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Title: Characterization of sludge for pyrolysis conversion process based on biomass composition analysis and simulation of pyrolytic properties.

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Abstract:

Pyrolytic behaviour of sludge is highly complex and obscure because of its heterogeneous and diverse composition. Therefore, an analytical procedure is proposed to categorize 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 categorized, quantified and characterized 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.

Keywords: Sludge; Pyrolysis; Biomass composition; Model compounds; Simulation

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 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 CO₂, cellulose produced more CO while lignin produced more H₂ and CH₄ when pyrolyzed (Yang et al., 2007). Another gasification study showed that the composition of syngas (H₂, CO, CO₂ and CH₄) 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. 25L of liquid samples (P, S and R) and 20kg 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 collected from Ulu Pandan (Us-R and Us-D) and Changi (Cs-P, Cs-S, and Cs-Y) WRPs in Year 2013 for comparison. In total, 14 different sludge samples were collected. Samples were dewatered by centrifuge and dried in oven at 105°C for 24 hours based on ASTM E871. Dried samples were milled to reduce the particle size to smaller than 1.00 mm (Sluiter et al., 2010).

2.2. Categorisation and quantification procedure of biomass composition in sludge

Biomass composition of sludge was divided into six categories, which were ethanol extractives (Ex-EtOH), water extractives (Ex-H₂O), protein, alkaline hydrolysed residues (AHR), acid digested residues (ADR) and other organic matters (OOM). Flowchart for extraction and isolation procedures is illustrated in Figure 1. Ethanol extraction was carried out with reference to ASTM E1690 to quantify hydrophobic extractives and to improve the efficiency of subsequent water extraction by removing hydrophobic materials and disrupting the membrane structures of microorganism. (Thipkhunthod et al., 2007). 20.00 ± 1.00g of

sludge was placed in cellulose thimble for Soxhlet extraction by using ethanol (ACS Grade, 95% purity) for 24 hours. Solid residue was dried at 60°C for 24 hours. Weight loss after ethanol extraction was recorded as Ex-EtOH. Water extraction was carried out subsequently on ethanol-extracted residue (EER) to remove hydrophilic materials. 20.00 ±1.00g of EER was extracted using deionized water for 6 hours (Ruiz et al., 2005). Solid residue was dried at 60°C for 24 hours and weight loss after water extraction was recorded as Ex-H₂O. Solid residue after ethanol and water extraction was classified as extractives free residue (EFR). Solubility of protein in ethanol and water was demonstrated to be very low after protein polymers unfolded (Pace et al., 2004). Therefore, protein content was estimated by determination of nitrogen content of EFR and then multiplied by a factor of 6.25 (Jimenez et al., 2013; Ruggieri et al., 2008; Simonne et al., 1997). Alkaline hydrolysis and acid digestion were carried out separately on EFR. Sequential treatment of 10.00 ±0.50g EFR was carried out in 300 ml of 0.5M NaOH followed by 0.5%, 1.0%, 1.5%, 2.0%, and 3.0% of H₂O₂ in 200 ml 0.5M NaOH, and 200 ml of 2M NaOH at 55°C for 2 hours at each step to determine AHR which represented components in sludge similar to cellulose (Sun et al., 2004). Soluble extractive was removed by centrifugation and washing after each step of treatment. Solid residue was retained and dried in oven at 105°C. Weight of final residue was recorded as AHR after gravimetric correction of ash residues (combustion of sample at 950°C for 3 hours) and nitrogenous content (total nitrogen determination and calculated with multiplication factor of 6.25). Acid digestion of EFR was carried out according to ASTM 1721 to determine ADR, which represented lignin, aromatics compounds and humic substances in sludge. OOM was calculated by difference after considered the above five categories of organic composition and total inorganic content (TI) in sludge. OOM represented residual organics that potentially consisted of diverse groups of compounds. After considered the main components (lipids, sugars, protein, cellulose, lignin or humic

compounds) in five sludge constituents (Ex-EtOH, Ex-H₂O, Protein, AHR and ADR), polysaccharides and hemicelluloses were suggested as the main components in OOM.

