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

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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.

Keywords: Composition; Model compounds; Pyrolysis; Synthetic sludge; Kinetics

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 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 hours. 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 hours 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 25K/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 $W_s P_s = \sum_{i=1}^n W_i P_i$ 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.

2.3. Synthetic sludge formation

Synthetic sludge was formed by physically mixing of selected model compounds with reference to the results on model compounds characterisation, thermochemical characteristics

150 simulations, thermal degradation behaviours study and weight% data determined by sludge
 151 biomass composition analysis as described in previous studies and also Supporting Materials
 152 of this study, as illustrated in Table 1 [20]. Selection of model compounds was carried out
 153 based on literature and hypothetical consideration to form synthetic sludge with simplified
 154 composition by using common and simple compounds. Asolectin, cholesterol and glyceryl
 155 tri-palmitate were selected to represent phospholipids, sterol lipids and glycerol lipids
 156 respectively as components of EE in sludge, because these are the three most commonly
 157 found lipids groups in wastewater, microorganisms and sludge [23-26]. Sucrose was selected
 158 to represent WE in sludge because of its simplicity and dominant appearance in hydrophilic
 159 extractives of biomass [27, 28, 35]. Whey Isolates (Optimum Nutrition, ON) with protein
 160 content of 81.48wt% was selected as a simple mimic to represent heterogeneous and complex
 161 protein mixture in sludge [29]. For AHR and ADR, cellulose and lignin isolated from
 162 lignocellulosic biomass were selected respectively based on existing studies [15, 36, 37]. As
 163 lipids, simple sugars, protein, cellulose, and lignin were separately quantified based on the
 164 sequential extraction and isolation procedure, polysaccharides (other than cellulose) which
 165 include hemicellulose, glycogen, starch and others, were suggested as the main components
 166 in the residual organics categorised as OOM. Therefore starch, glycogen and xylan were
 167 selected to represent storage or structural polysaccharides in sludge. Starch and glycogen
 168 were common storage polysaccharides while xylan was commonly used as model compounds
 169 for hemicellulose in thermal analysis. Properties of synthetic sludge were determined and
 170 compared to CsY sludge, as illustrated in Table 2. Ash residue (formed from combustion of
 171 sludge at 550°C) was mixed with model compounds mixture to represent inorganic contents
 172 in synthetic sludge. Thermochemical characteristics of synthetic sludge were calculated based
 173 on properties of model compounds used and their respective composition in the synthetic
 174 sludge. This calculation 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 [20]. FTIR spectra of synthetic sludge with and without ash residues were collected. Condensed phase (solids and liquids) spectra were analysed according to absorbance bands recorded in library databases and previous publications [26, 36, 38-41].

3. Results and Discussion

3.1. Synthetic sludge study

Simulation of thermal degradation behaviours of lipids mixture was carried out based on the superposition principle with the measured data of individual model compounds, as illustrated in supporting materials. The approximate proportions of asolectin, cholesterol and glyceryl tri-palmitate were adjusted to be comparable to TG-DTG data of EE from CsY.

Results of simulation showed that acceptable representation of complex waste mixture could be achieved with minor deviations observed. CsY-EE thermally degraded in slightly broader temperature region and lower degradation rates as compared to the lipids mixture simulated suggested that EE from sludge consisted more diverse components that degraded at different temperatures. Mass of volatile matters and fixed residues remained for EE agreed well with simulated data of model compounds. Lipids with lower and higher thermal stability than selected model compounds could be considered if further improvements needed to form the synthetic mixture. Since EE could be easily isolated from sludge, further kinetics modelling and compositional study could also be carried out directly with EE samples. WE consisted of hydrophilic materials with slightly lower thermal stability than sucrose. These compounds could be simple organic alcohols, acids and amines. Further chemical compounds identification could help to improve the representation of WE similar to the model compounds mixture formed for EE. For simplicity and the aim for proof of concept instead of optimisation, sucrose was selected to form synthetic sludge in this study. Main components

