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Title: Comparison study on thermal degradation behaviours and product distributions for various types of sludge by using TG-FTIR and fixed bed pyrolysis

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Abstract

Compositions and characteristics of sludge were highly complex and distinctive compared to other traditional feedstock resulted in limited understanding about impacts of sludge compositions on thermal degradation behaviours and product distributions in thermochemical conversion processes. Therefore, comparison study was carried out for 14 different sludge samples collected based on type, plant, and batch categorisation from all existing Water Reclamation Plants in Singapore. Complementary Thermogravimetric analysis coupled with Fourier-Transform Infrared Spectrometry (TG-FTIR) and fixed bed pyrolysis in a horizontal quartz tube reactor coupled with GC-FID/TCD/TCD system and char solids characterisation were applied. Model-free isoconversional methods with multiple heating rates TG were used to determine of kinetic parameters. Results showed that degradation behaviours and products released from sludge varied according to both operating conditions applied and characteristics of sludge. During pyrolysis, various components in sludge were degraded at different temperature regions with varying

reactivity and products evolution therefore causing apparent activation energy, E and volatile compounds released dependence on temperature and conversion degree. Correlations of pyrolysis yield distributions with characteristics of sludge were formed. Qualitative similarities and quantitative variations of different sludge samples were also identified and discussed which suggested present of waste mixtures with comparable components but in varying amounts. Separation of primary and secondary degradation region of sludge solids by using 500°C as temperature boundary could also contribute to improve kinetics parameters estimation and models development.

1. Introduction

Management of sludge was considered as an important issue with increasing significance caused by population growth, urbanization, industrialization and rising demand on wastewater treatment and water reclamation [1]. Significant amount of moisture, ash residues, nitrogen, sulphur, toxic organic compounds and heavy metals presence in sludge caused significant concern from both economics and environmental perspectives [2, 3]. Thermochemical conversion processes such as pyrolysis, gasification and incineration were considered as potential solutions in near future. However no general agreement was achieved on the most efficient method for sludge treatment and final disposal [4, 5]. Considered as advanced thermochemical conversion processes, pyrolysis and gasification attracted great interests on scientific research and engineering applications. Pyrolysis and gasification were capable to convert solid wastes into valuable products and to recover the hydrogen and carbon resources from sludge residues compared to heat generation during incineration. Additionally, reducing environment at temperature of 500-1000°C reduced the volume of waste, decomposed toxic organic compounds, fixed the heavy metals presence and minimised formation of dioxins, furans, SO_x and NO_x [6, 7].

Direct gasification of sludge involved combination of primary thermal degradations, oxidation and reduction reactions which were having completely different mechanisms and kinetics. Therefore, analytical and experimental studies of the highly complex thermochemical conversion processes should be carried out separately to provide more accurate data for system modelling and optimisation. In addition, gasification of sludge also produced tar as by-products which would limit the potential applications of synthetic gas. This is because of significantly higher temperature applied in gasification than pyrolysis could promote the production of polyaromatic hydrocarbons (PAH) from secondary reactions of volatile compounds released [8]. However gasification of pyrolysed char produced from sludge could generate product gas with significantly lower tar contents while maintaining comparable energy efficiency and heating values of synthetic gases [9, 10]. Sequential thermochemical conversion systems which separated different reaction stages based on the characteristics of feedstock also showed potentials to improve pollutants reduction, increase selectivity on targeting products in addition to the improvements on modelling and control for process optimisation [11-13]. Alternative design of sequential conversion systems could also be developed with detail understanding on thermal degradation behaviours of sludge.

Thermally induced degradations occurred in all thermochemical conversion processes and considered as primary reactions. Thermal degradation behaviours including mass loss kinetics and products evolution during the reactions were important aspects in process modelling and reactor design [14]. Kinetics analysis could be carried out based on the mass loss data measured by using thermogravimetric analysis (TG) and corresponding differential data (DTG) derived for determination of rate equations, description of reaction mechanisms, and predictions of reaction behaviours for any complex time-temperature profiles [15]. Thermal degradation behaviours of sludge were found to be very different

from traditional feedstock in thermochemical conversion processes and highly complex caused by heterogeneous and diverse compositions [16, 17]. Differences in sources of the wastewater and treatment technologies also resulted in significant variations on the characteristics of sludge produced [1, 17]. Existing studies on sludge showed that kinetic parameters of sludge thermal degradations varied significantly among the published results. Activation energy, E of thermal degradation by pyrolysis ranged from 17 kJ/mol to 332 kJ/mol while pre-exponential factor, $\log_{10} A$ ranged from 0.50 to 12.80 and reaction order of the selected models, n ranged from 0.92 to 15.00 for different sludge samples analysed [16, 18-20]. Observations of varying activation energy and high reaction orders for the fitted models suggested multiple and complex reactions occurred during thermal degradation of sludge [20]. Single heating rate experiment and single step model generally applied may not accurately describe the mass loss kinetics of the highly complex sludge thermal degradations which consisted of different components reacted in multiple degradation stages. In addition, model fitting methods used for kinetics modeling were also facing issues on the fit of multiple statistically equivalent models with significantly different activation energies and mechanisms [21]. Therefore, model-free isoconversional methods by using multiple heating rates thermogravimetric analysis could be considered as alternative tools for kinetics analysis of sludge. Multiple heating rates TG with simultaneous correlation could also minimise errors in kinetics parameter analysis [22]. Wide interval of heating rate used also contributed to results with higher reliability and closer to intrinsic kinetic characteristics of the samples [16]. Isoconversional methods also eliminated the necessity to guess the functional form of the reaction models therefore further improve the reliability and repeatability of the estimation of activation energy [23, 24]. Improved isothermal predictions on complex time-temperature profiles could be obtained by using non-isothermal data and kinetics parameters obtained in isoconversional

methods as compared to model fitting methods [21, 24]. Existing studies on experimental pyrolysis of different types of sludge at different reaction temperatures also showed distinct amounts of yields while different chemical compounds produced and distributed in solids, liquids and gases [25, 26]. However, limited understanding established on the impacts of characteristics of sludge on the corresponding pyrolysis performances and products generations.

Hence, TG-FTIR and fixed bed pyrolysis were carried out for thermal degradation behaviours and products evolution analysis on 14 different sludge samples collected from Water Reclamation Plants (WRPs) in Singapore based on plant, type and batch categorisation. Existing studies extensively focus on anaerobic digested sludge as final solid residues from wastewater treatment plants [4]. In this study, comparison analysis extended to different types of sludge in order to achieve a more comprehensive understanding on the sludge generated from different stages of wastewater treatment processes and also originated from different sources of wastewater. Analytical study was carried out at non-isothermal condition by using multiple heating rates TG-DTG, model-free isoconversional methods and products evolution analysis with interconnected TG-FTIR system. Experimental study was carried out in fixed bed reactor at isothermal condition where yield distributions, gas compositions and total energy requirements were measured and calculated. Gas compositions were determined by GC-FID/TCD/TCD system for identification and calculation of relative abundance of main gaseous compounds detected. Physical and chemical properties of sludge samples and char residues included heat capacity, heating value, and elemental composition were characterized. Complementary analysis by TG-FTIR and fixed bed pyrolysis provided important information on thermal degradation behaviours of sludge and corresponding products distribution characteristics useful for process design and optimisation. Comparison

analysis revealed and discussed the qualitative similarity and quantitative differences among different types of sludge samples collected provided insights on impacts of sludge compositions to thermal degradation behaviours and products evolution.

2. Material and methods

2.1. Sludge sampling and pre-treatment

Sludge samples were collected from four existing Water Reclamation Plants (WRPs) in Singapore namely Ulu Pandan (U), Changi (C), Jurong (J) and Kranji (K). Five different types of samples were collected namely primary (P), secondary (S), raw (R), dewatered (D) and dried sludge (Y). At least 25L liquids for P, S and R and 20kg solids for D and Y were collected. Two batches of sludge were collected for Ulu Pandan (Us-R and Us-D) and Changi (Cs-P, Cs-S, and Cs-Y) WRPs for comparison. In total, 14 different sludge samples collected and analysed. Sludge samples were categorised by types based on the considerations of treatment processes applied while by plants and batches based on sources and time variations of characteristics of wastewater. Sludge samples collected were dried in oven at 105°C for 24 hours and milled to pass through screen of 1.00 mm in diameter.