2.3. Selection of model compounds

Model compounds were selected based on literature and hypothetical consideration. The purpose of this selection is to demonstrate the possibility of simulating sludge properties with simple model compounds. For Ex-EtOH, compounds were selected from three most common lipids groups found in wastewater, microorganisms and sludge. These compounds are glycerol lipids, sterol lipids and phospholipids (Jardé et al., 2005; Réveillé et al., 2003; Siddiquee and Rohani, 2011; Sud et al., 2007). Asolectin, cholesterol and glyceryl tri-palmitate were selected to represent phospholipids, sterol lipids and glycerol lipids in Ex-EtOH of sludge respectively. For Ex-H₂O, sucrose was selected to represent easily soluble hydrophilic materials. Composition of Ex-H₂O can be highly complex. Organic alcohols, acids, amines and other intracellular substances were found in water extractives (Baham and Sposito, 1983; Chen et al., 2007; Chen et al., 2010). Sucrose was selected for its simplicity and dominant appearance in hydrophilic extractives of biomass (Chen et al., 2007; Chen et al., 2010). Protein existed as heterogeneous and complex mixture in sludge. Whey Isolates (Optimum Nutrition, ON) with protein content of 81.48wt% was selected as a mimic to represent protein mixture in sludge (Jimenez et al., 2013). Cellulose and lignin isolated from lignocellulosic biomass were selected as model compounds for AHR and ADR based on previous studies (Sluiter et al., 2010; Sun et al., 2004; Thipkhunthod et al., 2007). Three types of storage or structural polysaccharides (starch, glycogen and xylan) were used to represent OOM. Whey Isolates was obtained from local distributor and all other model compounds were purchased from Sigma-Aldrich.

2.4. Characterisation of sludge components and model compounds

Details of characterisation methods used in this study could be found in previous studies (Chan and Wang, 2016a, b). FTIR spectra of sludge samples and model compounds were collected by using Attenuated Total Reflection (ATR) with diamond crystal of FTIR System (Bruker) and were analysed according to absorbance bands recorded in library database and previous publications (Edalatmanesh et al., 2010; Réveillé et al., 2003; Sluiter et al., 2010; Smidt et al., 2011; Smidt and Meissl, 2007; Smith, 1998). Heating values (HHV) was determined by Calorific Bomb (IKA C2000) according to ASTM E711. HHV of extractives were calculated by difference between HHV of sludge and extracted residues (EER, EFR) and based on weight% of extractives. Elemental content (CHNSO) of sample was measured by Vario EL Cube (Elementar). Elemental content of Ex-EtOH and Ex-H₂O were estimated qualitatively as supplementary data by comparing elemental composition measured for sludge with corresponding solvent extracted residues. Comparison made between ash residues of solvent extracted residues and sludge samples suggested no significant amount of inorganics dissolved into extractives. Mechanical dewatering of wet sludge through either filter-press or centrifugation process could have removed water-soluble salts and inorganic compounds from sludge into reject water and recycled back into the plants. These observations were similar to previous extraction study (Boocock et al., 1992). Volatile matter (VM), fixed carbon (FC = 100% - VM - Ash), fixed residues (FR = 100% - VM - IM) and heat of pyrolysis ($\Delta H_{\text{pyrolysis}}$) were determined by thermogravimetric analysis with differential scanning calorimetry (TGA-DSC) system of STA 449 Jupiter[®] (Netszch). Ash content was measured by combustion of sludge at 950°C while inorganic matter (IM) was estimated by IM = 100% - CHNSO content. Heat capacity (C_p) of model compounds and sludge components were estimated based on reference compounds in literature (Boerio-Goates, 1991; Dupont et al., 2014; Kim and Parker, 2008; Mark, 2007; Morad et al., 2000). Mean values for properties of model compounds are showed in Table 1.

2.5. Simulation study of pyrolytic properties

Properties of waste mixture could be calculated based on composition of individual compounds with superposition principle (Tillman, 2012). Therefore simulation was carried out by applying $W_s P_s = \sum_{i=1}^n W_i P_i$ where W_s ($W_s = 100$ wt%) and W_i were wt% on db while P_s and P_i were mean values of the parameters for sludge and individual components respectively. Heat capacity, heating value, heat of pyrolysis, distribution of volatiles and char residues (as represented by VM/FC or VM/FR ratios) and CHNSO content of organic matters were simulated and compared to direct measurements on sludge samples. Errors of the estimated data were determined by using Bias Error $\epsilon_{\text{Bias}} = \text{Data}_{\text{measured}} - \text{Data}_{\text{calculated}}$,

Absolute Error $\epsilon_{\text{Abs}} = \sqrt{\epsilon_{\text{Bias}}^2}$ and Percentage of Error $\epsilon_{\%} = \frac{\epsilon_{\text{Abs}}}{\text{Data}_{\text{measured}}} \times 100\%$.

