Comprehensive characterisation of sewage sludge for thermochemical conversion processes - Based on Singapore survey

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Abstract:

Recently, sludge attracted great interest as a potential feedstock in thermochemical conversion processes. However, compositions and thermal degradation behaviours of sludge were highly complex and distinctive compared to other traditional feedstock led to a need of fundamental research on sludge. Comprehensive characterisation of sludge specifically for thermochemical conversion was carried out for all existing Water Reclamation Plants in Singapore. In total, 14 sludge samples collected based on the type, plant, and batch categorisation. Existing characterisation methods for physical and chemical properties were analysed and reviewed using the collected samples. Qualitative similarities and quantitative variations of different sludge samples were identified and discussed. Oxidation of inorganic in sludge during ash forming analysis found to be causing significant deviations on proximate and ultimate analysis. Therefore, alternative parameters and comparison basis including Fixed Residues (FR), Inorganic Matters (IM) and Total Inorganics (TI) were proposed for better understanding on the thermochemical characteristics of sludge.

Keywords:

Sludge; Thermochemical conversion; Characterisation; Singapore; Comparison analysis

1. Introduction

Sewage sludge management was considered as an important issue with increasing significance due to rising demand on wastewater treatment and reclamation in Singapore and globally. Global annual production of sludge was achieving more than 20 million tonnes of dry matter and was increasing with the population growth, urbanization and industrialization (Spinosa, 2007). According to the waste statistic reported by National Environment Agency

of Singapore, 160,200 tonnes of sludge were generated in year 2012. Sludge residues generated from four operating Water Reclamation Plants (WRPs) were incinerated and ash residues were subsequently landfilled in Pulau Semakau, the only operating landfill in Singapore. High moisture content, toxic organic compounds and heavy metals resulted in sludge to be considered as a serious waste management concern (Kim and Parker, 2008; Nipattummakul et al., 2010). Existing technologies for sludge treatment and final disposal were mechanical dewatering, thermal drying, agricultural utilization, composting, landfilling, land reclamation and incineration (Fytili and Zabaniotou, 2008). However, dewatering and drying processes were facing issues on low dewatering effectiveness and high energy consumptions (Jin et al., 2004). Restrictions were set on agricultural reuse due to the concerns of pathogens, heavy metals and organic pollutants in sludge (Fonts et al., 2012). Land disposal of the sludge was costly and facing limitation on the availability of landfill. Furthermore, sludge disposal before removing all the organic contents would cause potential greenhouse gases emission from microorganism activities (Ning-Yi et al., 2013). While incineration plants reduced the volume of sludge significantly, large amount flue gas generated from incineration needed to be treated and incurred high cost. Therefore, innovative sludge management methodology needed to take care of the sludge with economic and environmental friendly considerations and in the same time to discover possibilities on resource recovery.

Currently, there were great interests to study the feasibility of thermochemical conversion processes to convert municipal solid waste and sludge into oil through pyrolysis and into synthetic gas through gasification (Arena, 2012; Manara and Zabaniotou, 2012). Compared to incineration, advanced thermochemical conversion processes were capable to convert waste into valuable product instead of heat and to recover the hydrogen and carbon resources from the residues. Pyrolysis and gasification of sludge could also reduce the

64 volume of waste, degrade toxic organic compounds and fix the heavy metals present which
65 reduced the need and cost of landfilling (Marrero et al., 2004). Furthermore, reducing
66 environment present in pyrolysis and gasification could reduce the formation of dioxins,
67 furans, SO_x and NO_x (Arena, 2012). However, thermal degradation behaviours of sludge
68 found to be different from traditional feedstock such as coal. Fundamental research on sludge
69 as a feedstock for advanced thermochemical conversion such as pyrolysis and gasification
70 was needed for more efficient utilization of sludge (Fytili and Zabaniotou, 2008). Due to the
71 complex nature of sludge, characterisation should be carried out specifically to meet the need
72 of the targeted treatment and disposal methods (Sanin et al., 2011). Moreover, differences in
73 the sources of the wastewater and wastewater treatment technology resulted in significant
74 variations on the characteristics of sludge produced (Fytili and Zabaniotou, 2008; Spinosa,
75 2007). Therefore, characterisation of domestic sludge specifically for thermochemical
76 conversion processes was necessary for sludge generated from all WRPs which function as
77 both wastewater treatment and water reclamation facilities in Singapore. Previous studies
78 extensively focus on anaerobic digested sludge as the final solid residues from wastewater
79 treatment plants (Fonts et al., 2012). In this study, comparison analysis extended to different
80 types of sludge samples in order to achieve a more comprehensive understanding on the
81 sludge generated from different stages in wastewater treatment processes. Properties for
82 sludge handling and storage including physical appearance, pH and density were determined.
83 Characterization of wastes also should consider both physical and chemical properties for
84 applications in thermochemical processes (Arena, 2012). Therefore, physical properties
85 included heating value, proximate analysis, heat capacity and chemical properties included
86 ultimate analysis, functional groups analysis based on FTIR spectra and inorganic
87 compositions were determined for all sludge samples collected. Further analyses were carried
88 out based on measured data included heating value correlation, residual energy analysis, char

residues analysis, mass balance equations, oxidation of inorganic compounds and ash sintering temperatures. Hence, a comprehensive analytical procedure for sludge was proposed with alternative parameters and comparison bases for general sludge characterisation based on the existing literatures and supporting experimental results from collected sludge samples.

2. Material and methods

2.1. Sludge samples collection and pre-treatment

Sludge samples were collected from Water Reclamation Plants (WRPs) in Singapore. There were four existing plants namely Ulu Pandan (U), Changi (C), Jurong (J) and Kranji (K). Five different types of sludge were collected namely primary (P), secondary (S), raw (R), dewatered (D) and dried sludge (Y). At least 25L of liquids sample for P, S and R and 20kg of solids sample for D and Y were collected for each round of sampling. Two batches of sludge samples were collected for Ulu Pandan (Us-R and Us-D) and Changi (Cs-P, Cs-S, and Cs-Y) WRPs for comparison on different time of collection. In total, 14 different sludge samples collected and analysed in this study. Sludge samples collected were dried in oven at 105°C for 24 hours and subsequently milled to pass through a screen of 1.0 mm in diameter. Sludge samples in powder form were then mixed manually to obtain homogenous sample.

2.2. Physical appearance, pH and density analysis

Physical appearance of sludge was observed and recorded based on colour, odour, and structural form. pH test was carried out according to US EPA Method 9054D. Bulk density of the sludge was estimated by dividing the weight of sample measured in a measuring cylinder with a fixed sample volume of 20 cm³. Pellet density of sludge was measured for pellet pressed in a die with 12.17 mm diameter at 5 MPa for 1 minute.

2.3. Physical properties analysis

2.3.1. Heating value analysis

Higher Heating Value (HHV) of sludge was determined by Calorific Bomb (IKA C2000) according to ASTM E711. Lower Heating Value (LHV) could be obtained after deducting energy loss in water vaporisation by using $LHV = HHV - 2.26 \times (9H / 100)$ where H represented the weight percentage of hydrogen in the sample, 2.26 represented the heat of vaporisation of water in MJ/kg and the digit nine referred to the water produced during combustion in relation to the hydrogen content of the sample. HHV and LHV of sludge sample were recorded and calculated in dry basis (db), dry ash free basis (daf), and inorganic contents free basis (icf). The daf basis heating values were calculated based on Ash₅₅₀ content of sludge. The icf basis heating values were calculated based on Total inorganic content (TI) which was the summation of inorganic matter (IM), halogens content and inorganic CHNSO content in sludge. Both daf and icf basis were used to quantify the intrinsic characteristics and improved understanding of the organic matters in sludge. Ash content was frequently used as an approximation to the amount of inorganic compounds in sludge. However, ash content overestimated the inorganic content present in sludge due to the oxidation of inorganic elements as found in this study. Therefore, icf basis was suggested to be used as an improved estimation basis to quantify heating values of organic matters in sludge for comparison analysis.