of EFR remained after extractions were protein, cellulose, lignin and other polysaccharides. Therefore these four groups of model compounds were also used for simulation and compared to TG-DTG data of EFR. Since the compounds in EFR were more diverse and complex than model compounds selected, thermal degradation of EFR were distributed at different temperatures with lower degradation rates. Based on the simulations of model compounds and comparison to TG-DTG of biomass components of CsY sludge, acceptable representation of sludge thermal degradation behaviours was achieved. All selected model compounds were mixed physically to form synthetic sludge for further analysis. Composition of CsY and synthetic sludge are showed in Table 1. Thermochemical characteristics of synthetic sludge were calculated and compared to direct measurements of CsY in Table 2. Results showed that generally good agreements achieved with overestimated C contents and underestimated S contents as observed and discussed in previous study [20].

FTIR analysis was carried out for CsY sludge, synthetic sludge with and without ash residues of CsY. Results are showed in Figure 1 and Table 3. Peaks identified on FTIR spectra of all three samples were comparable indicated similar functional groups and compounds could be presence. FTIR spectra also showed that mixing of organic model compounds with inorganic ash residues significantly reduced resolution of peaks. Inorganic bounded O-H groups with wavenumber of 3700 and 3620 cm^{-1} could only be observed in CsY sludge but not in synthetic sludge. This was because residual inorganic-bounded moisture contents remained in sludge after drying at 105°C but removed after combustion at 550°C. Broad peaks at 3600–3100 cm^{-1} region contributed by O-H and N-H functional groups suggested the presence of alcohols, acids, amides and amines. Multiple peaks as showed in 3100–2600 cm^{-1} region were caused by C-H groups of unsaturated hydrocarbons and aromatics at 3076 cm^{-1} and saturated hydrocarbons, ethers, and lipids at 2925 and 2855 cm^{-1} . C=O functional groups could be observed for aldehydes, ketones, carboxylic acids, and esters

at 1710 cm^{-1} . C=O and N-H groups for amides and protein observed at 1635 and 1535 cm^{-1} . Multiple peaks showed in the region of 1450–1350 cm^{-1} could be attributed to C-H groups for saturated hydrocarbon, ethers, and lipids at 1445 cm^{-1} and O-H groups for acids and alcohols at 1415 cm^{-1} . Peak at 1375 cm^{-1} could be caused by C-N groups of primary amides, S-O groups of sulphur organic compounds and O-H groups of alcohols and polysaccharides. Peak at 1314 cm^{-1} could be caused by C-N groups of amines, S-O groups of sulphur organic compounds and O=C-O groups of carboxylic acids and esters. Broad peaks and multiple narrow peaks could be observed in the region of 1250–950 cm^{-1} for FTIR spectra of CsY sludge and synthetic sludge respectively. Considering the organic composition in sludge samples, peaks at 1220 cm^{-1} , 1158 cm^{-1} and 1030 cm^{-1} could be contributed by C-O functional groups for polysaccharides, alcohols and esters and by C-O-C groups of polysaccharides and ethers. Peak at 1028 cm^{-1} showed -P=O- groups for phosphates, nucleic acids and phospholipids while peak at 913 cm^{-1} could be caused by C-H groups of unsaturated hydrocarbon and aromatics, O-H groups of carboxylic acids and C-O-C groups of glycosidic linkage for polysaccharides. When considering inorganic composition, peaks at 1080 and 1008 cm^{-1} corresponding to the inorganic functional groups in phosphates, silicates, sulphates, and clay minerals. In the region of 850–600 cm^{-1} , multiple peaks could be identified for minerals and silicates at 797 cm^{-1} , for carbonates and nitrates at 779 cm^{-1} , amides, amines and halogenated compounds at 750 cm^{-1} , aromatics and alcohols at 694 cm^{-1} and sulphates at 668 cm^{-1} .