3. Results and Discussion

3.1. Biomass composition analysis of sludge

Results of biomass composition analysis on dry basis (db) are illustrated at Table 2. Data of total inorganic content free basis (icf) was then calculated for direct comparison among different sludge samples made on organic-only basis. Biomass composition analysis showed variations for all sludge samples according to the differences in types (P, S, R, D and Y), plants and batches. Mean weight% (icf) of sludge constituents were $5.97 \pm 2\%$ AHR, $11.27 \pm 4\%$ Ex-EtOH, $12.81 \pm 4\%$ Ex-H₂O, $17.14 \pm 7\%$ ADR, $20.83 \pm 9\%$ OOM and $31.98 \pm 6\%$ protein. Results in this study are comparable to earlier studies where about 33-50% of protein, 6-10% of lipids and 3-20% of carbohydrates or fibers were found in biological sludge samples after secondary treatment while relatively lower protein content at 18-24% and higher lipids content at 10-18% were found in primary, raw and digested sludge (Inoue et al., 1996; Jimenez et al., 2013; Manara and Zabaniotou, 2012).

Different orders of relative abundance could be observed when comparing the mean values calculated for three groups of sludge, i) all 14 sludge samples, ii) samples collected

225 before AD (R, P and S) and iii) samples collected after AD (D and Y) respectively. Protein
226 and AHR were relatively most and least abundant respectively. Weight% (icf) of Ex-EtOH
227 and OOM were significantly lower in AD digested samples. This could be caused by the
228 consumption of lipids and polysaccharides during anaerobic digestion as suggested by earlier
229 study (Li et al., 2014). These two components were higher in secondary sludge samples
230 suggested the accumulation of lipids and polysaccharides in sludge solids during activated
231 sludge process. Weight% (icf) of protein, AHR and ADR were significantly higher in sludge
232 samples collected after AD (D and Y) compared to before AD (R, P and S). This is probably
233 because non-biodegradable matters and aromatic compounds remained in sludge during AD
234 processes (Li et al., 2014). Ex-H₂O content was higher in sludge after AD probably because
235 the digestion process degraded polysaccharides into simple sugars, organic alcohols and acids
236 that could be extracted by water. For sludge samples collected from Changi WRP, primary
237 sludge (P) showed higher Ex-H₂O content while secondary sludge (S) showed higher Ex-
238 EtOH content. Dried sludge (Y) was relatively low in both extractives. Protein content was
239 found to be significantly higher in primary sludge, slightly lower in dried sludge and
240 significantly lower in secondary sludge. These observations suggested that high protein
241 content settled into primary sludge through sedimentation from wastewater influent and
242 partially digested during AD. Ex-H₂O content between two batches of Ulu Pandan raw sludge
243 (U-R and Us-R) and Ex-EtOH content between two batches of Changi primary sludge (C-P
244 and Cs-P) were varied significantly. Extractives content among two batches of Ulu Pandan
245 dewatered sludge (U-D and Us-D), Changi secondary (C-S and Cs-S) and dried sludge (C-Y
246 and Cs-Y) were more consistent. These observations suggested that raw and primary sludge
247 were affected by variation of wastewater characteristics significantly as primary sludge
248 formed from direct settling of solids and collection of floated greases in the wastewater. Raw
249 sludge formed from mixing of primary and secondary sludge and therefore affected

significantly by properties variation of wastewater. However, secondary and AD digested sludge were more consistent which suggesting potential self-regulating effect on characteristics of sludge generated during aerobic and anaerobic biodegradation processes. Lower total extractives in sludge after AD (D and Y) indicated the accumulation of inorganic content, structural biomass components recalcitrant to biodegradation and other non-biodegradable materials. The ratios of nitrogen content of EFR to sludge varied from 0.66 to 0.91 with an overall mean of 0.75 ± 0.07 . This observation agreed well with the previous estimation of only about 70-80% protein-nitrogen was found in sludge (Kristensen, 1990; Vriens et al., 1989). Therefore, estimation of sludge protein content with EFR can be considered as an alternative method. However, it is recommended to compare this method with direct quantification of amino acids in sludge in future study.