2.3.1.1. HHV correlation analysis

A unified correlation for calculating the HHV in db of a sample from its elemental composition was developed in previous study (Channiwala and Parikh, 2002) as showed. $HHV_{\text{calculated}} = 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.0151N - 0.0211A$ where C,H,S,O,N and A represent the carbon, hydrogen, sulphur, oxygen, nitrogen and ash mass percentage in the sample respectively. Both data for O determined by direct measurement and by difference method were used in the HHV correlation development and were considered to be interchangeable. However, significant differences could be observed for oxygen content

and inorganic content data determined by different methods for sludge samples in this study. Therefore, two calculations of HHV with the above correlation were carried out. Calculation 1 was based on direct measurement of oxygen content and indirect calculation of inorganic matters (IM). Calculation 2 was based on oxygen contents determined using by difference method and direct measurement of Ash₉₅₀. Two different calculation methods were analysed by using the following statistics parameters. Bias error, $\epsilon_{\text{Bias}} = \text{HHV}_{\text{measured}} - \text{HHV}_{\text{calculated}}$, absolute error, $\epsilon_{\text{Abs}} = \sqrt{(\epsilon_{\text{Bias}})^2}$ and error percentage, $\epsilon_{\%} = \epsilon_{\text{Abs}} / \text{HHV}_{\text{measured}} \times 100\%$.

2.3.1.2. Residual energy analysis

Residual energy analysis was carried out based on the heating values of sludge in db and moisture content of the sludge as received. Residual energy content was determined by $Q_{\text{Residual}} = Q_o - Q_w$ where, total sludge energy content, $Q_o = m_o h_o$ and evaporation energy loss, $Q_w = m_w h_w$ were calculated. m_o and m_w were the mass fraction of solid and moisture respectively and $m_o + m_w = 1$. h_o was LHV in db, and latent heat of evaporation, $h_w = 2.26 \text{ MJ/kg}$. At zero residual energy, moisture content was said to be at the critical level as described by $m_{w,\text{critical}} = 1 - h_w / (h_o + h_w)$ where any reduction of moisture content below this level would result in net positive residual energy for recovery from sludge. However, this theoretical estimation needed to be considered together with practical energy loss during recovery depending on efficiency of the system used. h_o could be replaced by $h_{\text{effective}}$ when net recoverable energy determined. Therefore the practical level of Q_{Residual} and $m_{w,\text{critical}}$ would be lower.

2.3.2. Proximate Analysis

Proximate analysis measured moisture content, volatile matter, fixed carbon and ash content in the sludge according to physical tests. Moisture measured in as received basis by the loss of weight after evaporating the water content at 105°C for 24 hours. Ash contents of the dried samples, Ash₅₅₀ and Ash₉₅₀ were recorded as the weight remained after being

combusted in a furnace at 550°C and 950°C for 3 hour respectively. 550°C was the temperature commonly used to separate between volatile solids and fixed solids in the sludge while 950°C was the temperature used in the proximate analysis of coal and biomass. Organic matters in the sludge would be combusted at 550°C while inorganic contents would be partially decomposed, partially unreacted and partially oxidised to form ash residues. Further decomposition and oxidation would occur as Ash₅₅₀ heated to 950°C as suggested by the results of proximate and ultimate analysis in this study. Volatile matter (VM) of the dried sample was determined as the loss of weight after being heated in crucible using STA 449 Jupiter[®] (Netszch) to 950°C and maintained for 7 minutes in an inert environment with 60ml/min nitrogen gas flow according to ASTM D7582. Multiple heating rates programme with 5, 10, 15, 20, 25 K/min were applied and mean was calculated. Fixed carbon (FC) was estimated by difference from the dry sample mass after subtracted Ash₉₅₀ and VM. However, oxidation of inorganic compounds during ash forming analysis would be expected to cause overestimation of inorganic residues present in char and then underestimation of FC. Fixed Residues (FR) was proposed to improve the estimation on the residues remained in the sludge solid samples after pyrolysis. Fixed Residues (FR) was estimated by difference from the dry sample mass after subtracted inorganic matter (IM) and VM. IM was calculated based on ultimate analysis in this study. Ratio of Ash₉₅₀/IM and apparent degree of oxidation (O_D) describing the oxidation of IM to ash residues were also calculated by assuming the Ash₉₅₀ represented the oxidised IM after combustion. Therefore, $O_D = (Ash_{950} - IM)/IM \times 100\%$. For comparison purposes, CHNS data of char samples at 950°C, Char₉₅₀ was used as representative data to account for the amount of non-inorganic residues. CHNS₉₅₀ calculated based on the CHNS analysis of char produced from sludge pyrolysis in inert nitrogen gas environment at 500°C for 40 minutes and subtracted by the CHNS of Ash₅₅₀ that would decomposed into volatiles at 950°C. The oxygen contents of char samples were assumed to

be negligible because most of the oxygen contents in the sludge were released at 950°C. Most of the oxygen remained in the char would be in the form that bounded with inorganic compounds and be categorised as part of IM.

In order to analyse the impacts of the presence of IM, O_D and the intrinsic distribution ratio, $R=VM/FR$ on the apparent distribution ratio of sludge samples, $R^*=VM/FC$, simulations based on the relationships of these four parameters were developed. Amount of VM released determined by the intrinsic distribution ratio, R after considered the weight of IM. For sample consisted organic matters only $VM/FR = R = R: 1$, therefore $VM = (R/R + 1) \times 100\%$. For sample consisted both organic and inorganic matters, $VM = (100\% - IM) \times (R/R + 1)$ and $Ash = IM \times (O_D/100 + 1)$ for oxidation of inorganic matters. Based on the above stated relationships, $\frac{R^*}{R} = \frac{(100-IM)}{100 + [R - R(\frac{O_D}{100} + 1) - (\frac{O_D}{100} + 1)] \times IM}$ could be derived. Three independent variables which were IM, R and O_D accounted for the variations in the dependent variable R^*/R . Three separate sets of simulations were carried out by using one of the parameter as independent variable and fixing other two parameters as constants using data from proximate analysis in this study as reference values for IM, R and O_D respectively.

2.3.3. Heat capacity analysis

Heat capacity analysis was carried out in Differential Scanning Calorimetry (DSC) of STA 449 Jupiter[®] (Netsch) by using cellulose, aluminium, zinc and gold as reference materials. Heat capacity of sludge was calculated based on the correlation between heat capacity and heat flux measured, $C_s = [(\Phi_s - \Phi_0 / \Phi_{ref} - \Phi_0) \times (m_{ref} / m_s)] C_{ref}$ where C_s and C_{ref} were the heat capacity in kJ/kg-K of sludge samples and reference materials respectively while Φ_s , Φ_{ref} and Φ_0 were the heat fluxes in mW measured by DSC for

samples, reference materials and empty crucible as baseline respectively. m_s and m_{ref} were the mass in mg of sample and reference materials respectively (Höhne et al., 2003).