Thermal degradation behaviours of synthetic sludge with and without ash residues were determined and compared to CsY sludge and simulation calculated based on TG-DTG data of individual model compounds selected. Results were illustrated on Figure 2. Synthetic sludge formed from mixture of model compounds and simulation calculated showed comparable properties suggested that superposition principle could be applied for thermal

degradation behaviours analysis with minimal deviations and interaction effects observed. Almost completely overlapping mass loss curves were observed and slightly higher char residues formed for synthetic sludge as compared to calculated simulation. Synthetic sludge with ash residues and CsY sludge also showed comparable mass loss curves suggested acceptable representation of real waste sample with mixture of selected model compounds. VM/FR ratios of the four TG-DTG data ranged from 2.52 to 2.90 suggested high similarities in distribution of volatile compounds and solid char residues. Compared to synthetic sludge without ash residues, relatively lower released of volatiles in primary degradation region from 100°C to 500°C could be observed for synthetic sludge mixed with ash residues caused by thermal degradation of inorganics at higher temperature. DTG profiles showed that CsY sludge thermally degraded with relatively lower maximum degradation rates at around 300-320°C and higher degradation rates at temperature around 400-500°C. Significant mass loss also observed at secondary degradation region of 500-950°C caused by decomposition of inorganics and secondary char degradation reactions. These observations illustrated the highly complex and diverse composition in real wastes mixture as compared to synthetic sludge formed from few selected compounds.

3.2. Multiple heating rates TG-DTG and kinetics analysis

Results of multiple heating rates TG-DTG and kinetics analysis of CsY and synthetic sludge are illustrated in Figure 2 and 3. Impacts of heating rates within the range of 5-25 K/min used in this study on TG-DTG of synthetic sludge were comparable to CsY. Thermal degradation of CsY and synthetic sludge could be generally divided into primary and secondary degradations where majority of the volatile compounds released during primary degradations at low temperature region of 100-500°C with high mass loss rate. Continuous decomposition occurred during secondary degradations at high temperature region of 500-950°C with low mass loss rate. Weight% on db recorded at 500°C and 950°C and relative%

275 of volatiles released at both primary and secondary degradation regions remained generally
276 consistent with random deviations at different heating rates. Based on the multiple heating
277 rates TG, highly similar and poorly separated mass loss curves from 100°C to 950°C could be
278 observed for CsY at different heating rates used while improved separation could be observed
279 for synthetic sludge. Poor separation of mass loss curves for sludge indicated that heat
280 transfer conditions less affected thermal degradation of sludge samples as compared to other
281 biomass feedstock[13] and could be caused by following reasons. (a) Random errors among
282 the mass loss data caused by heterogeneity in composition and therefore resulted in less
283 significant shift of TG curves to higher temperature at higher heating rates. (b) High
284 activation energy for sludge degradation reactions therefore highly sensitive to the
285 temperature and less affected by heating rates used. Separation of mass loss curves of
286 synthetic sludge improved as compared to CsY indicated that controlled and simplified
287 composition reduced random errors caused by heterogeneity in real wastes mixture since
288 comparable activation energy measured for synthetic sludge and CsY as showed in the results
289 of kinetics study. Variations in sludge composition and mass of char residues formed at
290 different heating rates also caused random crossing on mass loss curves as observed for all
291 sludge samples collected and comparable to previous study[13]. This issue also reduced in
292 multiple heating rates TG of synthetic sludge. Heterogeneity of composition in sludge
293 samples could also be observed as the DTG profiles plotted randomly varied at different
294 heating rates. Improved consistency could be observed for synthetic sludge. Shifts of initial
295 and terminate temperatures for primary degradation region, peaks at maximum degradation
296 rate and other apparent peaks to slightly higher temperatures and degradation rates could be
297 found in DTG profiles for both samples when higher heating rates were used. Higher heating
298 rates also caused thermal degradation of samples occurred in much shorter time intervals and
299 therefore slightly lower resolution of the three apparent peaks observed at around 220-280°C,