2.2. TG-FTIR analysis

TG-FTIR was carried out in STA 449 Jupiter[®] (Netsch) connected with FTIR system (Bruker). Systematic errors were controlled and reduced by the following methods. Temperature signals calibration by using reference metals. Blank run with empty crucible for background correction to reduce buoyancy effects on mass measured. Initialization stage at 100°C with continuous nitrogen flow for 30 minutes to remove any residual moisture in the pre-dried sample and to purge out any residual air inside the heating chamber. 9.00 ±0.50mg of sludge placed in alumina crucible and heated from 100°C to 950°C by using multiple heating rates of 5, 10, 15, 20, and 25 K/min according to thermal analysis data collection procedure suggested by ICTAC Kinetics Committee [22]. No lid

for crucible was used to avoid secondary char formation reactions. Continuous flow of nitrogen gas at 60 ml/min was supplied to provide inert environment and to remove volatile compounds released from the heating chamber. TG was connected to FTIR equipped with Mercury-Cadmium-Telluride (MCT) detector by transfer-line and flowcell maintained at 200°C with time of transfer estimated at about 5 minutes. Correction was carried out accordingly to estimate the corresponding reaction temperature causing the released of volatile compounds as recorded in FTIR spectra. TG mass loss data in mass% and corresponding DTG data in %/min were measured on dry basis (db). For comparison among different sludge samples with varying amounts of inorganic matters and char residues, TG and DTG on volatile basis (vb) were calculated and compared. TG and DTG in vb were calculated by $M_{vb} = \left[1 - \frac{100 - M_{db}}{100 - Char_{db}} \right] \times 100\%$ and $R_{vb} = \left[\frac{100}{100 - Char_{db}} \right] \times R_{db}$ where M_{vb} and M_{db} were TG mass loss data on vb and db respectively, R_{vb} and R_{db} were DTG degradation rates on vb and db respectively and $Char_{db}$ was the mass of char residues on db. DTG data recorded in %/min were divided by heating rate, β and converted to %/°C where $R_{\%/^{\circ}C} = R_{\%/min} / \beta$ for comparison. Degree of conversion could be calculated by $\alpha = (m_i - m) / (m_i - m_f)$, using initial mass of sludge samples (m_i), final mass of char residues (m_f) and mass of solids remained (m) at any time or temperature for corresponding conversion. Mean TG, DTG and α were calculated based on the data collected from experiments of five different heating rates. Kinetics computational procedure developed by ICTAC Kinetics Committee was adopted and applied to analyse all the sludge samples collected [15]. Both differential method by Friedman analysis and integral method by Ozawa-Flynn-Wall (OFW) analysis were applied. Apparent activation energy, E as a function of conversion, α calculated according to mathematical expressions developed in previous studies with Netzsch analytical software [21, 23, 24]. Identification of functional groups and volatile compounds was based on the gaseous phase TG-FTIR

spectra as compared to model compounds recorded in library database and previous publications [27-30]. TG-FTIR spectra at different temperatures within primary degradation regions of three types of sludge from Changi WRP were selectively illustrated and analysed. Direct comparison of ten important peaks identified was carried out after the absorbance normalized to mass of organic matters present in respective samples.

2.3. Fixed bed pyrolysis

20.00 $\pm$ 2.00g of sludge sample was placed on quartz crucible and inserted into horizontal quartz tube. Nitrogen gas was supplied at flow rate of 600 ml/min to maintain inert environment in fixed bed pyrolysis reactor and to flush out volatile compounds released during thermal degradations of sludge. Pyrolysis reactor was hold at 100°C as initial temperature for 10 minutes and then further heated up to reaction temperature at 500°C by using heating rate of 25K/min. Reactor maintained at final temperature for 24 minutes. Char solids were then collected at room temperature. Pyrolysis temperatures of sludge were selected based on primary degradation region identified in multiple heating rates TG-DTG analysis. Selection of pyrolysis temperature also supported by char reactivity and energy efficiency studies which indicated that pyrolysis at high temperature would reduce both reactivity of char solids and energy efficiency of the process [31, 32]. Total energy required for pyrolysis was calculated based on heat capacity of sludge and heat of reactions during pyrolysis measured by Differential Scanning Calorimetry (DSC) carried out in STA 449 Jupiter[®] (Netszch). Heat capacity of sludge, C_p was measured with the used of reference materials at temperature interval lower than initial temperature for sludge thermal degradations from 70°C to 120°C. Heat capacity was used to calculate energy required to raise the temperature of sample from initial room temperature at 25°C to operating temperature of pyrolysis at 500°C. Heat of reactions for sludge was measured by DSC within primary degradation region ranged from 200°C to 500°C. Linear baseline

was established for DSC signals recorded and the area under the curve was calculated as heat of pyrolysis. Mass of char solids collected was recorded as total solids yield. Solid residues remained were commonly known as char residues and consisted of three major components which were inorganic matters (IM) initially present in sludge, unreacted organic matters and char formed during pyrolysis. Residual char was the summation of unreacted organic matters and char formed during pyrolysis. Residual char was calculated by the difference between total solids yield and IM in sludge. Sludge samples and char solids collected were further characterized by considering both physical and chemical properties included heat capacity, heating value and elemental compositions. Heat capacities of sludge samples, char solids and ash residues were measured similarly by DSC in STA 449 Jupiter[®] (Netsch). Higher Heating Value (HHV) was determined directly by Calorific Bomb (IKA C2000) according to ASTM E711. Elemental compositions analysis of solid residues carried out with direct determination of CHNS contents and indirect calculation of O contents by difference using IM contents calculated from mass balance equation in ultimate analysis of sludge [33]. Inorganic matters free basis (imf) data were also calculated based on IM contents. Significant oxidation could be observed during ash forming analysis and therefore estimation of inorganic contents in char solids was carried out by using IM [33]. Volatile compounds released during pyrolysis were allowed to condense in condensation tubes connected in series and placed in ice bath. Mass of condensable liquids was recorded as liquid yield. Gas yield was calculated by difference. Gas samples were collected using gas bag at the outlet of the pyrolysis system and were tested using GC-FID/TCD/TCD gas chromatograph (Agilent Technologies 7890B) equipped with one flame ionisation detector and dual thermal conductivity detectors with HayeSep Q, HayeSep C, HayeSep R, Molesieve 13X, and Molesieve 5A columns to quantify main permanent gas components included hydrogen (H₂), carbon monoxide (CO),

carbon dioxide (CO₂), methane (CH₄) and C₂ to C₅ hydrocarbon gases released during sludge pyrolysis [8, 34]. Temperatures of all three detectors were set at 250°C. FID 1 was used to detect methane and C₂ to C₅ gases, TCD 2 for N₂, CO₂, CO and TCD 3 for H₂. Oven programme was started with initial temperature at 60°C hold for 1 minute followed by ramping with 20°C/min to 80°C, then ramped with 30°C/min to 190°C and hold for 1.333 minutes with total run time of 6.9997 minutes. Splitting ratio of 80:1 was used. For FID, air flow set at 350 ml/min, hydrogen flow at 40 ml/min and makeup flow by nitrogen at 27 ml/min were applied. Helium (TCD 2) and nitrogen gas (TCD 3) were used at reference flow of 45ml/min and makeup flow of 2 ml/min. Calibration was carried out by using a standard gas mixture at periodic intervals with 64.2% N₂, 12.0% H₂, 5.0% Methane, 1.0% CO, 3.0% CO₂, 0.1% O₂ and 14.7% C₂-C₅ gases. The detected hydrocarbon gases during pyrolysis of the sludge were ethane, ethylene, acetylene, propane, propylene, propadiene, methyl acetylene, butane, butene, butylenes, butadiene, methyl butane, pentane and pentene. All detected hydrocarbon gases were in relatively low abundance and therefore summarised as C₂ to C₅ gases. Relative abundance in volume percentage was calculated by assuming volume of other gas components such as NH₃, HCN, HCl, H₂S, and SO₂ were insignificant when compared to main gas components detected.