2.4. Chemical properties analysis

2.4.1. Ultimate analysis

CHNS were determined by using Vario EL cube (Elementar) according to the ASTM E870 and O was determined both by direct measurement using the same equipment and by calculation using the method of by difference. Direct measurement of O was carried out by pyrolysis according to ASTM D5622. Ultimate analysis carried out through direct determination provided the approximately total measurement of the $CHNSO_{Total}$ contents as the summation of both organic and inorganic CHNSO contents. $CHNSO_{Inorganic}$ contents of sludge were determined by ultimate analysis on Ash_{550} and calculated in dry sludge basis. $CHNSO_{Organic}$ was calculated by using $CHNSO_{Total} \cong CHNSO_{Organic} + CHNSO_{Inorganic}$ as mass balance approximation for CHNSO contents in sludge. Testing environment of O direct determination partially measure oxygen from inorganic oxides due to strong resistant to decomposition. Therefore, direct determination of $CHNSO_{Total}$ could approximately represent the total CHNSO of organics and inorganics in sludge other than the inert oxides. Inert oxides were categorized as IM in this study. Significant amount of oxides also formed in ash residues after combustion but due to the strong resistant to decomposition of the oxides, the amount of oxygen added to the ash through oxidation was assumed to be insignificantly increased the oxygen contents in direct measurement of $CHNSO_{Inorganic}$. Therefore, $CHNSO_{Inorganic}$ measured would mainly account for the decomposition of carbonates and sulfates that remained after combustion of sludge at 550°C (Vassilev and Tascon, 2003). In addition to the $CHNSO_{Total}$ measured, sludge also consisted of IM and halogens. Released of halogens through combustion was measured and the IM was calculated by difference. The approximated mass balance for sludge samples could be represented by $CHNS_{Total} +$

$O_{Total} + Inorganic\ Matter + Halogens \cong 100\%$. Quantification of the total amount of inorganics present in the sludge carried out by $Total\ Inorganics \cong CHNSO_{Inorganic} + Inorganic\ Matter + Halogens$. Using by difference method, oxygen contents could also be determined by using $CHNS_{Total} + O_{difference} + Ash_{950} + Halogens \cong 100\%$.

However, determination of O_{Total} and $O_{difference}$ of the sludge samples showed significant deviations based on the results obtained in this study. Both values cannot be used interchangeably. During ash formation analysis, sludge was combusted where high temperature and oxidative environment transformed inorganics into ash residues that remained as solids and into volatile inorganics that released and removed. Mass balance could be described by $Inorganic\ Matter + O_{oxidation} = Ash_{950} + Volatile\ Inorganics$. Assuming negligible volatile inorganics released other than the carbonates and sulfates that already being accounted in $CHNSO_{Inorganic}$ compared to the residues remained during ash formation analysis, then $Inorganic\ Matter + O_{oxidation} \cong Ash_{950}$. This assumption was based on previous studies showing that most of the inorganic compounds of sludge retained in solid residues during thermochemical conversion processes (Fytili and Zabaniotou, 2008; Hernandez et al., 2011). This assumption also supported by the inorganic elements analysis of sludge in this study which demonstrated that most of the inorganic elements in sludge were non-volatile ash forming elements. The deviation found for oxygen contents determined by two different methods could be represented by $O_{Total} - O_{difference} = O_{deviation}$. By using the mass balance equations above, deviations of oxygen contents could be described as $O_{deviation} \cong Ash\ Residues_{950^{\circ}C} - Inorganic\ Matters \cong O_{oxidation}$. Therefore, deviations found in two methods for oxygen contents determination could be accounted by the oxidation of inorganic compounds in sludge. Molecular formula of sludge was determined by converting the dry basis CHNSO contents into normalized molar basis.

2.4.2. Functional groups analysis

FTIR spectra of sludge and Ash₅₅₀ were collected at Mid-infrared region (MIR) from 4000cm⁻¹ to 600cm⁻¹ by using Attenuated Total Reflection (ATR) with diamond crystal in FTIR System (Bruker). Spectra were analyzed according to library database and previous publications (Smidt and Meissl, 2007; Smith, 1998).

2.4.3. Inorganic compositions analysis

2.4.3.1. Inorganic elements analysis

Sludge samples weighted 0.5 ±0.05g were combusted in Calorific Bomb (IKA C2000) with 5ml of Na₂CO₃ solution (50g/L) according to ASTM D808 then tested by Ion Chromatography System (Dionex ICS-1100) to quantify fluoride, chloride and bromide contents. For other inorganic elements analysis, sludge samples were treated with acids digestion in Ethos One Microwave Digestion System (Milestone) according to US-EPA Method 3052 and DIN EN 13346 then send to Optima 8000 ICP-OES Spectrometer (Perkin-Elmer) for inorganic elements detection. Inorganic elements were categorised into three groups which were major ash forming elements, minor elements, and trace elements according to the respective mass composition present in the sludge. Major ash forming elements and their corresponding oxides in sludge identified in previous studies were SiO₂, Al₂O₃, TiO₂, Fe₂O₃, CaO, MgO, Na₂O, K₂O, and P₂O₅ (Dunnu et al., 2010; Liang Wang et al., 2012; Werle, 2014). Silica in sludge was calculated based on the weight difference between Ash₉₅₀ and other oxides. It was assumed that inorganics other than major ash forming elements were present in an insignificant amount in Ash₉₅₀. Silicon element in sludge was calculated based on its weight% in silica. Inorganic elements detected that having average weight% of more than and less than 50 mg/kg in dry sludge basis were categorised in minor and trace elements respectively.

2.4.3.2. Ash sintering analysis

Fusibility test adequately predicted sintering of ashes from biomass therefore adopted in this study to analyze the sintering characteristics of ash residues from sludge samples (Llorente and Garcia, 2005). Calculation of ash residues sintering characteristic temperatures were carried out with reference to ASTM D1857 where temperatures of four fusion stages were considered. The four different temperatures were initial deformation temperature (IDT), softening temperature (ST), hemispherical temperature (HT), and fluid temperature (FT). The difference between IDT and FT was calculated as fusion temperature range. Base-to-acid ratios calculated by $R_{B/A} = \text{Base}/\text{Acid}$ and $R_{B+P/A} = \text{Base}_{\text{with phosphate}}/\text{Acid}$ were used as indicators to estimate the sintering characteristics of ash residues. Base was the mass summation of basic oxides included Fe_2O_3 , CaO , MgO , Na_2O , and K_2O with and without P_2O_5 while Acid was the mass summation of acidic oxides included SiO_2 , Al_2O_3 , and TiO_2 . Linear correlations of $R_{B/A}$ and $R_{B+P/A}$ with the four fusion temperatures were formed based on the data from previous studies on fusibility of ash residues from sludge in both oxidizing and reducing environments (Dunnu et al., 2010; Liang Wang et al., 2012; Werle, 2014) and were used to calculate fusion temperatures of the sludge samples collected.