300 300-320°C and 400-420°C. Distribution of apparent activation energy, E in kJ/mol of CsY
301 and synthetic sludge determined by Friedman and Ozawa-Flynn-Wall (OFW) analysis were
302 highly similar indicating acceptable representation of complex wastes mixture with selected
303 model compounds on thermal degradation behaviours study. In average, E values calculated
304 for synthetic sludge were slightly lower than CsY by 5.04% and 3.10% while standard
305 deviations of the E values calculated reduced significantly by 62.78% and 67.63% for
306 Friedman and OFW analysis respectively. As illustrated in Figure 2, E data of both samples
307 were closely similar at conversion below 0.50 and started to deviate when standard deviations
308 for E of CsY increased significantly. These observations suggested that synthetic sludge
309 showed comparable thermal degradation kinetics while with significantly reduced random
310 errors of measurements and in calculations.

311 3.3. Products evolution analysis

312 Based on TG-FTIR spectra collected, distinct characteristics of volatile compounds
313 released according to reaction temperatures and types of samples could be observed. Main
314 functional groups detected were O-H, N-H, C-O, C-H, H-C≡N and C=C groups. Gaseous
315 compounds identified were methane (CH₄), carbon dioxide (CO₂), carbon monoxide (CO),
316 water vapour (H₂O), ammonia (NH₃), hydrogen cyanide (HCN), and carbonyl sulphide
317 (COS). Broad and multiple apparent peaks at the range of 3032-2876 cm⁻¹ could be observed
318 for CsY-EE and lipids indicated presence of C-H functional groups from different
319 compounds with diverse chemical structures. Peaks for CH₄ at 3016 cm⁻¹ and C=C groups at
320 950 cm⁻¹ were also identified in EE and lipids. C-O groups at 1032 cm⁻¹ identified in EE and
321 asolectin. For WE and sucrose, comparable peaks at 3016 cm⁻¹ for CH₄, 2359 cm⁻¹ for CO₂,
322 2173 cm⁻¹ for CO, 1541 cm⁻¹ for H₂O and 1176 cm⁻¹ for C-O groups were observed. However
323 additional peaks at 966 cm⁻¹ for NH₃, 712 cm⁻¹ for HCN and 2066 cm⁻¹ for COS could also
324 be observed during WE pyrolysis because of the highly complex composition with significant

amount of nitrogen and sulphur containing compounds as suggested in previous study.

Therefore, representation of WE could be improved with additional nitrogen and sulphur model compounds based on further analysis of WE. With more than 40wt% on icf basis of protein in EFR, TG-FTIR spectra showed high similarity to whey isolates in wavenumbers of peaks identified suggested compatibility of selected model compound to represent protein mixture in sludge. However, the relative absorbance for NH_3 and HCN were significantly lower because of the volatiles contribution on CO_2 , CO , H_2O and CH_4 from other biomass components in EFR such as cellulose, xylan, polysaccharides and lignin. Thermal degradation of model compounds for lignocellulosic biomass also showed gas evolution characteristics comparable to previous pyrolysis research where hemicellulose released higher yield of CO_2 , cellulose produced relatively more CO while lignin generated significant amount of CH_4 [21]. 1176 cm^{-1} for C-O groups were also detected at low temperature for both EFR and glycogen. For AHR and ADR, mainly C-H, CH_4 , CO_2 , CO and H_2O were identified with relatively low absorbance probably caused by low organic contents and low degradation rates in wide temperature region. C=O groups at 1792 cm^{-1} and C-O groups at 1107 cm^{-1} were identified in cellulose probably caused by condensable volatile compounds but not identified in AHR. Strong CH_4 peak at 3016 cm^{-1} and C-O groups at 1033 cm^{-1} were identified for lignin. In general, products released during pyrolysis for model compounds were comparable to sludge components with deviations observed caused by complex composition in sludge. TG-FTIR spectra of components isolated from sludge also showed improved resolutions and peaks identification compared to direct analysis on sludge.