3. Results and Discussion

3.1. TG-FTIR analysis

3.1.1. Multiple heating rates TG-DTG analysis

Results of multiple heating rates TG-DTG were summarised with mean values calculated on db and vb as showed in Table 1 and Figure 1. Characteristics of all sludge samples collected were quantitatively varied but qualitatively similar as highly comparable mass loss curves in TG and generally overlapping degradation rate profiles in DTG could be observed. Thermal degradation of sludge generally divided into primary and secondary

degradation regions where majority of volatile compounds released at low temperature with high degradation rate and continuous degradation occurred at high temperature with low degradation rate similar to pyrolysis of lignocellulosic biomass where main weight loss occurred at specific temperature range depending on the compositions and followed by slow and continuous weight loss [27]. Impacts of heating rates on TG-DTG were generally comparable for all 14 different sludge samples studied. Poorly separated TG mass loss curves and highly similar DTG profiles from 100°C to 950°C with slight alterations of apparent peaks of degradation, initialization and terminating temperatures could be observed for all sludge samples at different heating rates used. Sludge samples were less affected by the heat transfer conditions compared to other biomass feedstock therefore less affected by heating rate applied [20]. Poor separation of TG curves could be also due to random errors caused heterogeneity in compositions. Heterogeneity of the compositions in sludge could be observed as the DTG profiles randomly varied at different heating rates. In addition, thermal degradations of the organic matters in sludge could be highly sensitive to the temperature indicating high activation energy, E therefore less affected by the heating rates used. Variations in mass of char residues formed at different heating rates also caused random crossing on mass loss curves.

By comparing mean TG measured and DTG calculated, variations observed on db where different weight% of volatile compounds released and char solids remained were mainly caused by differences in IM contents. Variations in vb were significantly smaller and mainly caused by the differences in organic and inorganic compositions of the sludge. For comparison purposes, initial and terminate temperatures of decomposition in primary degradation region were determined when reached degradation rate of $-0.02\%/^{\circ}\text{C}$ as arbitrary indicator. Initial and terminating temperatures were comparable among different sludge samples at mean values of $164.4 \pm 11.0^{\circ}\text{C}$ and $551.9 \pm 16.7^{\circ}\text{C}$ respectively. Both

initial and terminating temperatures of sludge samples collected after anaerobic digestion (AD) treatment included dewatered (D) and dried (Y) sludge were slightly higher as compared to sludge samples before AD included raw (R), primary (P), and secondary (S) sludge. Initial and terminating temperatures in primary degradation region could be used as important indicators for further analysis. Application of DSC analysis to measure the heat capacity of sludge should be carried out at temperature below the initial degradation while experimental pyrolysis could be designed based on the terminating temperatures to produce volatile compounds and char residues for subsequent applications. Degradation profiles with multiple apparent broad peaks could be observed for all sludge samples collected. Three apparent broad peaks were located at $276.8 \pm 5.2^{\circ}\text{C}$ with R_{db} of $-0.28 \pm 0.05\%/^{\circ}\text{C}$, at $326.2 \pm 10.7^{\circ}\text{C}$ with R_{db} of $-0.33 \pm 0.12\%/^{\circ}\text{C}$ and at $414.7 \pm 11.1^{\circ}\text{C}$ with R_{db} of $-0.13 \pm 0.02\%/^{\circ}\text{C}$. Peaks observed in DTG could represent the compositions in sludge as different components degraded with different characteristics [35]. Comparison on DTG of all sludge samples suggested that comparable compositions with varying amounts could be present. Temperatures at maximum degradation varied from 274.9°C to 346.4°C with R_{db} ranged from $-0.16\%/^{\circ}\text{C}$ to $-0.61\%/^{\circ}\text{C}$. Maximum R_{vb} and corresponding temperatures for primary sludge were similar to dewatered and dried sludge. Secondary sludge showed significantly higher R_{db} and v_b at around 340°C and much lower R_{db} and v_b above 400°C as compared to all other sludge samples. Raw sludge showed mixed behaviours of primary and secondary sludge. Dewatered and dried sludge also showed relatively higher R_{db} at temperature above 400°C . However both maximum degradation rates and their corresponding recorded temperatures were generally lower for sludge samples collected after AD treatment. These observations indicated that thermal degradations of sludge after AD were more distributed which suggested the present of more diverse compositions and more recalcitrant organic matters or other non-biodegradable materials that decomposed at

higher temperature. Primary degradation region of sludge generally occurred from 100°C to 500°C while secondary degradation region occurred from 500°C to 950°C. The selection of 500°C as the temperature boundary was supported by (a) significant reduction of degradation rates in DTG profiles and change of slope on TG data could be directly observed on Figure 1 after the main degradation region at around 500°C for all 14 sludge samples tested at different heating rates of 5, 10, 15, 20, 25K/min. (b) Observations of increased degradation rates in DTG profiles at temperature around 550 to 600°C and above indicating decomposition of inorganic compounds and secondary char degradation. (c) Temperature of $473.1 \pm 46.0^\circ\text{C}$ with range of 414.9 to 608.5°C at conversion degree, $\alpha = 0.80$ stated in Table 1 which suggested the main decomposition region generally occurred before and around the average temperature calculated. (d) Arbitrary average terminating temperature at DTG rate of 0.02%/min for comparison purposes found at $551.9 \pm 16.7^\circ\text{C}$ with range of 524.1 to 589.2°C. Therefore, 500°C was used to unify the results from (a), (b), (c) and (d) and also for 14 different sludge samples as an average temperature boundary. (e) Heat capacities of char solids and ash residues collected from pyrolysis of CsY at 200, 300, 400, 500°C and combustion at 550°C were also determined for comparison. Results showed that heat capacity of sample reduced gradually from 1.53 (CsY sludge), 1.41 (Char₂₀₀), 1.25 (Char₃₀₀), 1.21 (Char₄₀₀), to 1.08 J/g-K (Char₅₀₀ and Ash₅₅₀) on dry basis. These observations suggested that thermal decomposition reduced C_p of sludge but the reduction stopped at 500°C pyrolysis indicating the end of primary degradation of organic matters in sludge. Weight% on db at the end of primary and secondary degradation regions at 500°C and 950°C respectively were recorded and used for calculation of relative% of volatiles released in these two regions. In average, more than 50 weight% of solids on db degraded during thermal degradation of sludge and more than 80 relative% of total mass loss caused by released of volatile compounds in primary

degradation region. Lower relative% for volatiles released before 500°C could be observed for sludge samples collected from Jurong WRP because of significant amount inorganics decomposition at higher temperature such as carbonates and sulphates. In general, the weight% on db for char residues at 500°C and 900°C for sludge samples after AD treatment were higher mainly due to the present of more inorganic matters. More volatile compounds released in relative% during secondary degradation region for dewatered and dried sludge samples could also be observed indicating relatively more secondary char degradation, recalcitrant organic matters degraded at higher temperature and inorganics decomposition occurred. Isolation and identification of thermal degradation behaviours of individual group of components could help to improve the understanding on pyrolysis of sludge. Heterogeneity in organic and inorganic compositions of sludge samples also indicated the importance of the usage of representative samples and the potential advantages of forming synthetic sludge with controlled and modifiable composition to improve the accuracy and consistency of thermal degradation behaviours study.