3. Results and Discussion

3.1 Physical appearances, pH and density

Physical appearances of dried and milled sludge samples collected from WRPs were comparable to previous study (Sanin et al., 2011). Results showed that type of sludge which corresponding to the treatment method was the main factors affecting the physical appearances. Primary and raw sludge were brown in colour with strong odour. Secondary sludge was yellowish brown in colour with slight odour. Dewatered and dried sludge were blackish brown in colour with musty smell. Considering the physical structure of sludge, secondary sludge was in fluffy form and different from granular powder form of primary sludge and anaerobic digested sludge. Raw sludge was having the mixed appearance of

primary and secondary sludge. Results showed that anaerobic digested sludge was stabilized with less odour compared to pre-digested sludge. pH was considered as one of the important aspects for safe handling and storage. pH of sludge was slightly acidic and ranged from 4.44 to 5.84 comparable to previous study (Hernandez et al., 2011). The slightly acidic nature of sludge would not cause problems to the handling process in using sludge as feedstock for subsequent thermochemical conversion. Bulk and pellet density of the sludge were important parameters in the aspect of sludge transportation and the design of feeder to the reactor (Dogru et al., 2002). Bulk density of sludge samples varied significantly and measured at mean and standard deviation (SD) of $0.66 \pm 0.22 \text{ g/cm}^3$ with relative standard deviation of 33.67 RSD% comparable to previous study (Ruggieri et al., 2008). Primary sludge showed highest bulk density of 0.93 g/cm^3 while secondary sludge showed lowest bulk density of 0.22 g/cm^3 . Bulk density of the raw sludge was lower than anaerobic digested sludge probably due to the present of low density secondary sludge. The pellet density of different sludge samples were more consistent and measured at $1.38 \pm 0.09 \text{ g/cm}^3$ with 6.58 RSD%. Pellet density of sludge increased with higher ash content. Strong linear correlation with $R^2 = 0.8176$ existed between Ash_{950} and pellet density but weak linear correlation of $R^2 = 0.2922$ found between Ash_{950} and bulk density. This suggested that the physical forms played a more important role in determination of bulk density for sludge. Significant variation existed in bulk densities of different type of sludge and could cause complex handling and transportation issues. Variation in bulk density mainly resulted by the type of the sludge and partially by the ash contents. This issue could be solved by pelletizing. Transportation volume could also be reduced by 50% with high consistency since the density doubled in average during pelletizing and highly comparable after pelletized.

3.2 Physical properties

3.2.1. Heating value analysis

Heating value was considered as one of the important parameters for energy audit and modelling in thermochemical conversion processes (Dogru et al., 2002). Energy efficiency could be calculated based on heat generated in incineration, chemical energy stored in syngas in gasification and energy distribution in char residues, liquids and gases during pyrolysis with respect to the data of heating values. Higher Heating Value (HHV) and Lower Heating Value (LHV) of sludge were showed in dry basis (db), dry ash free basis (daf), and inorganic content free basis (icf) in Table 1. HHV and LHV (db) of sludge samples varied significantly at 17.41 ± 2.36 MJ/kg with 13.56 RSD% for HHV and at 16.23 ± 2.22 MJ/kg with 13.67 RSD% for LHV. Inverse correlations were found for both HHV and LHV in db with the ash content and total inorganic content (TI) since the heating value was contributed mainly by organic matters in sludge. Present of inorganics was the main factor causing significant variation in dry basis HHV and LHV as Ash₅₅₀ varied from 15.28wt% to 51.06wt% and TI varied from 10.71wt% to 44.09wt% for different sludge samples. Heating values of sludge higher than 12 MJ/kg indicated that all dry sludge samples were suitable for thermochemical conversion processes (Arena, 2012; Tsai and Chou, 2006). Heating values in daf and icf basis were more consistent with 5.38 RSD% in average. The consistency in HHV and LHV of both daf and icf basis showed that the energy contents of organic matters among different sludge samples were similar. As Ash₅₅₀ overestimated the amount of inorganics in the sludge due to oxidation, daf basis heating value was higher than the icf basis. Therefore, icf basis proposed as an alternative basis to estimate and compare heating values of organic matters in sludge. The LHV in icf basis of 20.91 MJ/kg also found to be closely comparable to previous study that estimated LHV of organic matters in sludge to be 19.62 kJ/kg organics (Ptasinski et al., 2007). Sludge after Anaerobic Digestion (AD) was having lower heating values in dry basis mainly because of the present of more inorganics. Removal of organic matters during AD caused concentration effect on inorganics. Mean values of HHV and LHV in daf and icf basis

of sludge samples before AD were slightly higher than sludge samples collected after AD indicated AD process transformed the organic matters into compounds with slightly lower heating values.

3.2.1.1. HHV correlation analysis

Results of HHV correlation were also showed in Table 1. By using oxygen content directly measured instead of determined from the by difference method and by using IM instead of Ash₉₅₀ to represent the inorganics in sludge, mean of $\epsilon_{\%}$ calculated was reduced from 5.11% to 3.86%. Bias errors analysis showed that data of $\epsilon_{\text{Bias}1}$ were randomly distributed with positive and negative values for all sludge samples but data of $\epsilon_{\text{Bias}2}$ were negative for most sludge samples. This observation demonstrated that Calculation 2 was making over-predictions as observed in previous study for sludge (Channiwala and Parikh, 2002). Mean values of $\epsilon_{\text{Bias}1}$ and $\epsilon_{\text{Bias}2}$ were 0.02 MJ/kg and -0.66 MJ/kg respectively also supported the observation made. Calculation 2 overestimated HHV of sludge mainly because of the underestimation of oxygen content as discussed in the ultimate analysis of this study. Used of IM helped to reduce the underestimation on HHV calculated by reducing the overestimation of inorganics in sludge caused by oxidation during ash forming experiment. ϵ_{Abs} less than 1.0 MJ/kg in average indicated the usage of HHV correlation was acceptable. Results also indicated that sludge was comparable to other feedstock when correlation between heating value and elemental composition was considered.

3.2.1.2. Residual energy analysis

Dewatered and dried sludge showed positive residual energy contents from 0.24 to 12.44MJ/kg indicated net recoverable energy contents while wet sludge samples included primary, secondary and raw sludge showed negative residual energy contents of -0.89 to -1.91MJ/kg indicated the need of moisture removal before energy recovery. Critical moisture content, $M_{w,\text{critical}}$ calculated based on LHV (db) of sludge samples were ranging from 84.46

to 89.54 wt%. In order to be able to recover energy from the sludge, moisture content of sludge needed to be reduced to below the critical level. Based on the equations of Q_{Residual} and $M_{w,\text{critical}}$, recoverable energy from sludge reduced greatly and the demand of LHV (db) of sludge increased tremendously when the moisture content of sludge above 80wt%. Therefore, further improvement on dewatering processes and the potential of re-utilization of the water vapour generated during drying were important aspects to be considered to sustain the wastewater treatment system and energy recovery from sludge.

3.2.2. Proximate analysis

Results of the proximate analysis of all the sludge samples collected showed in Table 2. Moisture contents of the wet sludge samples included raw, primary and secondary sludge from different plants were high and ranged from 93.30wt% to 98.40wt% as received. Moisture contents of sludge dewatered by mechanical dewatering processes were varied significantly and ranged from 73.40wt% to 86.40wt%. Thermal drying reduced the moisture contents of two batches of dried sludge from Changi WRP to an average of 5.60wt%. Dewatering facilities existed in all four WRPs but thermal dryer operating with energy supplied by combustion of biogas generated from onsite anaerobic digestion existed only at Changi WRP. Thermogravimetric Analysis (TGA) showed that VM was generally the most abundance components in sludge. VM in db ranged from 47.56wt% to 71.07wt% for different sludge samples. FC and FR were important parameters used to determine the non-inorganic residues remained in the char after the sludge was pyrolysed at 950°C in an inert environment. FC underestimated the non-inorganic residues caused by the apparent weight gained of inorganics in char by oxidation when combusted. FR and IM were proposed to replace FC and Ash₉₅₀ to provide an improved quantification on the residues remained after pyrolysis. Calculated data showed that FC of sludge showed mean of $10.51 \pm 3.32\text{wt}\%$ while FR showed much higher mean of $18.71 \pm 3.47\text{wt}\%$. Calculated FC data underestimated the non-

inorganic residues in char as represented by the $\text{CHNS}_{\text{char}}$ from -9.40wt% to -2.46wt% with mean difference of -6.35wt%. FR data randomly under- and over-estimated non-inorganic residues in char from -2.66wt% to 5.96wt% with mean difference of 1.85wt%. FR slightly overestimated the residues in average could be accounted by the random errors of the experiments and the heterogeneity of sludge characteristics. Therefore, use of FR and IM for quantification of non-inorganic and inorganic residues in char after thermal degradation in inert environment could improve the accuracy of the estimation.