Qualitative and semi-quantitative comparison on TG-FTIR spectra for synthetic sludge and CsY showed highly similar characteristics as illustrated in Figure 4 (a), (b) and Figure 5. Absorbance measured were normalised to the mass of organic matters in CsY and synthetic sludge samples respectively. At low temperature of around 200°C , only water vapour and

carbon dioxide were significantly detected and accompanied by small amounts of carbon monoxide, ammonia and C-O containing compounds for both synthetic sludge and CsY comparable to the findings in previous study [42]. All ten identified peaks could be clearly observed when temperature elevated to about 250°C agreed well with the first apparent peak showed in DTG profiles. Absorbance of C=C functional groups and HCN increased significantly from about 200°C and reached plateau at around 300°C for both samples and further increased at above 400°C only for CsY. Released of water vapour was gradually increased as temperature elevated to 500°C. Released of water vapour during pyrolysis could be caused by dehydration of organic components [43-45]. Dehydration of hydrated inorganic compounds in sludge could also contribute to the released of water vapour as suggested by comparison made for FTIR spectra of sludge samples and char solids in previous study. Since synthetic sludge consisted of pre-combusted ash residues from CsY and insignificant amount of other inorganics, the released of H₂O was lower than CsY. CO₂, CO, C-O functional groups and NH₃ detection reached maximum at temperature region from 300°C to 400°C corresponding to the second apparent peak in DTG profiles. Synthetic sludge released more CO at lower temperature than CsY agreed well with the relatively higher degradation rates in DTG profiles at 280-320°C. Methane and compounds with C-H and C=C-H groups released significantly at temperature higher than 400°C correlated to apparent peaks in DTG profiles where potentially recalcitrant organic matters, non-biodegradable materials and char residues decomposed [10, 31, 46]. In general, TG-FTIR results of synthetic sludge and CsY were highly comparable with slight variations by qualitative and semi-quantitative comparison.

Conclusions

In this study, distinctive thermal degradation behaviours and products released for sludge samples collected, synthetic sludge, model compounds and components from different biomass categories were characterised. Simulations were carried out successfully based on

375 data measured for individual components indicated applicability of superposition principle
376 and suggested potential benefits to construct a library database for common organic
377 compounds to be used as a reference tool. By comparing the results obtained for sludge to
378 model compounds selected, compatibility of model compounds to represent sludge biomass
379 components was observed. Acceptable representation was achieved with discrepancy
380 identified for further improvement on biomass composition analysis and model compounds
381 selection. Reduced random errors on multiple heating rates TG-DTG and improved
382 consistency in kinetics study could also be observed by using synthetic sludge as compared to
383 real waste sample collected. Comparable products evolution observed on TG-FTIR spectra of
384 volatiles released for CsY and synthetic sludge also supported the applicability of synthetic
385 sludge. Hence, synthetic sludge was formed with acceptable representation to the collected
386 real waste sample based on biomass composition analytical procedure and model compounds
387 selection. Formation of synthetic sludge provided an alternative tool to analyse and
388 understand thermochemical characteristics of sludge with reduced heterogeneity and random
389 errors. With the application of this component-based methodology to analyse real sludge
390 samples, components of different types of sludge could be further studied separately and
391 individually for more precise and comprehensive understanding of sludge conversion in
392 thermochemical systems. Synthetic sludge with modifiable composition could also be used as
393 a research tool for complex modelling and performance study since properties of feedstock
394 could be manipulated as a control parameter. By quantitatively adjusting the mass of the
395 components in synthetic sludge and by observing the corresponding performance of sludge
396 conversion, the impacts of sludge composition on thermochemical processes can be further
397 quantified. In addition, thermochemical conversion modelling technique can incorporate this
398 component-based method to simplify the modelling system and improve the consistency of
399 the results. However, it is important to note that synthetic sludge should be only considered

as an alternative tool to complement the research on real waste sludge instead of replacement. Complexity in composition and presence of interaction reactions among compounds in sludge would further complicate the real performance of thermal reactors. Therefore, subsequent verification and comparison with actual sludge are recommended when this proposed methodology is applied in thermochemical conversion processes.