3.1.2. Kinetics analysis

Activation energy for thermal degradation of sludge was determined by integral method using Ozawa-Flynn-Wall (OFW) analysis and differential method using Friedman analysis. Plots of activation energy, E related to conversion, α for sludge samples collected were showed in Figure 2. E increased steadily at the initial conversion stage where $\alpha < 0.20$ and maintained generally consistent values with gradually increasing trends then followed by reducing trends in the main degradation region where $0.20 < \alpha < 0.80$. Significant fluctuation of E with generally reducing trends could be observed at the terminating stage of thermal degradation where $\alpha > 0.80$. Increasing of E from initial conversion stage to main degradation region could be explained by the residual components during thermal degradation were increasingly refractory while reducing trends

in the values of E could indicate the present of reversible reactions [15, 36]. Reversible reactions could be caused by simultaneous mass loss and mass gain at high temperature where volatiles released from sludge solids or secondary char degradation reactions and solids formation through carbonization of volatile compounds and char forming reactions. Significant carbonization products could be observed on the upper parts of the crucible distance from the solid residues after the end of pyrolysis suggested the reversibility of the mass loss by carbonization of volatiles released. Negative values of E observed mainly caused by the crossover of TG mass loss curves due to the heterogeneity of sludge compositions [20]. Kinetic parameters determined in main degradation region of $0.20 < \alpha < 0.80$ showed good repeatability and predictability while significant errors could be observed at the initial and ending stages [24]. These variations could be caused by the differences in the compositions of sludge and also the random experimental errors due to heterogeneity of sludge as complex mixtures of waste materials. Activation energy at different conversion calculated based on both differential and integral isoconversional methods showed high similarity. In general, activation energy determined by Friedman analysis slightly higher than OFW method with difference between the mean values at 19.7kJ/mol or 10.88% and comparable to the systematic deviations found previously [36]. Kinetics analysis on thermal degradation behaviours of sludge based on model-free isoconversional methods showed that significant variation of apparent activation energy with conversion could be identified and suggested the occurrence of complex processes in all 14 different sludge samples collected. Therefore, multiple-steps models and individual components analysis needed to further clarify the details on thermal degradations of sludge. Apparent activation energy determined in non-isothermal analysis could be used directly for isothermal predictions and complex time-temperature profiles determination by including the temperature-conversion data of T_α at corresponding α calculated based on

multiple heating rates mass loss curves [37]. Considering the relationship of temperature-conversion, results showed that thermal degradation of sludge could be generally divided into three different sections. The first section could be considered as initialization section where sludge started to be thermally degraded in the temperature region of $150.5 \pm 23.9^{\circ}\text{C}$ to $270.2 \pm 9.8^{\circ}\text{C}$ with conversion ranged of 0.01 to 0.20 as showed in Table 1. Second section could be classified as major degradation section where main degradation of sludge occurred in this section where temperature ranged from $270.2 \pm 9.8^{\circ}\text{C}$ to $473.1 \pm 46.0^{\circ}\text{C}$ and conversion ranged from 0.20 to 0.80. Third section could be considered as minor degradation section where sludge slowly and continuously degraded to form char residues over temperature range of $473.1 \pm 46.0^{\circ}\text{C}$ to $919.2 \pm 13.2^{\circ}\text{C}$ where conversion increased from 0.80 to 0.99. Degradation of recalcitrant organic matters, decomposition of inorganics and secondary char degradations occurred in this section. Similar results could be obtained for all sludge samples at different heating rates with slight variations in temperature boundaries of the three sections. Generally, temperature-conversion relationships agreed well with selected temperature of 500°C as boundary to separate between primary and secondary degradation regions of sludge suggested in the multiple heating rates TG-DTG analysis. Temperatures for sludge samples collected from Jurong WRP at conversion, $\alpha = 0.80$ were much higher compared to all other plants because of significant amount of inorganics decomposed at relatively higher temperature compared to organic matters that generally decomposed at temperature below 500°C .

3.1.3. Products evolution analysis

Since raw sludge showed mixed characteristics of primary and secondary sludge while dewatered sludge similar to dried sludge, TG-FTIR spectra for Cs-P, Cs-S and Cs-Y from 150°C to 500°C within primary degradation region were selectively illustrated in Figure 3. Ten selected peaks from TG-FTIR spectra as main functional groups detected at

(a) 3032 cm^{-1} for C=C-H, (b) 3016 cm^{-1} for CH_4 , (c) 2974 cm^{-1} for C-H, (d) 2359 cm^{-1} for CO_2 , (e) 2173 cm^{-1} for CO, (f) 1541 cm^{-1} for H_2O , (g) 1176 cm^{-1} for C-O, (h) 966 cm^{-1} for NH_3 , (i) 951 cm^{-1} for C=C and (j) 712 cm^{-1} for HCN were compared. Absorbance measured were normalised to mass of organic matters present in respective sludge samples for comparison. Distinct characteristics of volatile compounds released according to the reaction temperatures and types of sludge could be observed. 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 comparable to the findings in previous study [12]. All ten identified peaks could be observed when temperature elevated to about 250°C agreed well with the first apparent peak showed in DTG. Absorbance of C=C functional groups and HCN increased significantly from about 200°C and reached plateau at around 300°C while released of H_2O gradually increased as temperature elevated to 500°C. Released of H_2O during pyrolysis could be caused by dehydration of organic components and in-situ formation of pyrolytic water [26, 38, 39]. In addition, dehydration of hydrated inorganic compounds in sludge [40] could also contribute to the released of water vapour as suggested by comparing FTIR spectra of sludge samples and char solids. Peaks identified in FTIR spectra of sludge and char solids at 3700 cm^{-1} corresponding to O-H for inorganic compounds reduced in absorbance as temperature increased and diminished from the solids residues collected after pyrolysis at 500°C. CO_2 , CO, C-O functional groups and NH_3 detection reached maximum at temperature region from 300°C to 400°C corresponding to the second apparent peak in DTG. Significant amount of methane and compounds with C-H and C=C-H functional groups released at temperature higher than 400°C correlated to the apparent peaks in DTG profiles where potentially recalcitrant organic matters, non-biodegradable materials and char residues decomposed [16, 41]. Similar released of volatiles compounds

detected for Cs-P and Cs-Y while significant quantitative differences could be observed for Cs-S. Higher absorbance detected at 2359 cm^{-1} , 2173 cm^{-1} and 1176 cm^{-1} indicated more CO_2 , CO and C-O containing compounds released from Cs-S during thermal degradation but lower absorbance detected at 966 cm^{-1} indicated relatively less NH_3 released. More C-H and C=C-H containing compounds also released from Cs-Y at above 400°C . Comparable released of methane, H_2O , HCN, and C=C functional groups could be observed for all three types of sludge.

3.2. Fixed bed pyrolysis

3.2.1. Yield distributions analysis

Yield distributions for fixed bed pyrolysis at 500°C of 14 different sludge samples collected were showed on db and imf in Table 2. Yield distributions were quantitatively different and qualitatively similar among different sludge samples analysed and were also comparable to findings in previous research on pyrolysis of sludge [4]. Yield distributions on db showed significant variations in solids, liquids and gases yields. Variations were caused by differences in IM contents and characteristics of organic compositions in sludge. Solids recorded highest weight% on db followed by liquids and gases due to the present of high amounts of inorganics. In average, $\text{Char}_{500\text{C}}$ consisted of 36.66% and 47.27% of inorganic matters for sludge samples collected before and after anaerobic digestion (AD) treatment respectively. Impacts of IM on yield distributions could be caused by apparent effects of weight% of IM present and interaction effects with the organic components. Weight% of IM increased the apparent solid yields and reduced the apparent liquid and gas yields. IM could also promote char forming reactions and catalytic decompositions which increased solids yield and reduced liquids yield [4]. Biomass compositions of the sludge samples collected from different stages in wastewater treatment could also affect the yield distributions due to differences in the intrinsic characteristics of organic matters present.