Though ash contents could lead to errors in estimation of FC in char and heating values of organic matters in sludge as discussed earlier, Ash_{550} and Ash_{950} were considered as important engineering parameters that accurately determined the amount of solid residues remained after the samples being treated in oxidative thermochemical conversion processes such as incineration and air gasification at different temperature. Ash_{550} and Ash_{950} of sludge varied significantly for different sludge samples. Ash contents found to be higher in anaerobic digested sludge mainly caused by biodegradation of organic matters during AD. Ash_{550} generally recorded higher values than Ash_{950} , except for primary sludge samples from Changi WRP for both batches. Reduction of the weight for Ash_{950} was resulted by the decomposition and volatilization of carbonates, sulphates and volatile inorganics at higher temperature. However, both oxidation and decomposition of inorganics occurred at elevated temperature in oxidative environment as observed in mineral phase transformation study of sludge (Hernandez et al., 2011). The results of C-P and Cs-P samples suggested that more weight gained from oxidation of inorganic matters at 950°C and less weight loss from decomposition above 550°C. This observation supported that measurement of ash contents overestimated the inorganic contents in sludge and also suggested the application of different temperatures during ash contents analysis for more accurate estimation of ash residues remained according to the operating temperature of thermochemical system.

VM/FC or VM/FR ratios were indicators for the distribution of volatile matters released and char residues formed. VM/FC ratio of sludge samples were relatively high compared to common feedstock in thermochemical conversion processes (Channiwala and Parikh, 2002). For coal, VM/FC ratios measured were very low and ranged from 0.01 to 1.07. For biomass and other wastes, VM/FC ratios ranged from 3.16 to 5.21. For sludge samples in this study, VM/FC ratios varied significantly from 4.31 to 11.34 with mean and SD of 6.45 ± 2.24 much higher than the other feedstock. On the other hand, VM/FR ratios ranged from 2.44 to 5.40 with mean and SD of 3.40 ± 0.78 comparable to the biomass and other wastes. This observation further supported the hypothesis of FC underestimation for sludge characterisation. Compared to sludge, underestimation of FC in the char caused by the oxidation of inorganics was insignificant in coal and other biomass could be due to the following reasons. Ash contents were generally lower in coal and biomass compared to sludge and therefore the impacts of inorganics oxidation on VM/FC ratio were lower too. Decomposition of inorganics at elevated temperature compensated for the oxidation of remaining inorganics in coal therefore no significant apparent weight gained by ash residues. Theoretical amount of ash contents in coal were more than IM. However, ash contents measured were generally comparable or lower than IM due to the decomposition and volatilization of inorganics in coal (Vassilev and Tascon, 2003). Inorganics in sludge were in leachable organic fractions which could be easily oxidised (Hernandez et al., 2011). Mean values of ratio of $\text{Ash}_{950}/\text{IM}$ at 1.47 ± 0.20 and O_D at $47.07 \pm 19.59\%$ indicated significant oxidation of inorganics could be observed. Simulations based on the proposed intrinsic distribution ratio, $R = \text{VM}/\text{FR}$ were developed to illustrate the above reasons that caused the sludge to behave distinctively. Simulations of R^*/R at (a) $\text{O}_D = 45\%$ with variations in IM and R, (b) $\text{IM} = 20\text{wt}\%$ with variations in R and O_D , and (c) $R = 3.50$ with variations in O_D and IM were showed in Figure 1. Simulations were developed using mean values of the data

obtained from sludge which were $IM = 19.65\text{wt}\%$, $R = 3.40$, and $O_D = 47.07\%$ as reference values. All simulations showed that the deviation of R^* from R increased as the IM , R and O_D increased. Simulations demonstrated that the deviations became significance at $R^*/R > 1.20$ when in general, $IM > 10.00\text{wt}\%$, $R > 1.00$, and $O_D > 20.00\text{wt}\%$ respectively. Proximate analysis showed that characteristics of sludge were in the range where significant deviations observed.

3.2.3. Heat capacity analysis

Heat capacity was considered as an important parameter to calculate the energy requirement for heating the feedstock from initial to operating temperature in thermochemical processes for different temperatures used in pyrolysis, gasification and incineration respectively. Heat capacities of all sludge samples increased gradually as temperature elevated similar to the observation found in previous studies on biomass (Chen et al., 2014; Dupont et al., 2014). Mean heat capacity was calculated based on the average of all recorded data at different temperature. Heat capacity of sludge calculated at mean and SD of $1.68 \pm 0.26 \text{ J/g-K}$ lower than the assumed value of around 2.00 J/g-K made in previous studies (Agarwal et al., 2015; Kim and Parker, 2008). However, significant variation could be observed as heat capacity varied from 1.33J/g-K to 2.18J/g-K for different sludge samples. Direct measurement of the heat capacity for the feedstock therefore improved the accuracy of energy audit and modelling for different sludge samples used as feedstock. Heat capacity of sludge before AD measured at mean and SD of $1.78 \pm 0.27 \text{ J/g-K}$ higher than after AD at $1.55 \pm 0.21 \text{ J/g-K}$. This observation mainly caused by present of more inorganic contents in sludge after AD as heat capacity of inorganics generally lower than organics (Kim and Parker, 2008).

3.3 Chemical Properties

3.3.1. Ultimate analysis

Results for ultimate analysis of sludge by direct measurements were showed in Table 3. Carbon (C), Hydrogen (H), Nitrogen (N) and Oxygen (O) contents of sludge samples in Singapore were comparable to other studies but Sulphur (S) contents were relatively higher (Dunnu et al., 2010; Ptasiński et al., 2007). Based on the ultimate analysis for sludge samples, C was the dominant element measured at $38.08 \pm 5.15\text{wt}\%$ followed by O at $25.75 \pm 2.68\text{wt}\%$, H at $5.71 \pm 0.72\text{wt}\%$, N at $5.29 \pm 1.29\text{wt}\%$ and S at $5.17 \pm 0.43\text{wt}\%$ according to the weight% in db. Based on ultimate analysis for Ash₅₅₀ recorded in dry sludge basis, S was the dominant element measured at $1.46 \pm 0.53\text{wt}\%$ followed by O at $0.71 \pm 0.38\text{wt}\%$, C at $0.22 \pm 0.06\text{wt}\%$, N at $0.04 \pm 0.01\text{wt}\%$, and H at $0.01 \pm 0.00\text{wt}\%$. By comparing the two ultimate analyses, O and S contents were observed as partially contributed by the inorganics in sludge samples at 5.67% and 13.54% respectively. The C, H and N contents were mainly contributed by organic matters. Contribution from inorganics in sludge on total C, H and N contents were in average at only 0.58%, 0.18% and 0.78% respectively. By using ultimate analysis for sludge and ash samples, CHNSO contents of the organic matters in sludge samples could be calculated by difference. The data for CHNSO_{organic}, CHNSO_{inorganic}, CHNSO_{Total}, halogens contents, inorganic matters (IM) and total inorganic contents (TI) were also showed in Table 3. By determination of CHNSO_{Total} and halogens contents released during combustion, IM could be calculated by approximated mass balance as described. IM represented the main part of the inorganic compounds present in sludge which included the inorganic elements in various forms included inert oxides, heavy metals, minerals, and volatile inorganics. Compared to the ash contents measured for sludge samples, IM and TI contents were lower indicated the apparent weight gained during ash formation analysis. Therefore, IM and TI were proposed to be used as indicators to represent the amount of inorganics in sludge samples. IM was suitable to be used as approximate to account for the inorganics remained in the char residues after pyrolysis at 950°C while TI was suitable to be used as approximate to