Figure 2(a) and (b) shows that HHV, LHV, and carbon content correlated positively with Ex-EtOH. These observations supported the representation of Ex-EtOH as lipids and hydrocarbons components in the sludge, which has relatively higher energy and carbon content. Ex-EtOH could be used as a potential indicator for estimation of HHV, LHV, and carbon content of sludge. Nitrogen content correlated positively with Ex-H₂O, protein and the summation of these two constituents as illustrated in Figure 2 (c). These observations suggested that Ex-H₂O and protein were main contributors to the nitrogen content in sludge. Significant amount of amines, amino acids and other nitrogen containing compounds were soluble in water as supported by FTIR analysis. Solid and liquid yields of sludge pyrolysis at 500°C correlated strongly with the content of Ex-EtOH and OOM. As Ex-EtOH and OOM content (icf) increased in the sludge samples collected, solids yields decreased and liquid yields increased as illustrated in Figure 3 (a) and (b). However, no significant correlation between Ex-EtOH and OOM with gas yields could be observed. These observations suggested that Ex-EtOH and OOM thermally degraded with higher mass loss and formed

dominantly condensable volatile compounds. These behaviours were similar to pyrolytic degradations of lipids and polysaccharides. The identified correlations suggested that physical and chemical properties of sludge could be quantified and explained by using the analytical procedure applied in this study. Further study needed to analyse and quantify the characteristics of individual category of biomass composition for better understanding on pyrolytic conversion of sludge. Furthermore, interaction effects among different components and interference of inorganic constituents in sludge may also contributed to the inconsistency of the results that required further analysis for identification and quantification.

Inorganic content is a main component in sludge that can influence its pyrolytic properties. Therefore, it is important to consider the potential of inorganic compounds in promoting char forming reactions and catalytic decompositions of organic matters in sludge (Chan and Wang, 2016a; Fonts et al., 2012). In addition, dehydration of hydrated inorganic compounds in sludge could contribute to the released of water vapour as suggested by FTIR spectra of sludge samples, char solids and ash residues at 3700 and 3620cm⁻¹ for inorganic bounded O-H groups (Anca-Couce, 2016; Conesa et al., 1998; Shen et al., 2009; Vassilev and Tascon, 2003). H₂O released from inorganic compounds and generated from dehydration of organic components during pyrolysis are commonly categorised as pyrolytic water. Earlier studies also demonstrated that most of the inorganic compounds of sludge retained in solid residues during thermochemical conversion processes (Fytili and Zabaniotou, 2008; Hernandez et al., 2011). This assumption is supported by the inorganic elements analysis of sludge in another study for these 14 sludge samples used, which demonstrated that most of the inorganic elements in these samples collected were non-volatile ash forming elements (Chan and Wang, 2016b). However, carbonates, sulphates and volatile inorganic compounds could devolatilize at elevated temperature. Therefore, CHNSO_{Inorganic} and halogens (fluoride, chloride and bromide) released at high temperature should be determined and differentiated

from the decomposition of organic constituents in sludge (Chan and Wang, 2016b). This procedure is applied in the current study to estimate CHNSO_{Organic} content. Solid residue remained after pyrolysis is commonly known as char residues and consisted of three major components, which are inorganic compounds, unreacted organic matters and char formed during pyrolytic degradation. Ash content was frequently used as an approximation to the inorganic content in sludge samples or char solids. However, ash content could overestimate the amount of inorganic compounds because of the oxidation of inorganic elements during ash forming combustion test as inorganic compounds in sludge were in leachable organic fractions which could be easily oxidised (Hernandez et al., 2011). Therefore the estimation of inorganic content in sludge was carried out by using total inorganic content (TI), which was the summation of inorganic matter (IM), halogens content and inorganic CHNSO content in sludge. IM is the estimation inorganic residue remained in the char solids after pyrolysis. Details of the mathematical expression of these parameters and related data of sludge samples used in this study were described in previous publications (Chan and Wang, 2016a, b).