Different organic components such as lipids, proteins, and carbohydrates could produce distinctive yield distributions. Yield distributions on imf basis were calculated for comparison by removing the apparent effects of weight% of inorganic matters on the data. In average, liquids recorded highest weight% on imf followed by solids and gases. Total volatiles and liquids yield from dewatered and dried sludge samples after treated by AD were lower than before AD which included raw, primary and secondary sludge samples on both db and imf. Solid yields on db and imf were higher for AD digested sludge indicated more IM remained and also more residual char formed during pyrolysis. Gas yields for sludge samples before AD treatment were lower on imf basis indicated that organic matters present released relatively less permanent gases but slightly higher on db as relatively higher weight% of organic matters present. After treated by AD, sludge consisted of higher inorganic contents and the organic matters remained would produce lower amounts of liquids and higher amounts of residual char and gaseous compounds. Distribution ratios volatile/solid and liquid/gas calculated in average at 1.97 and 2.05 respectively indicating about two-thirds of organic matters in sludge decomposed into volatile compounds during pyrolysis and about two-thirds of volatile compounds were liquids. However significant variations could be observed as V/S ratios ranged from 1.48 to 2.74 and L/G ratios ranged from 1.07 to 3.18. Both ratios were higher for sludge samples before AD at 2.20 and 2.26 while lower for after AD at 1.66 and 1.77 respectively. In general, significant variations in yield distribution for pyrolysis could be observed. Differences in organic and inorganic compositions of sludge were suggested to be having significant impacts on the results of pyrolysis. Since decomposition during pyrolysis at 500°C mainly accounted by organic matters, further analysis on the biomass compositions of sludge could help to understand and predict the yield distributions from pyrolysis of different types of sludge.

Correlations for yield distributions with weight% of IM and CHNSO elemental compositions in sludge were established and showed in Figure 4. Yield distributions on db and imf were used to form linear regression plots and to illustrate increasing and reducing trends of solid, liquid and gas yields as weight% of IM present in sludge samples varied. On db, solid yields increased with R^2 of 0.8606 while liquid yields decreased with R^2 of 0.78024 when the weight% of IM increased. These observations showed apparent effects of increased IM contents on yields since weight% on db of organic matters available for thermal decomposition reduced. On imf, only weak correlations were observed. Solid yields increased with R^2 of 0.3193 while liquids yields decreased with R^2 of 0.4066 respectively when the weight% of IM increased. No significant correlations between gas yields and IM contents could be obtained although slight decreasing trend for db and increasing trend for imf could be observed. Observations of data on imf showed that interaction effects of IM with volatile compounds could be present for promoting char formation, liquids cracking and gas production but less significant as compared to the apparent effects of weight% found in yield distributions on db. These observations could be also explained by the variations in biomass compositions of sludge which determined the intrinsic characteristics of yield distribution and also the differences in inorganic compositions which determined the effectiveness of interactions between organic and inorganic components. Since variation of IM contents was not the only parameter that changed when comparing different sludge samples, organic and inorganic compositions study was important to determine other factors affecting yield distribution of sludge pyrolysis. Solid, liquid, and gas yields on imf basis were correlated with total weight% of element on db, on imf and organic weight% of element on imf for CHNSO elements separately and collectively. Results showed that relatively strong correlations with could only be observed on solid and liquid yields with carbon (C) element and could not be

found in all other elements examined individually [42]. No significant correlation could be formed for gas yields with any individual CHNSO elements. However, relatively weak correlations could be found between gas yields and summation of HNSO contents. Correlations also found to be improved statistically when considered organic C contents on imf as compared to total C contents on both db and imf. By using organic element contents on imf, apparent effect of weight% of IM and inorganic CHNSO contents on elemental compositions could be removed. CHNSO of organic matters were determined by difference using CHNSO of sludge samples and ash residues measured [33]. Results of correlation analysis showed that increasing organic C contents on imf caused reducing solids yield with R^2 of 0.5351 and increasing liquid yields with R^2 of 0.6395 during pyrolysis at 500°C. These observations indicated that sludge samples with higher C contents consisted more organic matters that would be degraded thermally into condensable liquids during pyrolysis. By considering the compositions of sludge, high C contents components could be originated from lipids, hydrocarbons and plastic materials. These materials were having strong tendency in forming volatile matters through endothermic devolatilization instead of forming char solids by exothermic char forming reactions. Since total CHNSO contents on imf were equal to 100%, increased of C contents could also be represented by decreased of summation of HNSO contents. Therefore, results also could indicate that present of more functional groups with HNSO elements could promote char formation reactions and caused higher solids yield during pyrolysis. Correlation of gas yields also showed similar results supporting the observations for char formation reactions where sludge samples with higher organic HNSO contents on imf recorded higher gas yields during pyrolysis with R^2 of 0.3705. CHNSO contents were contributed by different organic components in sludge having distinct characteristics in

pyrolysis. Therefore simple and direct correlations with the yield distributions were difficult to obtain.

3.2.2. Gas compositions analysis

Results of gas compositions analysis were showed in Table 2. Qualitative similarities and quantitative variations could be generally observed. CO₂ present with the highest relative abundance of $52.64 \pm 5.71\%$ in average comparable to the pyrolysis of lignocellulosic biomass [13]. H₂ present with mean relative abundance of $20.89 \pm 6.61\%$ and then followed by CO at $11.35 \pm 3.48\%$, CH₄ at $9.26 \pm 1.91\%$, and C₂ to C₅ gases at $5.80 \pm 1.37\%$. Mean heating values of product gases calculated at $12.10 \pm 3.05 \text{ MJ/m}^3$ for HHV and at $10.98 \pm 1.88 \text{ MJ/m}^3$ for LHV on N₂ free basis. Significant quantitative variations in all the gas components detected indicating differences in compositions in sludge samples would impact the gases compounds released. In average, sludge samples collected after AD treatment showed relative abundance with lower CO and CO₂, higher H₂ and similar CH₄, and C₂ to C₅ gases detected as compared to sludge samples collected before AD. However variations could be clearly observed for sludge samples from different WRPs and the average values calculated were for indications only. Raw sludge samples from Ulu Pandan WRP (U-R and Us-R) released significant higher amount of H₂ and different from all other sludge samples collected before AD treatment while sludge samples from Jurong WRP (J-R and J-D) released significantly lower amount of CO and CH₄. Secondary sludge from Changi WRP (C-S and Cs-S) showed comparable gas compositions among the two batches of samples but primary sludge samples showed reduction of CO released by more than 50% when compared C-P to Cs-P. Present of 32.24% in average of H₂ and CO in the gases released during pyrolysis could reduce the reactivity of char solids during carbon dioxide and steam gasification processes due to inhibition reactions [32]. These gases could be separated when sludge samples were first pyrolysed with volatile-solid separation

then the char solid residues were subsequently gasified or incinerated. These observations also supporting the application of sequential thermochemical conversion processes.

3.2.3. Energy requirements and energy contents analysis

Results of energy requirements analysis were showed in Table 3. Heat of reaction for different sludge samples were slightly endothermic or near autothermic and ranged from 22 to 78 J/g. No significant endothermic or exothermic peak could be identified in DSC data collected at primary degradation region from 200°C to 500°C. Near autothermic characteristics of sludge pyrolysis indicated that endothermic devolatilization and exothermic char forming reactions occurred concurrently [20, 43]. Heating requirement to raise the temperature of sludge found to be the main energy needed when compared to heat of reaction measured. In average, heating requirement and heat of reaction represented 94.33% and 5.67% respectively of the total energy requirement at $0.85 \pm 0.13 \text{ kJ/g}$. Higher total energy requirements observed for sludge samples collected before AD treatment mainly due to higher heat capacities measured because of more organic matters present[25]. C_p of Cs-Y dried sludge from Changi WRP, Char_{500C} formed during pyrolysis and Ash_{550C}, ash residues after combustion at 550°C were also measured and compared. Average values of C_p decreased from 1.53J/g-K for Cs-Y to 1.08J/g-K on db for both Char_{500C} and Ash_{550C} while reduced to 0.61J/g-K and 0.43J/g-K on dry sludge basis for Char_{500C} and Ash_{550C} respectively. Reduction of C_p indicated destruction of organic matters with higher C_p into residual char with lower C_p . Heat capacities on db of Char_{500C} and Ash_{550C} were similar further suggested that residual char solids formed from organic matters at 500°C were having comparable C_p with inorganics. On dry sludge basis, heat capacities of char solids and ash residues reduced more significantly as compared to Cs-Y sludge due to the concurrent reductions on both heat capacities measured and mass of solids remained. Energy requirements for heating reduced by 29.41% on db and 60.13%