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Abbreviations

CsY, Dried sludge from Changi WRP; WRP, Water Reclamation Plant; 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%;

References:

1. Spinoso, L., *Wastewater Sludge: A Global Overview of the Current Status and Future Prospects*. 2007: Iwa Publishing.
2. Fytli, D. and A. Zabaniotou, *Utilization of sewage sludge in EU application of old and new methods-a review*. Renewable and Sustainable Energy Reviews, 2008. **12**(1): p. 116-40.
3. Manara, P. and A. Zabaniotou, *Towards sewage sludge based biofuels via thermochemical conversion – A review*. Renewable and Sustainable Energy Reviews, 2012. **16**(5): p. 2566-2582.
4. Nipattummakul, N., I. Ahmed, S. Kerdsuwan, and A.K. Gupta, *High temperature steam gasification of wastewater sludge*. Applied Energy, 2010. **87**(12): p. 3729-3734.
5. Kim, Y. and W. Parker, *A technical and economic evaluation of the pyrolysis of sewage sludge for the production of bio-oil*. Bioresource Technology, 2008. **99**(5): p. 1409-1416.
6. Chan, W.P. and J.-Y. Wang, *Comprehensive characterisation of sewage sludge for thermochemical conversion processes – Based on Singapore survey*. Waste Management, 2016. **54**: p. 131-142.
7. Fonts, I., G. Gea, M. Azuara, J. Abrego, and J. Arauzo, *Sewage sludge pyrolysis for liquid production: a review*. Renewable and Sustainable Energy Reviews, 2012. **16**(5): p. 2781-805.
8. Arena, U., *Process and technological aspects of municipal solid waste gasification. A review*. Waste Management, 2012. **32**(4): p. 625-639.