3.2. Characterisation of sludge components isolated and model compounds selected

Energy content distributions and HHV results for extractives (Ex-EtOH and Ex-H₂O) were calculated from direct measurements for ethanol and water extracted residues (EER and EFR). Variations in HHV could be observed for all extractives and solvent extracted residues among different samples collected because of differences in inorganic content and composition of organic matters. With lipids as major components, Ex-EtOH was having higher mean HHV of 42.41 ± 6 MJ/kg and contributed higher proportion of energy content of $20.67 \pm 7\%$ to sludge. With carbohydrates as major component, Ex-H₂O was having lower mean HHV of 21.24 ± 5 MJ/kg and contributed lower proportion of energy content of $11.70 \pm 4\%$ to sludge. Main portion of sludge energy content at $67.63 \pm 5\%$ remained in EFR. In general, HHV results supported that the Ex-EtOH and Ex-H₂O were comparable among

different sludge samples collected and could be represented by lipids and simple carbohydrates compounds respectively. Mean elemental content (normalized molar basis) were used to form molecular formula for sludge ($C_{1.00}H_{1.8045}N_{0.1202}S_{0.0518}O_{0.5109}$), EER ($C_{1.00}H_{1.7797}N_{0.1353}S_{0.0481}O_{0.7147}$), and EFR ($C_{1.00}H_{1.8100}N_{0.1290}S_{0.0456}O_{0.6838}$). Based on the three molecular formula calculated for solids, average molecular formula for extractives can be estimated after considered the change in CHNSO content and weight% of extractives. Ex-EtOH has relatively higher H and S while lower N and O molar content. Ex-H₂O has higher N, S and O while lower H molar content. Higher H/C ratio in Ex-EtOH suggested lipids as main components while nitrogen content indicated the presence of phospholipids. Lower H/C ratio in Ex-H₂O suggested sugars as main components while high N/C ratio indicated the presence of nucleic acids, amines and nitrogenous compounds, which agreed well with FTIR spectra analysis. Sulphur containing compounds were extracted by both extractions.

Table 1 shows the results on characterisation of model compounds. VM was the main component in these compounds. Lipids released highest amount of VM during pyrolytic degradation followed by polysaccharides, protein and lignin. Variation could also be observed within lipids and polysaccharides groups. Triglycerides and cholesterol mainly consisted of C and H and released higher VM. Asolectin as a model compound for phospholipids consisted of phosphorus and relatively higher N and O content while formed more FC during pyrolysis. Starch, glycogen, and cellulose were glucose polymers but showed different characteristics during pyrolytic degradations because of their overall molecular structures. Polysaccharides with branched, heterogeneous and amorphous structure were observed to form more solid residues classified as FC such as xylan and glycogen. Main components in lignocellulosic biomass, which were xylan, cellulose and lignin, behaved distinctively in almost all aspects. $\Delta H_{\text{pyrolysis}}$ varied from endothermic to exothermic for different model compounds. Pyrolysis reactions for lipids and protein were endothermic, for

lignin was exothermic and could range from endothermic to exothermic for different types of polysaccharide. $\Delta H_{\text{pyrolysis}}$ for model compounds reduced from endothermic value to exothermic value with increasing char yield comparable to results found in previous studies of biomass (Rath et al., 2003; Yang et al., 2007). Based on the correlation ($\Delta H_{\text{pyrolysis}} = 11.15 \text{ Char}_{\text{yield}} - 773.03$, $R^2 = 0.59$) formed between $\Delta H_{\text{pyrolysis}}$ and char yield by analyzing model compounds used in this study, autothermic pyrolysis was estimated to be occurred at VM \approx 70.44%, FC \approx 29.56% and VM/FC ratio \approx 2.38. This observation could be caused by a mixed of endothermic volatile formation processes and exothermic char formation reactions during pyrolysis (Brown and Stevens, 2011). Heating values of model compounds showed significant categorical characteristics and closely related to carbon content ($\text{HHV} = 0.59 \text{ C} - 10.02$, $R^2 = 0.97$ where HHV is higher heating values in MJ/kg and C is carbon content in weight%). Lipids showed highest HHV followed by lignin, protein, and polysaccharides.

FTIR spectra of Ex-EtOH, Ex-H₂O, AHR and ADR are showed in Figure 4. In general, high similarities could be observed among different categories of biomass composition from different sludge samples. These observations suggested that components isolated from different sludge samples were comparable and having similar functional groups in the respective categories. For Ex-EtOH, broad peak at 3200cm⁻¹ indicated O-H functional groups of carboxylic acids, alcohols, sterol lipids and phospholipids. Strong and narrow peaks indicated significant amount of C-H groups, at 3048 cm⁻¹ for unsaturated hydrocarbon and aromatics while at 2926, 2854 cm⁻¹ for saturated hydrocarbon, ethers and lipids. Strong peaks at 1730 cm⁻¹ indicated C=O groups of aldehyde, ketone, carboxylic acids, esters and lipids while multiple peaks at 1461 and 1370 cm⁻¹ indicated C-H groups of saturated hydrocarbon, ethers and lipids. Multiple peaks observed and overlapped in fingerprint regions of 1300-600 cm⁻¹ therefore detailed and specific peak identifications was not applicable. However, comparison could be made to the FTIR spectra for specific compounds in the