on dry sludge basis when Char_{500C} solid residues instead of Cs-Y sludge samples were heated to operating temperature of gasification or incineration at 750°C and above indicating the advantage of sequential thermochemical conversion process. HHV results of Char_{500C} on db and imf were also showed in Table 3 with significant variations observed. Mean HHV of Char_{500C} measured at 11.84 ± 2.60 MJ/kg on db comparable to previous studies [34, 44]. On imf, mean HHV_{char} calculated at 19.83 ± 2.23 MJ/kg slightly lower than HHV_{sludge} at 21.62 ± 1.13 MJ/kg suggested the intrinsic energy contents of organic matters in sludge reduced when thermally degraded to form char residues. HHV of char solids correlated positively with carbon contents and negatively with IM contents. These observations indicated that energy contents of char contributed mainly by C as supported by results of ultimate analysis of char. Residual HHV in relative% showed that in average $31.21 \pm 3.54\%$ of energy contents which equalled to 5.38 ± 0.56 MJ/kg-of-sludge remained in the char solids after pyrolysis at 500°C. In general, char solids for sludge samples collected after AD treatment showed lower values but higher residual percentage of HHV agreed with the higher IM contents and solid yields observed. These observations indicated the differences in organic compositions affected not only energy contents in sludge but also char solids formed in pyrolysis.

3.2.4. Elemental compositions analysis

Results of elemental compositions analysis on Char_{500C} on db were showed in Table 4. According to mass contents, element with highest weight% was carbon (C) measured at 30.69 ± 7.61 wt% followed by oxygen (O) at 20.35 ± 4.86 wt%, nitrogen (N) at 3.97 ± 0.98 wt%, sulphur (S) at 3.43 ± 0.66 wt% and hydrogen (H) with only 1.09 ± 0.3 wt% on db. IM also present with significant amounts of 40.48 ± 11.04 wt% in average. C contents calculated on imf showed 51.56% in average and significantly lower than lignocellulosic biomass pyrolysed at similar conditions indicated the impact of

characteristics of feedstock on char formed [32]. Variations could be observed for all
 sludge samples from different plants, types and batches. Similar S contents, higher IM
 contents, and lower CHNO contents found in dewatered and dried sludge collected after
 AD as compared to raw, primary and secondary sludge samples collected before AD
 treatment. Based on CHNSO data calculated on normalised molar basis, sludge before and
 after AD treatment were highly similar while sludge after AD consisted slightly more S
 and O. Significantly more S and O contents were found in samples collected from Jurong
 WRP (J-R and J-D) mainly due to the present of more inorganic components such as
 sulphates and carbonates. By comparing mean molecular formula formed for Char_{500C}
 ($C_{1.00}H_{0.42}N_{0.11}S_{0.05}O_{0.52}$) to sludge ($C_{1.00}H_{1.80}N_{0.12}S_{0.05}O_{0.51}$) determined in characterisation
 study, significant reduction of H relative abundance could be observed. Residual CHNSO
 contents of char solids in relative percentage to the initial contents in respective sludge
 samples were also calculated and showed in Table 4. In average, less than 10% of H but
 more than 30% of C, N, S and O contents were remained in the char solids agreed with the
 molecular formula formed. Sludge after AD treatment generally retained more CHNSO
 contents during pyrolysis probably due to relatively more char solids formed as suggested
 in yield distributions analysis of pyrolysis and relatively more inorganic contents with
 carbonates and sulphates degraded only at higher temperature as suggested in ultimate
 analysis of ash residues. Significant released of 65.14% N and 68.55% S contents in
 average could be observed after pyrolysis of sludge at 500°C. Subsequent utilization of
 char solids by gasification and incineration could potentially face lower concerns of NO_x
 and SO_x pollutants as compared to direct utilization of sludge since the total amount of N
 and S reduced in char solids as fuel bound nitrogen contents were more important in NO_x
 formation compared to nitrogen gas present in the air at temperature below 1500°C [45,
 46]. However the relative amount of N and S were remained similar on char solids.

Therefore further analysis to identify the released of volatile compounds with comparison study of sludge and char gasification could contribute in clarification of this concern.

4. Conclusions

Complementary TG-FTIR and fixed bed pyrolysis showed that thermal degradation behaviours and product distributions of all 14 different sludge samples collected were qualitatively similar and quantitatively different as summarised in Table 5 which suggested the present of waste mixtures with comparable components but in varying amounts. Thermal degradation behaviours and products distribution of sludge also found to be varied according to both operating conditions applied and heterogeneous compositions of sludge. Various components in sludge were degraded at different temperature regions with varying reactivity and products evolution. Competitive reactions such as formation of char and carbonization of volatile compounds further complicated the thermally induced degradation of sludge. Activation energy distributions, E for different sludge samples were also varied according to the pyrolysis temperature and the conversion degree, α . Therefore, understanding on mechanism and modelling of the thermochemical conversion processes would face limitations if only operating conditions were considered in details. In order to understand and describe the complex behaviours of sludge thermal degradation, individual contributing components and corresponding characteristics needed to be identified and studied. In addition to the components with different characteristics, primary and secondary decomposition of sludge at low and high temperature and the degradation kinetics of organic and inorganic contents in sludge should be studied separately in details. Therefore, further analysis should consider the physical and chemical properties of sludge in the aspects of biomass components and inorganic compositions present with respective reactivity and characteristics in thermochemical conversion processes. 500°C could be

used as temperature boundary to separate primary and secondary degradation region of sludge solids to improve estimations of kinetics parameters and models development.

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Table 1: Summary of multiple heating rates TG and DTG analysis of sludge samples collected.

Sample Label	Initial Temp °C	Maximum Degradation		Terminate Temp °C	Weight% on db		Volatiles released in relative%		Temperature °C at conversion α			
		Temp °C	Rate %/°C		500°C	950°C	100°C - 500°C	500°C - 950°C	0.01	0.20	0.80	0.99
U-R	137.3	340.7	-0.40	558.8	41.96	31.42	84.63	15.37	195.8	277.2	459.3	910.9
U-D	162.0	277.5	-0.28	589.2	50.37	38.87	81.20	18.80	153.4	270.7	488.2	915.4
C-P	161.5	318.4	-0.31	545.9	47.23	37.57	84.55	15.45	156.1	262.1	458.8	925.3
C-S	185.4	346.4	-0.61	553.0	41.40	32.76	87.13	12.87	185.8	290.6	443.3	889.4
C-Y	165.9	318.6	-0.26	547.5	57.95	48.56	81.75	18.25	150.9	273.1	481.7	944.3
J-R	161.5	322.4	-0.29	551.6	52.47	40.29	79.58	20.42	127.4	267.7	506.7	917.4
J-D	171.9	320.4	-0.16	570.4	66.07	53.14	72.43	27.57	128.4	284.6	608.5	926.4
K-R	163.8	327.8	-0.33	540.5	44.24	35.76	86.80	13.20	167.4	261.2	441.8	914.9
K-D	163.3	310.9	-0.26	543.0	53.00	43.29	82.89	17.11	154.4	260.2	468.3	934.3
Us-R	162.4	342.0	-0.38	540.6	39.21	29.71	86.47	13.53	139.4	262.2	445.3	907.9
Us-D	156.4	274.9	-0.32	573.3	45.39	34.37	83.20	16.80	120.0	262.7	468.8	919.8
Cs-P	162.1	278.2	-0.33	536.8	45.09	36.72	86.79	13.21	127.9	260.2	443.8	927.4
Cs-S	168.4	334.3	-0.54	524.1	39.86	32.61	89.26	10.74	174.3	272.1	414.9	909.3
Cs-Y	179.4	325.4	-0.24	551.6	58.74	48.93	80.80	19.20	125.7	278.9	493.4	925.7
Mean $\pm$ Standard Deviations												
All Sample	164.4 ± 11.0	317.0 ± 24.0	-0.34 ± 0.12	551.9 ± 16.7	48.78 ± 8.02	38.86 ± 7.19	83.39 ± 4.23	16.61 ± 4.23	150.5 ± 23.9	270.2 ± 9.8	473.1 ± 46.0	919.2 ± 13.2
Before AD	162.8 ± 13.1	326.3 ± 21.8	-0.40 ± 0.11	543.9 ± 10.9	43.93 ± 4.38	34.61 ± 3.55	85.65 ± 2.87	14.35 ± 2.87	159.3 ± 26.0	269.2 ± 10.5	451.7 ± 26.1	912.8 ± 11.8
After AD	166.5 ± 8.1	304.6 ± 22.5	-0.25 ± 0.05	562.5 ± 18.0	55.25 ± 7.25	44.53 ± 7.02	80.38 ± 4.00	19.62 ± 4.00	138.8 ± 15.7	271.7 ± 9.3	501.5 ± 53.4	927.7 ± 10.4

Table 2: Yield distributions. Solids, liquids and gases on dry basis (db), inorganic matters free basis (imf) and gas compositions in volume%.