account for the total inorganics initially present in the sludge samples. CHNSO contents were important input used to form molecular formula for sludge and used in simulations of thermochemical conversion processes (Domínguez et al., 2006). Molecular formula of sludge samples were calculated based on the data from ultimate analysis and showed in Table 4. The mean of the ratios for H/C at 1.80, O/C at 0.51, H/O ratio at 3.55 and H/N at 15.88 were comparable to previous studies for different sludge samples analysed (Ptasinski et al., 2007; Ruggieri et al., 2008). Variations in molecular formula could be observed for different sludge samples but most of them showed high similarities. The mean molecular formulas summarized for sludge, organic matters and ash residues were determined as $C_{1.00}H_{1.80}N_{0.12}S_{0.05}O_{0.51}$, $C_{1.00}H_{1.81}N_{0.12}S_{0.04}O_{0.48}$ and $C_{1.00}H_{0.70}N_{0.15}S_{1.16}O_{5.11}$ respectively. Molecular formulas for sludge sample and organic matter calculated were highly similar since $CHNSO_{Inorganic}$ only represented small part of the $CHNSO_{Total}$. Significantly lower H, slightly higher N and significantly higher S and O observed for ash residues indicated present of mainly carbonates, nitrates and sulphates with inorganic bounded moisture contents but absent of C-H functional groups generally found in organic matters.

Results of oxygen contents determined by two different methods were also showed in Table 4. Significant differences quantified as $O_{deviation}$ could be observed between O_{Total} and $O_{difference}$. The differences in O contents determined could range from 5.09wt% to 11.37wt% with mean and SD of 8.20 ± 2.43 wt% in db. Since $O_{difference}$ calculated based on the Ash_{950} , $O_{deviation}$ mainly caused by the apparent weight gained of inorganics during the ash formation analysis as suggested by the mass balance equations developed. $O_{difference}/O_{Total}$ ratio showed an average of 0.68 ± 0.11 indicated the calculated $O_{difference}$ only accounted about 68% in average of the total O contents present in the sludge samples and O/C ratio in the molecular formula of sludge would reduced from 0.51 to 0.31. Slightly higher of $O_{deviation}$ for sludge samples after anaerobic digestion (AD) could be caused by higher amount of IM therefore

more oxidation of inorganics occurred. Therefore different O contents should be applied according to the reaction environment of thermochemical systems. Total O contents released from sludge and available in the thermochemical system would be represented by O_{Total} if oxidation reactions of inorganics were insignificant. However, if sludge samples were treated in an oxidation environment similar to the ash formation analysis then O_{Total} would still representing the total O contents released from the sludge samples but $O_{\text{difference}}$ would be more suitable to account for the O contents available in the system for thermochemical reactions other than the inorganics oxidation. Therefore, direct measurement of O_{Total} was recommended for sludge molecular formula formation and modelling analysis for pyrolysis and gasification in reducing environment such as CO_2 and H_2O . Indirect calculation of $O_{\text{difference}}$ was recommended for combustion and gasification with the present of oxidative environment for system modeling, stoichiometric analysis and equivalence ratios calculations. The phenomenon of significant $O_{\text{deviation}}$ determined for sludge samples in this study was distinctive when compared to other feedstock such as lignocellulosic biomass and coal. High oxygen contents and low amount of inorganic matters were generally found in lignocellulosic biomass causing the $O_{\text{oxidation}}$ to be insignificant compared to the O_{Total} present in the biomass. Decomposition of inorganic components in coal caused the mass of ash residues determined comparable to the initial mass of inorganics (Vassilev and Tascon, 2003). Therefore no significant underestimation of oxygen contents could be observed in coal. Low oxygen and high carbon contents in coal led to high stoichiometric requirement and oxygen input for complete combustion also reduced the importance of initial oxygen contents as compared to sludge.

3.3.2. Functional groups analysis

FTIR spectra provided information of functional groups detected and indirectly indicated the group of chemical compounds present. This information was more crucial for

advanced thermochemical system such as pyrolysis and gasification as characteristics of products from advanced thermochemical conversion processes were important for subsequent utilization of pyrolysis oil, char, and syngas (Zhuo et al., 2000). Figure 2 showed the FTIR spectra of all sludge samples collected and Ash₅₅₀. Qualitative similarities and quantitative variations found among different sludge samples and residues were comparable to previous research (Grube et al., 2006). By comparing the FTIR spectra of sludge samples and ash residues, the contribution of peaks by organic and inorganic could be identified and differentiated to provide better understanding on collected spectra. However complex mixture of various compounds in waste caused overlapping of peaks and diverse peaks shifting in FTIR spectra (Francioso et al., 2010). Multiple functional groups could contribute to a single peak observed in FTIR spectra and different chemical compounds could presence for a single functional group identified. Therefore, direct determination of chemical compounds and exact differentiation of the detected functional groups were difficult for waste mixtures by using FTIR analysis. Analysis carried out below aimed to provide as much information on functional groups and chemical compounds in sludge samples as possible.

Inorganic bounded O-H groups at 3700 and 3620 cm⁻¹ could be observed in sludge samples but not in ash residues. It showed that residual moisture remained in the sludge after drying at 105°C but removed after combustion at 550°C. Broad peaks at 3600–3100 cm⁻¹ region could be contributed by O-H and N-H functional groups suggested the present of alcohols, acids, amides and amines. Multiple peaks showed at 3100–2600 cm⁻¹ region were caused by C-H groups of unsaturated hydrocarbons and aromatics at 3076cm⁻¹ and saturated hydrocarbons, ethers, and lipids at 2925 cm⁻¹. C=O functional groups could be observed for aldehydes, ketones, carboxylic acids, and esters at 1710cm⁻¹. C=O and N-H groups for amides and proteins observed at 1635cm⁻¹ 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 carboxylic 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 could be observed in the region of $1250\text{--}950\text{ cm}^{-1}$ for both sludge samples and ash residues. By 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. By considering inorganic composition and ash residues of sludge, peaks at 1080 cm^{-1} and 1008 cm^{-1} corresponding to the inorganic functional groups in phosphates, silicates, sulphates, and clay minerals. In the region of $850\text{--}600\text{ cm}^{-1}$, 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} . In general, broad and overlapping peaks were observed throughout the FTIR spectra of sludge samples and ash residues suggested that complex mixture present in the waste and only apparent peaks could be identified. Therefore, extraction and isolation procedures would be required to separate different organic composition in sludge for better FTIR identification and more detail analysis on chemical compounds present in sludge samples.