9. He, C., A. Giannis, and J.-Y. Wang, *Conversion of sewage sludge to clean solid fuel using hydrothermal carbonization: Hydrochar fuel characteristics and combustion behavior*. Applied Energy, 2013. **111**: p. 257-266.
10. Font, R., A. Fullana, and J. Conesa, *Kinetic models for the pyrolysis and combustion of two types of sewage sludge*. Journal of Analytical and Applied Pyrolysis, 2005. **74**: p. 429-438.
11. Chan, W.P. and J.-Y. Wang, *Comparison study on thermal degradation behaviours and product distributions for various types of sludge by using TG-FTIR and fixed bed pyrolysis*. Journal of Analytical and Applied Pyrolysis, 2016. **121**: p. 177-189.
12. Bengoa, C., A. Fabregat, and J. Font, *Reduction, Modification and Valorisation of Sludge: Removals*. 2011: Iwa Publishing.
13. Urban, D.L. and M.J. Antal Jr, *Study of the kinetics of sewage sludge pyrolysis using DSC and TGA*. Fuel, 1982. **61**(9): p. 799-806.
14. Piatkowski, N. and A. Steinfeld, *Reaction kinetics of the combined pyrolysis and steam-gasification of carbonaceous waste materials*. Fuel, 2010. **89**(5): p. 1133-1140.
15. Thipkhunthod, P., V. Meeyoo, P. Rangsunvigit, and T. Rirksomboon, *Describing sewage sludge pyrolysis kinetics by a combination of biomass fractions decomposition*. Journal of Analytical and Applied Pyrolysis, 2007. **79**(1-2): p. 78-85.
16. Atienza-Martínez, M., I. Fonts, L. Lázaro, J. Ceamanos, and G. Gea, *Fast pyrolysis of torrefied sewage sludge in a fluidized bed reactor*. Chemical Engineering Journal, 2015. **259**: p. 467-480.
17. Calvo, L.F., M. Otero, B.M. Jenkins, A.I. García, and A. Morán, *Heating process characteristics and kinetics of sewage sludge in different atmospheres*. Thermochimica Acta, 2004. **409**(2): p. 127-135.
18. Inguanzo, M., A. Domínguez, J.A. Menéndez, C.G. Blanco, and J.J. Pis, *On the pyrolysis of sewage sludge: the influence of pyrolysis conditions on solid, liquid and gas fractions*. Journal of Analytical and Applied Pyrolysis, 2002. **63**(1): p. 209-222.
19. Francisca Gómez-Rico, M., R. Font, A. Fullana, and I. Martín-Gullón, *Thermogravimetric study of different sewage sludges and their relationship with the nitrogen content*. Journal of Analytical and Applied Pyrolysis, 2005. **74**(1-2): p. 421-428.
20. Chan, W.P. and J.-Y. Wang, *Characterisation of sludge for pyrolysis conversion process based on biomass composition analysis and simulation of pyrolytic properties*. Waste Management, 2018. **72**: p. 274-286.
21. Yang, H., R. Yan, H. Chen, D.H. Lee, and C. Zheng, *Characteristics of hemicellulose, cellulose and lignin pyrolysis*. Fuel, 2007. **86**(12-13): p. 1781-1788.
22. Hanaoka, T., S. Inoue, S. Uno, T. Ogi, and T. Minowa, *Effect of woody biomass components on air-steam gasification*. Biomass and Bioenergy, 2005. **28**(1): p. 69-76.
23. Sud, M., E. Fahy, D. Cotter, A. Brown, E.A. Dennis, C.K. Glass, A.H. Merrill, R.C. Murphy, C.R.H. Raetz, D.W. Russell, and S. Subramaniam, *LMSD: LIPID MAPS structure database*. Nucleic Acids Research, 2007. **35**(suppl 1): p. D527-D532.
24. Siddiquee, M.N. and S. Rohani, *Lipid extraction and biodiesel production from municipal sewage sludges: A review*. Renewable and Sustainable Energy Reviews, 2011. **15**(2): p. 1067-1072.
25. Jardé, E., L. Mansuy, and P. Faure, *Organic markers in the lipidic fraction of sewage sludges*. Water Research, 2005. **39**(7): p. 1215-1232.
26. Réveillé, V., L. Mansuy, É. Jardé, and É. Garnier-Sillam, *Characterisation of sewage sludge-derived organic matter: lipids and humic acids*. Organic Geochemistry, 2003. **34**(4): p. 615-627.