Sample Label	Yield distributions of fixed bed pyrolysis at 500°C												
	Weight% on db					Weight% on imf			Gas compositions in volume%				
	IM	Char	Total Solids	Liquid	Gas	Solid	Liquid	Gas	H ₂	CO	CO ₂	CH ₄	C ₂ - C ₅
U-R	8.35	30.63	38.98	46.43	14.59	33.42	50.66	15.92	33.16	9.47	44.78	8.41	4.18
U-D	14.78	32.90	47.68	35.30	17.02	38.61	41.42	19.97	17.09	10.77	59.17	8.15	4.83
C-P	18.36	27.18	45.54	33.69	20.77	33.30	41.26	25.44	16.31	13.48	52.24	10.75	7.12
C-S	9.88	28.72	38.60	42.66	18.74	31.87	47.34	20.79	13.29	16.93	56.11	8.13	5.54
C-Y	29.72	27.40	57.12	22.17	20.71	38.99	31.54	29.47	21.21	11.69	49.12	11.5	6.47
J-R	23.11	28.45	51.56	35.28	13.16	37.00	45.88	17.12	22.84	6.62	60.37	5.64	4.53
J-D	38.38	24.83	63.21	25.68	11.11	40.29	41.68	18.03	32.21	7.71	48.58	6.22	5.28
K-R	12.81	28.71	41.52	40.20	18.28	32.93	46.11	20.97	14.00	15.27	52.79	9.80	8.02
K-D	20.09	31.31	51.40	29.63	18.97	39.18	37.08	23.74	20.74	11.76	49.27	11.46	6.77
Us-R	15.77	22.55	38.32	43.78	17.90	26.77	51.98	21.25	22.58	10.23	49.16	10.99	7.04
Us-D	17.21	27.81	45.02	37.49	17.49	33.59	45.28	21.13	15.68	13.23	57.32	8.66	5.11
Cs-P	18.17	24.77	42.94	36.88	20.17	30.27	45.08	24.65	17.38	6.24	60.21	10.4	5.77
Cs-S	17.18	22.49	39.67	39.13	21.20	27.16	47.25	25.60	16.13	16.75	55.54	8.35	3.23
Cs-Y	31.33	24.73	56.06	25.97	17.98	36.00	37.82	26.18	29.82	8.78	42.26	11.22	7.25
Mean ± Standard Deviations													
All Sample	19.65 ±8.44	27.32 ±3.15	46.97 ±7.87	35.31 ±7.25	17.72 ±2.96	34.24 ±4.34	43.60 ±5.54	22.16 ±3.85	20.89 ±6.61	11.35 ±3.48	52.64 ±5.71	9.26 ±1.91	5.80 ±1.37
Before AD	15.45 ±4.87	26.69 ±3.06	42.14 ±4.54	39.76 ±4.39	18.10 ±2.88	31.59 ±3.42	46.94 ±3.32	21.47 ±3.65	19.46 ±6.57	11.87 ±4.33	53.90 ±5.33	9.06 ±1.79	5.68 ±1.65
After AD	25.25 ±9.28	28.16 ±3.35	53.42 ±6.69	29.37 ±5.97	17.21 ±3.26	37.78 ±2.50	39.14 ±4.76	23.09 ±4.24	22.79 ±6.75	10.66 ±2.06	50.95 ±6.25	9.53 ±.20	5.95 ±1.00

Table 3: Energy requirements for sludge pyrolysis at 500°C and heating values of char solids collected.

Sample Label	Heat Capacity Cp in J/g-K		Energy requirement, J/g			HHV of Char _{500C} , MJ/kg				
			Heating Requirement	Heat of Reaction	Total Energy Requirement	Dry basis		Imf basis	Dry sludge basis	Residual HHV in %
	Mean	SD				Mean	SD			
U-R	1.98	0.21	940	41	981	14.63	0.13	18.62	5.70	27.83
U-D	1.60	0.15	760	40	800	12.64	0.07	18.32	6.03	34.62
C-P	1.55	0.16	737	72	809	12.32	0.00	20.64	5.61	32.00
C-S	1.93	0.19	916	55	972	15.81	0.02	21.25	6.10	31.05
C-Y	1.57	0.18	745	44	788	9.22	0.16	19.22	5.27	36.41
J-R	1.74	0.16	829	36	864	9.26	0.13	16.78	4.77	27.88
J-D	1.35	0.13	642	46	719	6.44	0.04	16.40	4.07	30.86
K-R	1.61	0.15	763	22	785	13.28	0.05	19.20	5.51	26.86
K-D	1.33	0.14	632	33	664	10.61	0.01	17.41	5.45	34.82
Us-R	2.18	0.17	1034	66	1119	13.25	0.06	22.52	5.08	26.17
Us-D	1.90	0.20	902	78	997	13.55	0.04	21.93	6.10	34.88
Cs-P	1.36	0.22	645	48	693	12.39	0.07	21.48	5.32	29.23
Cs-S	1.90	0.27	903	50	953	13.51	0.14	23.83	5.36	28.73
Cs-Y	1.53	0.16	727	40	767	8.84	0.07	20.03	4.95	35.65
Mean ± Standard Deviations										
All Sample	1.68 ± 0.26		798 ± 125	48 ± 16	846 ± 132	11.84 ± 2.60		19.83 ± 2.23	5.38 ± 0.56	31.21 ± 3.54
Before AD	1.78 ± 0.27		846 ± 126	49 ± 16	895 ± 131	13.06 ± 1.92		20.54 ± 2.26	5.43 ± 0.40	28.72 ± 2.00
After AD	1.55 ± 0.21		734 ± 98	47 ± 16	781 ± 112	10.22 ± 2.62		18.89 ± 1.97	5.31 ± 0.75	34.54 ± 1.92

Table 4: Ultimate analysis of char solids collected after fixed bed pyrolysis at 500°C, Char_{500C}.