literature and model compounds of lipids. Strong peaks at 1226, 1170, 1045 and 960 cm^{-1} indicated the presence of lipids mixture comparable to the spectra of model compounds such as glyceryl tri-palmitate, asolectin and cholesterol. For Ex- H_2O , broad peaks extended from 3400–3000 cm^{-1} indicated the O-H and N-H groups from alcohols, acids, amides and amines. Weak peaks at 2949 cm^{-1} indicated that the proportions of C-H groups were lower. Strong broad peaks at 1620 cm^{-1} indicated N-H groups of amines and nitrogenous compounds while strong peaks at 1405 cm^{-1} indicated O-H groups of alcohols and carbohydrates. Multiple peaks at 1230, 1060, and 1000 cm^{-1} indicated C-O-C groups of carbohydrates and ethers. Signature peaks of protein compounds at 1654 and 1540 cm^{-1} (Grube et al., 2006) were absent in FTIR spectra of Ex-EtOH suggested that protein remained in sludge solids while non-protein nitrogen was extracted. For Ex- H_2O , broad peaks observed at 1650 – 1540 cm^{-1} region could be caused by amines, nucleic acids, amino acids, and other nitrogenous compounds instead of protein because of the low solubility of protein in water after unfolded during extractions (Pace et al., 2004). These observations supported the hypothesis that calculations based on EFR nitrogen content could improve the estimation of protein content in the sludge by excluding non-protein nitrogen content.

For AHR, FTIR spectra analysis showed mainly O-H, C-O, C-O-C and inorganic functional groups. O-H groups could be observed at 3700 cm^{-1} for inorganic bounded hydroxyl groups and at 3300 cm^{-1} , 1415 cm^{-1} , and at 913 cm^{-1} for O-H in organic matters. C-O and C-O-C groups of glycosidic linkage could be observed at peaks of 1220, 1158, 1030 and 912 cm^{-1} . For ADR, FTIR spectra analysis showed mainly C-H, C=O, C=C and aromatic rings functional groups. C-H groups observed at 2972 cm^{-1} and 2837 cm^{-1} , C=O and C=C groups in 1700-1600 cm^{-1} region with broad peaks at 1680 cm^{-1} and 1653 cm^{-1} while aromatic rings at 1510 cm^{-1} . By comparing dried sludge from Changi WRP (Cs-Y) with the respective solid residues and extractives, no qualitative difference could be observed among EER, EFR

and sludge. However, significant differences could be observed for Ex-EtOH, Ex-H₂O, AHR and ADR when compared to sludge. These observations suggested that complex and heterogeneous sludge could be better characterised after extraction and isolation procedures.

3.3. Simulation study of pyrolytic properties

Table 3 shows heat capacity simulation, C_p . Simulated data showed that the C_p of sludge was mainly contributed by organic components. Simulation based on composition of sludge improved estimation of C_p when compared to the method and estimated value used in previous studies (Agarwal et al., 2015; Kim and Parker, 2008). Considerably overestimation could be observed as these studies assumed a high mean heat capacity at 2.00 J/g-K for organic compounds in sludge. Protein and lipids were having C_p close to the value assumed but sugars, lignin and carbohydrates which including polysaccharides, xylan and cellulose were having lower mean C_p at around 1.32J/g-K for glucose and 1.56 J/g-K for lignocellulosic biomass. Therefore, lower C_p values assigned for these biomass components reduced the overall estimation. Percentage of ϵ_{Abs} reduced from 21.04% for calculation method used in earlier studies to 11.36% in this study for the 14 sludge samples collected. Biomass composition analysis categorised organic constituents in sludge into better-defined groups of compounds. This improved the understanding and estimation of pyrolytic characteristics of sludge. Protein contributed significantly to C_p probably because of its relatively high content in sludge and high heat capacity. Ex-EtOH and OOM contributed more to samples collected before AD (R, P and S) while ADR and inorganic content contributed more to samples collected after AD (D and Y). Table 4 shows HHV simulation of sludge. In average, ϵ_{Abs} of less than 1.00MJ/kg or 4.31% could be observed. This observation indicated good estimation of heating values by applying biomass composition analysis of sludge. Bias errors randomly distributed as positive and negative values indicated low systematic errors. In average, simulated data underestimated HHV of sludge by 0.31MJ/kg or