- 485 27. Chen, S.-F., R.A. Mowery, C.J. Scarlata, and C.K. Chambliss, *Compositional*
486 *Analysis of Water-Soluble Materials in Corn Stover*. Journal of Agricultural and Food
487 Chemistry, 2007. **55**(15): p. 5912-5918.
- 488 28. Chen, S.-F., R.A. Mowery, R.S. Sevcik, C.J. Scarlata, and C.K. Chambliss,
489 *Compositional Analysis of Water-Soluble Materials in Switchgrass*. Journal of
490 Agricultural and Food Chemistry, 2010. **58**(6): p. 3251-3258.
- 491 29. Jimenez, J., F. Vedrenne, C. Denis, A. Mottet, S. Deleris, J.P. Steyer, and J.A. Cacho
492 Rivero, *A statistical comparison of protein and carbohydrate characterisation*
493 *methodology applied on sewage sludge samples*. Water Res, 2013. **47**(5): p. 1751-62.
- 494 30. Heikkinen, J.M., J.C. Hordijk, W. de Jong, and H. Spliethoff, *Thermogravimetry as a*
495 *tool to classify waste components to be used for energy generation*. Journal of
496 Analytical and Applied Pyrolysis, 2004. **71**(2): p. 883-900.
- 497 31. Biagini, E., F. Barontini, and L. Tognotti, *Devolatilization of biomass fuels and*
498 *biomass components studied by TG/FTIR technique*. Industrial and Engineering
499 Chemistry Research, 2006. **45**(13): p. 4486-4493.
- 500 32. Orfão, J.J.M., F.J.A. Antunes, and J.L. Figueiredo, *Pyrolysis kinetics of*
501 *lignocellulosic materials—three independent reactions model*. Fuel, 1999. **78**(3): p.
502 349-358.
- 503 33. Ferrasse, J.H., S. Chavez, P. Arlabosse, and N. Dupuy, *Chemometrics as a tool for the*
504 *analysis of evolved gas during the thermal treatment of sewage sludge using coupled*
505 *TG–FTIR*. Thermochimica Acta, 2003. **404**(1–2): p. 97-108.
- 506 34. Tian, K., W.-J. Liu, T.-T. Qian, H. Jiang, and H.-Q. Yu, *Investigation on the*
507 *Evolution of N-Containing Organic Compounds during Pyrolysis of Sewage Sludge*.
508 Environmental Science & Technology, 2014. **48**(18): p. 10888-10896.
- 509 35. Baham, J. and G. Sposito, *Chemistry of Water-Soluble, Metal-Complexing Ligands*
510 *Extracted from an Anaerobically-Digested Sewage Sludge*. Journal of Environmental
511 Quality, 1983. **12**(1): p. 96-100.
- 512 36. Sluiter, J.B., R.O. Ruiz, C.J. Scarlata, A.D. Sluiter, and D.W. Templeton,
513 *Compositional Analysis of Lignocellulosic Feedstocks. 1. Review and Description of*
514 *Methods*. Journal of Agricultural and Food Chemistry, 2010. **58**(16): p. 9043-9053.
- 515 37. Sun, J.X., X.F. Sun, H. Zhao, and R.C. Sun, *Isolation and characterization of*
516 *cellulose from sugarcane bagasse*. Polymer Degradation and Stability, 2004. **84**(2): p.
517 331-339.
- 518 38. Edalatmanesh, M., M. Sain, and S.N. Liss, *Cellular biopolymers and molecular*
519 *structure of a secondary pulp and paper mill sludge verified by spectroscopy and*
520 *chemical extraction techniques*. Water Science and Technology, 2010. **62**(12): p.
521 2846-2853.
- 522 39. Smidt, E. and K. Meissl, *The applicability of Fourier transform infrared (FT-IR)*
523 *spectroscopy in waste management*. Waste Management, 2007. **27**(2): p. 268-76.
- 524 40. Smith, B.C., *Infrared Spectral Interpretation: A Systematic Approach*. 1998: Taylor
525 & Francis.
- 526 41. Smidt, E., K. Böhm, and M. Schwanninger, *The application of FT-IR spectroscopy in*
527 *waste management*. 2011: INTECH Open Access Publisher.
- 528 42. Hernández, A.B., J.H. Ferrasse, and N. Roche, *Limiting the Pollutant Content in the*
529 *Sewage Sludge Producer Gas through Staged Gasification*. Chemical Engineering &
530 Technology, 2013. **36**(11): p. 1985-1996.
- 531 43. Conesa, J.A., A. Marcilla, R. Moral, J. Moreno-Caselles, and A. Perez-Espinosa,
532 *Evolution of gases in the primary pyrolysis of different sewage sludges*.
533 Thermochimica Acta, 1998. **313**(1): p. 63-73.

44. Shen, J., X.-S. Wang, M. Garcia-Perez, D. Maurant, M.J. Rhodes, and C.-Z. Li, *Effects of particle size on the fast pyrolysis of oil mallee woody biomass*. Fuel, 2009. **88**(10): p. 1810-1817.
45. Anca-Couce, A., *Reaction mechanisms and multi-scale modelling of lignocellulosic biomass pyrolysis*. Progress in Energy and Combustion Science, 2016. **53**: p. 41-79.
46. Conesa, J.A., A. Marcilla, D. Prats, and M. Rodriguez-Pastor, *Kinetic study of the pyrolysis of sewage sludge*. Waste Management and Research, 1997. **15**(3): p. 293-305.