3.3.3. Inorganic composition analysis

3.3.3.1. Inorganic elements analysis

Inorganic compositions analysis provided basic data for pollution concerns of inorganics, ash residues expected to be generated and also potential of inorganics in participating in pyrolysis and gasification processes by promoting char formation during pyrolysis and catalytic reactions during gasification (de Lasa et al., 2011; Fonts et al., 2012). Summary of inorganic elements in sludge was showed in Table 5. Fluoride, chloride and bromide were detected and the summation of these elements was considered as total halogens released. Halogen contents determined were representing only the halogens that released during combustion. Halogens remained as solid form in ash residues were categorised as part of IM. Determination of halogens released provided the basis for pollution analysis and helped to improve the mass balance equations and theoretical calculations when calculating the IM and $O_{\text{difference}}$. Results showed that total halogens released during combustion varied among different sludge samples collected at $0.34 \pm 0.16\text{wt}\%$ in average. Major ash forming elements detected were similar to previous studies (Dunnu et al., 2010; Liang Wang et al., 2012; Werle, 2014). The measurements of inorganic elements present in sludge were important data to be used as basic information to analyse the potential of pollutions, risk of ash sintering and the usability of the ash residues formed after thermochemical conversion processes. In general, the contents of inorganic elements detected were quantitatively varying among different sludge samples but qualitatively similar. For major ash forming elements determined, Si, Al, Fe, Ca, and P were present in relatively higher amount in sludge samples while Ti, Mg, Na and K were present with less than $1.00\text{wt}\%$ in dry basis in average. For minor elements detected in sludge samples, Cu and Zn were present in relatively higher amount with more than 1000 mg/kg in average. For trace elements detected, Pb, Co, Mo, and V were present in higher amount with more than 10 mg/kg in average. Sludge samples from Jurong WRP were having significantly more minor and trace elements which consisted of heavy metals such as Cu, Zn, Cr, Ni and Pb compared to all other WRPs. This observation

mainly caused by the present of higher amount of inorganic compounds contributed from the influent of wastewater from industrial sources. Summary also showed that most of the inorganic elements present in the sludge samples were non-volatile ash forming elements at $14.77 \pm 4.97\text{wt\%}$ in db and $96.78 \pm 2.49\%$ in relative composition, followed by minor elements at $0.55 \pm 0.63\text{wt\%}$ (db) and $3.14 \pm 2.44\%$ and trace elements at $0.01 \pm 0.02\text{wt\%}$ and $0.07 \pm 0.06\%$. In order to further explain and understand the oxidation of inorganic compounds in sludge during ash formation analysis, correlations were established between O_D and inorganic elements present in sludge as illustrated in Figure 3. Relative weight% of inorganic element was calculated by using $\text{Relative Weight\%} = (\text{Welement}/\text{IM}) \times 100\%$. No significant correlation could be formed for individual elements but strong correlations were found when considered the summation of all inorganic elements detected or major ash forming elements with and without silica (Si) based on the results of inorganic compositions analysis. Strong positive correlations indicated that as relative weight% of inorganic elements increased, O_D would also increase. IM represented the inorganic contents in sludge after excluding $\text{CHNSO}_{\text{Inorganic}}$ and combustion released halogen contents. As the summation of detected inorganic elements approaching IM contents calculated then the oxygen contents bounded as oxides in IM would become lesser. Therefore the inorganic elements were in less oxidised forms and could participate in more oxidation reactions during combustion which resulted in higher O_D observed.

3.3.3.2. Ash sintering analysis

Fusion temperatures estimated by using $R_{B/A}$ and $R_{B+P/A}$ were highly similar with less than 50°C difference in average. Based on the calculation, IDT of sludge samples estimated at $1194 \pm 54^\circ\text{C}$, ST at $1218 \pm 24^\circ\text{C}$, HT at $1349 \pm 40^\circ\text{C}$ and FT at $1424 \pm 50^\circ\text{C}$ in average comparable to previous studies (Chiang et al., 2011; Petersen and Werther, 2005). However significant variations of about 150°C among different sludge samples could be observed.

Slightly higher of $R_{B/A}$ and $R_{B+P/A}$ could also be observed for sludge samples before anaerobic digestion which led to lower fusion temperatures. However these differences were relatively small and could be caused by the variations in the wastewater influent. More detail analysis needed to further clarify the impacts of the fluctuations in characteristics of inorganics to the ash sintering in order to optimize the utilization of sludge in thermochemical conversion processes. Low ash fusion temperature compared to other biomass such as wood which had a much higher initial deformation temperature at 1394°C was one of the main concerns in sludge gasification (Seggiani et al., 2012). High temperature in gasifier could produce higher quality syngas and higher H_2 to CO ratio in product gas but faced with the risk of ash sintering. Undesired ash sintering could cause declination in energy efficiency, increased in maintenance cost and frequent unscheduled shutdown of the system (Dogru et al., 2002; Liang Wang et al., 2012). Gasification with uniform operating temperature that was lower than ash slagging temperature reduced the risk of sintering and volatilization of inorganic elements into syngas (Lijun Wang et al., 2008). Therefore, improvements on performance for sludge thermochemical conversion at lower operating temperature or avoidance of local overheating would be beneficial in both ash handling issues and energy efficiency considerations. Detail feedstock characteristics analysis, innovative design on thermochemical process, proper selection of gasification agents and catalyst could contribute to this improvement. IDT and FT indicated the initial and complete deformation of ash residues at different temperature respectively. Therefore, IDT should be considered when ash sintering needed to be avoided while FT should be considered if sintered ash residues were expected as by-products. Fusion temperature range of the sludge samples collected found to be at $230 \pm 23^{\circ}\text{C}$ in average. Large fusion temperature range indicated the present of inorganic components that having significantly different melting temperatures. Care needed to be taken when estimating fusion temperatures of feedstock for thermochemical conversion based on

inorganic elements analysis. Ash fusion temperature could be depending on both chemical and mineral composition (Dunnu et al., 2010). In addition, degree of alteration on ash fusion temperature by individual element was not accounted in the application of ratios as indicators. Therefore, estimations of fusion temperature based on oxides ratios such as Base-to-Acid ratios ($R_{B/A}$ and $R_{B+P/A}$) were only applicable to samples with similar distribution of inorganic elements and mineral characteristics of the inorganic components.

4. Conclusion

In conclusion, sludge generated in Singapore WRPs could be classified as suitable feedstock for thermochemical conversion processes with 77.58% organic contents and LHV of 16.24MJ/kg in dry basis average. Comprehensive characterisation provided concrete data for optimisation and modelling in thermal treatment of sludge. Analytical procedure proposed in this study was comparable to existing characterisation methods and could be applied directly and complementary for sludge analysis. Qualitative similarities and quantitative variations were found in all the analyses carried out for 14 different sludge samples collected and could be accounted by differences in organic and inorganic compositions present. Existing characterisation methods for determination of sludge physical and chemical properties were analysed and reviewed using collected samples. Significant deviations were observed in oxygen contents determination, char residues analysis, estimated heating values of organic matters in sludge and other parameters related to the quantification of ash residues caused by decomposition of $CHNSO_{Inorganic}$ and oxidation of inorganic compounds. Results in this study showed that $O_{difference}$ accounted for only 68.13% of O_{Total} in sludge, FC accounted for only 56.17% of FR in char residues, HHV and LHV in daf basis were higher than in icf basis by 2.02 MJ/kg and Ash_{950} contents higher than IM by 47.07% in average. Therefore alternative parameters and comparison basis included FR, IM, TI and icf were proposed for

better estimation, reliable comparison and improved understanding on thermochemical characteristics of sludge.