1.78%. The overall underestimation could be explained by considering the higher mean values of HHV found for Ex-EtOH and Ex-H₂O at 42.41MJ/kg and 21.24MJ/kg as compared to model compounds for lipids and simple sugars at 35.86MJ/kg and 16.48MJ/kg respectively. HHV of sludge was mainly contributed by protein at 32.69% of total energy content. Ex-EtOH and OOM contributed significantly to HHV of sludge before AD while ADR contributed significantly to HHV of sludge after AD. Table 5 shows the results for heat of pyrolysis simulation and direct measurement by DSC for sludge. Relatively significant differences could be observed between $\Delta H_{\text{pyrolysis}}$ measured and calculated at 37.20% in average with absolute difference at 17.83J/g. Since the pyrolysis reactions of sludge were slightly endothermic and near autothermic, relative% of random errors were higher though only slight differences observed when consider the absolute values in the calculation of total energy requirement. Total energy requirement of $846 \pm 132\text{J/g}$ for sludge pyrolysis at 500°C was calculated through summation by considering both heating requirement ($\Delta Q_{\text{heating}} = C_p \Delta T$) and $\Delta H_{\text{pyrolysis}}$. Mean absolute error of simulation for $\Delta H_{\text{pyrolysis}}$ at 17.83J/g or 2.11% of the total energy requirement is acceptable. $\Delta H_{\text{pyrolysis}}$ was higher for sludge samples collected before AD because of higher organic content. Extractives and protein were contributed to the endothermic requirement of pyrolysis significantly. AHR and OOM contributed slightly because of low weight% of AHR and mixed of endothermic and exothermic reactions among model compounds used to represent OOM. ADR and lignin decomposed exothermically and reduced overall heat of pyrolysis of sludge.

Table 6 shows simulated data on distribution of volatile matters and char solids. Simulated VM/FC ratio supported the proposal in earlier studies on an alternative parameter, fixed residues (FR) to replace fixed carbon (FC) as an estimated value for char solids remained in sludge when pyrolysed at high temperature (950°C for 7 minutes) (Chan and Wang, 2016b). Good agreement was obtained when compared simulated VM/FC ratio (3.13

± 0.34) with VM/FR data (3.40 ± 0.78) from direct measurements of sludge samples. VM/FC ratios measured (6.45 ± 2.24) for sludge higher than VM/FR and simulated data because of the underestimation of FC caused by overestimation of ash content. Therefore, FR was proposed to replace FC because of overestimation of inorganic during ash residues quantification. In general, components in sludge contributed differently to the released of volatile matters and the formation of char solids. Volatiles released by all components in sludge with varying amounts while char solids mainly formed from three groups of components, which were protein, ADR and OOM. In average, these three groups represented 69.95% of organic components in sludge while accounted for 86.73% of FC formed. Ex-EtOH as simulated by using lipids model compounds decomposed mainly into volatiles and contributed less than 1.00% on FC though represented 11.27% of organic components in sludge. Since char formation could not be measured directly during thermogravimetric analysis, data from proximate analysis were generally used for kinetics equations and quantification of char formation reactions. However, characterisation study of complex waste mixture such as sludge showed that different components thermally degraded at different temperature regions therefore proximate analysis data for individual steps would be needed. Biomass composition analysis of sludge separated the sludge components into six different categories with distinct distributions of VM and FC provided important data for development of multiple step kinetics modeling study for sludge and other waste mixture.

Table 7 shows elemental content. Elemental composition showed comparable content and expected variations among sludge samples. Variations were expected because biomass composition analysis in this study focused only on main categories of biochemical components in sludge. $\text{CHNSO}_{\text{Organic}}$ data were calculated by difference using the $\text{CHNSO}_{\text{Total}}$ of sludge and $\text{CHNSO}_{\text{Inorganic}}$ of ash residues after combustion of sludge at 550°C . In general, overestimation could be observed for C and O content while