Sample Label	Ultimate Analysis of Char _{500C} on dry basis, Weight%										Residual CHNSO of Char _{500C} in relative%				
	C		H		N		S		O	IM	C	H	N	S	O
	Mean	SD	Mean	SD	Mean	SD	Mean	SD							
U-R	45.26	0.99	1.64	0.05	5.68	0.14	3.72	0.05	22.27	21.42	40.50	11.33	38.10	26.53	28.13
U-D	32.40	0.19	1.11	0.03	4.26	0.04	3.65	0.07	27.58	30.99	38.75	8.57	33.65	30.95	48.19
C-P	31.15	0.20	1.00	0.04	4.85	0.04	2.91	0.04	19.78	40.31	37.40	7.77	29.27	28.95	35.57
C-S	39.75	0.29	1.51	0.03	4.00	0.02	3.39	0.02	25.76	25.59	34.89	9.02	39.89	24.68	33.02
C-Y	23.66	0.40	0.87	0.02	3.06	0.06	2.94	0.04	17.44	52.02	42.63	10.18	34.75	34.95	42.55
J-R	22.25	0.28	0.73	0.04	2.99	0.05	4.73	0.05	24.47	44.82	30.87	6.33	35.63	45.41	53.96
J-D	16.18	0.17	0.48	0.01	1.96	0.02	4.71	0.04	15.95	60.72	37.27	7.49	38.57	54.79	48.34
K-R	33.71	0.08	1.07	0.03	4.45	0.05	3.24	0.06	26.67	30.86	31.96	6.79	32.83	24.74	43.56
K-D	27.51	0.21	0.84	0.02	4.03	0.07	3.13	0.14	25.41	39.08	38.73	7.21	31.15	29.86	52.18
Us-R	34.00	0.31	1.21	0.04	4.52	0.04	3.63	0.14	15.47	41.16	30.53	7.39	34.95	32.69	22.89
Us-D	34.99	0.18	1.24	0.02	4.71	0.02	3.59	0.06	17.25	38.23	39.87	9.51	35.88	35.21	29.00
Cs-P	31.20	0.11	1.11	0.03	4.69	0.02	2.58	0.08	18.11	42.32	34.92	8.29	29.62	20.19	30.89
Cs-S	34.64	0.55	1.44	0.05	3.42	0.03	3.08	0.06	14.11	43.30	34.16	9.68	39.23	22.51	20.32
Cs-Y	22.96	0.12	0.94	0.01	2.97	0.04	2.68	0.07	14.56	55.89	42.30	11.61	34.48	28.87	34.80
Mean ± Standard Deviations															
All Sample	30.69 ± 7.61		1.09 ± 0.31		3.97 ± 0.98		3.43 ± 0.66		20.35 ± 4.86	40.48 ± 11.04	36.77 ± 4.00	8.65 ± 1.64	34.86 ± 3.38	31.45 ± 9.22	37.38 ± 10.83
Before AD	33.99 ± 6.70		1.21 ± 0.30		4.33 ± 0.85		3.41 ± 0.65		20.83 ± 4.72	36.22 ± 8.97	34.40 ± 3.38	8.32 ± 1.64	34.94 ± 4.11	28.21 ± 7.93	33.54 ± 11.00
After AD	26.28 ± 6.85		0.91 ± 0.26		3.50 ± 1.01		3.45 ± 0.72		19.70 ± 5.41	46.16 ± 11.70	39.93 ± 2.14	9.09 ± 1.68	34.75 ± 2.45	35.77 ± 9.68	42.51 ± 8.96

Table 5: Summary on qualitative similarities and quantitative variations of different sludge samples collected and analysed.

Analysis	Qualitative similarities	Quantitative variations		
TG	Comparable mass loss curves. Primary and secondary degradation regions identified with volatiles released $V_{\text{primary}} > V_{\text{secondary}}$, degradation rates $R_{\text{primary}} > R_{\text{secondary}}$ and temperature, $T_{\text{primary}} < T_{\text{secondary}}$.	Volatiles released in relative%		
		Primary 100-500°C	72.43 – 89.26	
	Secondary 500-950°C	10.74 – 27.57		
	Formation of char residues affected by present of inorganic matters (IM), differences in sludge organic (Oc) and inorganic compositions (Ic). $[IM, Oc, Ic] \in Char$ and $Char_{950C} < Char_{500C}$.	Char, weight%	db	imf
		500°C pyrolysis	39.21 – 66.07	22.68 – 35.59
	950°C pyrolysis	29.71 – 53.14	13.94 – 24.09	
DTG	Similar degradation rate profiles with three apparent broad peaks in average where P1 at $276.8 \pm 5.2^{\circ}\text{C}$, P2 at $326.2 \pm 10.7^{\circ}\text{C}$ and P3 at $414.7 \pm 11.1^{\circ}\text{C}$. Comparable initial and terminating temperatures for primary degradation region at $164.4 \pm 11.0^{\circ}\text{C}$ and $551.9 \pm 16.7^{\circ}\text{C}$ with relative standard deviation (RSD) at 6.69 and 3.03% respectively.	Characteristic temperatures, °C		
		Initial	137.3 – 185.4	
		Terminating	524.1 – 589.2	
		Maximum DTG peak	274.9 – 346.4	
		Maximum rate, %/°C	-0.16 – -0.61	
E	At degree of conversion $\alpha < 0.20$, E increased steadily with $dE/d\alpha > 0$. At $0.20 < \alpha < 0.80$, E generally maintained consistent values and gradually increased then reduced with $d^2E/d\alpha^2 < 0$. At $\alpha > 0.80$, significant fluctuation of E with generally reducing trends observed.	Mean activation energy E, kJ/mol for $0.20 < \alpha < 0.80$		
		Differential-Friedman	58.7 – 319.4	
		Integral-OFW	52.4 – 288.0	
FTIR	Ten peaks as main functional groups were detected for all sludge samples at 3032 cm^{-1} for C=C-H, 3016 cm^{-1} for CH ₄ , 2974 cm^{-1} for C-H, 2359 cm^{-1} for CO ₂ , 2173 cm^{-1} for CO, 1541 cm^{-1} for H ₂ O, 1176 cm^{-1} for C-O, 966 cm^{-1} for NH ₃ , 951 cm^{-1} for C=C and 712 cm^{-1} for HCN.	Normalised absorbance		
		Baseline correction	0.000 – 0.101	
		Organic matters only	0.000 – 0.171	

Fixed bed pyrolysis	Yield distributions generally found as $Y_S > Y_L > Y_G$ in db and $Y_L > Y_S > Y_G$ in imf with slight variations for some samples. Distribution ratios in imf, $1.00 < V/S < 2.80$ and $1.00 < L/G < 3.20$.	Yield distribution, %	db	imf
		Solid yields, Y_S	38.32 – 63.21	26.77 – 40.29
		Liquid yields, Y_L	22.17 – 46.43	31.54 – 51.89
		Gas yields, Y_G	11.11 – 21.20	15.92 – 29.47
	Gas composition relative abundance from sludge pyrolysis was generally found in the order of $V_{CO_2} > V_{H^2} > V_{CO} > V_{CH_4} > V_{C_2-C_5}$ with slight variations for some samples.	Gas compositions in relative abundance, %		
		V_{CO_2}	42.26 – 60.37	
		V_{H^2}	13.29 – 33.16	
		V_{CO}	6.24 – 16.93	
		V_{CH_4}	5.64 – 11.50	
		$V_{C_2-C_5}$	3.23 – 8.02	
	In average, heating requirement and heat of reaction represented 94.33% and 5.67% respectively of total energy requirement at 0.85 ± 0.13 kJ/g where $\Delta H_{Heating} \gg \Delta H_{Reaction}$. Pyrolysis reaction of sludge found to be slightly endothermic or near autothermic, $\Delta H_{Reaction} \cong 0$ kJ/g.	Energy requirement for pyrolysis, kJ/g		
		Heating requirement Heat of reaction	0.632 – 1.034 0.022 – 0.078	
	Weight% in db of elements present in char solids generally found in the order of $C > O \gg N \approx S > H$ and residual% of elements as compared to initial sludge samples found as $C \approx O > N \approx S \gg H$ with slight variations for some samples.	Elemental contents	Weight%	Residual%
		C	16.18 – 45.26	30.53 – 42.63
O		14.11 – 27.58	20.32 – 53.96	
N		1.96 – 5.68	29.27 – 39.89	
S		2.58 – 4.73	20.19 – 54.79	
H		0.48 – 1.64	6.33 – 11.61	

Figure 1: Mean data for (a) TG (b) DTG on dry basis, (c) TG (d) DTG on volatile basis.

Figure 2: Apparent activation energy distributions, E in kJ/mol determined by using (a) OFW analysis and (b) Friedman analysis at different conversion degree, α .

Figure 3: Selected TG-FTIR spectra of (a) CsP, (b) CsS and (c) CsY in primary degradation region from 100°C to 500°C.

(c)

Figure 4: Correlations analysis on fixed bed pyrolysis of sludge for (a) solid, (b) liquid yields on db and imf with weight% of inorganic matters and (d) solid (e) liquid yields on imf with CHNSO contents in sludge.

(c)

(d)