and lignin. Whey Isolates (Optimum Nutrition, ON) was obtained from local distributor and all other compounds were purchased from Sigma-Aldrich. Model compounds and synthetic sludge were dried in oven at 60 °C for 24 h and used for analysis in the form as received.

2.2. Thermal degradation behaviours and products evolution analysis

Thermal degradation behaviours and products evolution analysis was carried out by using STA 449 Jupiter® (Netszch) connected with FTIR System (Bruker). Simultaneous Thermal Analyser (STA) was used to carry out thermogravimetric analysis (TG-DTG) and differential scanning calorimetry (DSC) simultaneously. Details of equipment settings, experimental procedure, operating conditions and data analysis methods were described in previous study [11,20]. 9.00 ± 0.50 mg of dried sample was placed in alumina crucible and heated using constant heating rate from 100 °C to 950 °C. Continuous nitrogen flow at 60 ml/min was supplied to provide inert environment inside heating chamber and to transfer volatile compounds evolved from thermal degradation for FTIR detection. Wavenumber of functional groups and corresponding suggested compounds for TG-FTIR gas phase spectra were determined based on library database and published literatures [21,31,33,34]. Multiple heating rates TG-DTG was carried out at 5, 10, 15, 20 and 25 K/min. Mean TG-DTG profiles of synthetic sludge and CsY were calculated based on the five sets of data collected respectively. TG-DTG data profiles and thermochemical properties of model compounds and isolated sludge components were measured and used for simulation by superposition principle, where $W_sP_s = \sum_{i=1}^{n} W_iP_i$ where W_s and W_i were wt% on db while P_s and P_i were mean for thermochemical parameters for sludge and individual components respectively.