underestimation could be observed for H, N and S content. In average, C and O simulations overestimated the content by 3.88wt% or 10.54% in relative percentage and 0.72wt% or 5.01% respectively while H, N and S simulations underestimated the content by 0.15wt% or 5.11%, 0.94wt% or 16.74% and 4.23wt% or 94.72% respectively. Since estimations of H and O agreed very well with the CHNSO_{Organic} data of sludge, the overestimation of C was probably related to the underestimation of N and S containing compounds. Underestimation of N content was caused by the selection of sucrose as model compound to represent Ex-H₂O. As water extraction removed non-protein nitrogen content therefore nitrogen containing compounds such as amines, amides, nucleic acids and other intracellular substances were not accounted in this simulation study. Significant underestimation of S content was caused by absent of individual categorisation for sulphur containing compounds in sludge. Sulphur containing compounds were highly diverse and consisted of amino acids, vitamins, thiols and enzymes that could be extracted during ethanol and water extractions. Polysaccharides with sulphur and alkylbenzene sulphonate from laundry detergents could also be found in sludge. However, OOM were represented by sulphur-free carbohydrates (glycogen, starch and xylan) in current study. Therefore, further analysis should be carried out to determine the main sulphur containing compounds in sludge so that suitable model compounds could be selected and added into the category of extractives and OOM respectively.

4. Conclusions

In conclusion, constituents in sludge could be categorized and quantified by using composition analytical procedure applied in this study. Different types of sludge (P, S, R, D and Y) showed qualitative similarities based on these generalized groups (treatment stages and technology applied) and quantitative variations for samples collected from different plants (U, C, J and K). This is because sources and properties of wastewater at different WRPs will also affect the characteristics of sludge generated. Therefore, localized and

specifically targeted waste characterization is always needed to complement the generalized research for sludge. Organic composition analysis can potentially provide additional information on relationship of composition and pyrolytic properties for sludge generated from different treatment stages and plants. Characterization of components isolated showed distinctive properties when compared to the sludge samples collected as waste mixtures. Correlation analysis also identified and discussed the impacts of organic composition on properties of sludge. These results provided insights of why existing studies carried out to compare different sludge samples were facing difficulties to identify significant impacts of sludge composition on characteristics and pyrolytic degradation behaviours. In addition, simulation with model compounds could satisfactory estimate the pyrolytic characteristics of sludge. Heat capacity of sludge is estimated with improved accuracy. Other simulated characteristics including heating value, heat of pyrolysis, distribution of volatiles and char, and elemental content showed good agreements with the measured data of 14 different samples. Combination of the data from sludge composition analysis and simulation of characteristics also provided insights on the contributions and specific characteristics of different components in sludge. These insights were important for understanding pyrolytic degradation behaviours of sludge and crucial for mechanisms determination and models development.

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List of symbols and abbreviations

AD	Anaerobic digestion
ADR	Acid digested residues
AHR	Alkaline hydrolysed residues

525	Ash ₉₅₀	Ash residues remained after combustion at 950°C
526	CHNSO _{Inorganic}	CHNSO content of Ash ₅₅₀
527	CHNSO _{Organic}	CHNSO content of organic matters in sludge
528	CHNSO _{Total}	Total CHNSO content in sludge
529	C _p	Heat capacity at constant pressure
530	db	Dry basis
531	ε _{Abs}	Absolute error
532	ε _{Bias}	Bias error
533	EER	Ethanol extracted residues
534	EFR	Extractives free residues
535	Ex-EtOH	Ethanol extractives
536	Ex-H ₂ O	Water extractives
537	FR	Fixed residues
538	icf	Total inorganic content free basis
539	IM	Inorganic matters
540	OOM	Other organic matters
541	SD	Standard deviations
542	TI	Total inorganic content
543	WRP	Water reclamation plant
544	wt%	Weight percentage (Weight%)
545	U-R	Raw sludge from Ulu Pandan WRP (Batch 1)
546	U-D	Dewatered sludge from Ulu Pandan WRP (Batch 1)
547	C-P	Primary sludge from Changi WRP (Batch 1)
548	C-S	Secondary sludge from Changi WRP (Batch 1)
549	C-Y	Dried sludge from Changi WRP (Batch 1)

550	J-R	Raw sludge from Jurong WRP
551	J-D	Dewatered sludge from Jurong WRP
552	K-R	Raw sludge from Kranji WRP
553	K-D	Dewatered sludge from Kranji WRP
554	Us-R	Raw sludge from Ulu Pandan WRP (Batch 2)
555	Us-D	Dewatered sludge from Ulu Pandan WRP (Batch 2)
556	Cs-P	Primary sludge from Changi WRP (Batch 2)
557	Cs-S	Secondary sludge from Changi WRP (Batch 2)
558	Cs-Y	Dried sludge from Changi WRP (Batch 2)

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