Comprehensive characterisation of sludge for thermochemical conversion processes carried out in this study also suggested the applications of different parameters and quantification methods for incineration, pyrolysis and gasification processes respectively due to differences in operating conditions and reacting environments where temperature and present of oxygen were two most important conditions to be considered for the properties discussed in this study. Distributions of sludge organic and inorganic components in inert (pyrolysis) and oxidative (combustion) environments at varying temperatures were significantly different while in gasification it would show intermediate distributions between pyrolysis and combustion depended on the gasifying agents used and operating conditions applied. Ash₅₅₀ and Ash₉₅₀ could be used to determine amount of solid residues remained after sludge thermally degraded in oxidative environment such as incineration and air gasification at different temperatures. IM was suitable to be used as an approximate to account for inorganics remained in char residues after pyrolysis at 950°C while TI was suitable to be used as an approximate to account for total inorganics initially present in sludge. Distinctive and complex characteristics of sludge also suggested importance of further fundamental research on compositions and thermal degradation behaviours studies.

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List of symbols and abbreviations

AD Anaerobic digestion

732	Ash ₅₅₀	Ash residues remained after combustion at 550°C
733	Ash ₉₅₀	Ash residues remained after combustion at 950°C
734	Char ₅₀₀	Char solids remained after pyrolysis in inert environment at 500°C
735	Char ₉₅₀	Char solids remained after pyrolysis in inert environment at 950°C
736	C _p	Heat capacity at constant pressure
737	CHNSO _{Inorganic}	CHNSO contents of Ash ₅₅₀
738	CHNSO _{Total}	Total CHNSO contents in sludge
739	db	Dry basis
740	dsb	Dry sludge basis
741	ε _{Bias}	Bias error
742	ε _{Abs}	Absolute error
743	FR	Fixed residues
744	FT	fluid temperature
745	HT	hemispherical temperature
746	icf	Total inorganic contents free basis
747	IDT	Initial deformation temperature
748	IM	Inorganic matters
749	$m_{w,critical}$	Critical moisture level at zero residual energy content
750	O _D	Apparent oxidation degree
751	$O_{deviation}$	Difference between O _{Total} and O _{difference}
752	O _{difference}	Oxygen contents in sludge calculated by difference
753	$O_{oxidation}$	Difference between IM and Ash ₉₅₀
754	O _{Total}	Oxygen contents in sludge determined by direct measurement
755	$Q_{Residual}$	Residual energy content
756	R	Intrinsic distribution ratio, VM/FR

757	R*	Apparent distribution ratio, VM/FC
758	R _{B/A}	Base (without phosphate)-to-Acid ratio of inorganic oxides
759	R _{B+P/A}	Base (with phosphate)-to-Acid ratio of inorganic oxides
760	ST	Softening temperature
761	TI	Total inorganic contents
762	WRP	Water reclamation plant
763	wt%	Weight percentage

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Table 1: HHV and LHV in db, daf and icf basis and HHV by Calculation 1 and 2 of sludge.

Sample Label	HHV (MJ/kg)			LHV (MJ/kg)			Calculation 1, MJ/kg				Calculation 2, MJ/kg			
	db	daf	icf	db	daf	icf	HHV 1	$\epsilon_{\text{Bias 1}}$	$\epsilon_{\text{Abs 1}}$	$\epsilon_{\% 1}$	HHV 2	$\epsilon_{\text{Bias 2}}$	$\epsilon_{\text{Abs 2}}$	$\epsilon_{\% 2}$
U-R	20.49	24.19	22.95	19.35	22.61	21.45	18.94	1.55	1.55	7.55	19.39	0.95	0.95	4.61
U-D	17.41	24.18	21.19	16.15	22.43	19.65	18.57	-1.16	1.16	6.67	19.51	-2.29	2.29	13.14
C-P	17.53	23.93	21.92	16.34	22.30	20.43	17.51	0.02	0.02	0.11	18.33	-0.64	0.64	3.63
C-S	19.66	24.17	22.34	18.34	22.55	20.84	20.14	-0.49	0.49	2.48	20.75	-1.24	1.24	6.32
C-Y	14.47	23.85	21.62	13.48	22.22	20.13	14.18	0.29	0.29	2.01	14.90	-0.52	0.52	3.58
J-R	17.13	26.96	23.50	15.92	25.06	21.84	17.55	-0.42	0.42	2.45	18.45	-1.57	1.57	9.17
J-D	13.19	26.95	23.59	12.36	25.26	22.11	11.91	1.28	1.28	9.70	12.70	0.17	0.17	1.30
K-R	20.52	26.59	24.14	19.19	24.87	22.57	20.57	-0.05	0.05	0.25	21.33	-0.89	0.89	4.35
K-D	15.66	23.19	20.27	14.44	21.39	18.69	17.22	-1.56	1.56	9.99	18.16	-2.61	2.61	16.64
Us-R	19.41	24.46	23.61	18.13	22.85	22.06	19.64	-0.23	0.23	1.20	19.96	-0.66	0.66	3.38
Us-D	17.48	23.14	21.80	16.29	21.56	20.31	17.93	-0.44	0.44	2.54	18.40	-1.07	1.07	6.11
Cs-P	18.20	24.53	22.73	17.03	22.95	21.27	17.64	0.56	0.56	3.09	18.30	-0.06	0.06	0.31
Cs-S	18.65	24.08	23.14	17.45	22.53	21.66	18.27	0.38	0.38	2.05	18.69	-0.07	0.07	0.35
Cs-Y	13.89	23.00	21.16	12.97	21.46	19.75	13.35	0.54	0.54	3.88	14.00	-0.15	0.15	1.08
Mean	17.41	24.52	22.43	16.24	22.86	20.91	17.39	0.02	0.64	3.86	18.06	-0.66	0.88	5.11
SD	2.36	1.34	1.14	2.24	1.29	1.12	2.55	0.85	0.52	3.28	2.50	0.95	0.72	4.39
%RSD	13.56	5.48	5.07	13.78	5.64	5.38	14.66	-	-	-	13.85	-	-	-

Table 2: Proximate analysis and residues analysis of sludge.

Sample Label	As Received	Dry Basis (db), Weight%							Difference in Weight%	
	Moisture Content	Volatile Matter (VM)	Fixed Carbon (FC)	Ash ₉₅₀	Ash ₅₅₀	Fixed Residues (FR)	Inorganic Matter (IM)	CHNS _{Char} at 950°C	FC - CHNS _{Char}	FR - CHNS _{Char}
U-R	98.40	69.99	16.24	13.77	15.28	21.66	8.35	21.29	-5.05	0.37
U-D	86.40	61.95	11.91	26.14	27.99	23.28	14.78	18.56	-6.65	4.71
C-P	93.30	63.36	8.36	28.28	26.74	18.28	18.36	17.75	-9.40	0.53
C-S	93.30	67.44	15.32	17.24	18.68	22.68	9.88	17.96	-2.64	4.72
C-Y	6.55	51.44	10.00	38.57	39.35	18.85	29.72	16.23	-6.24	2.61
J-R	97.90	60.53	5.34	34.13	36.48	16.36	23.11	14.33	-9.00	2.02
J-D	73.40	47.56	4.43	48.01	51.06	14.06	38.38	12.58	-8.16	1.47
K-R	97.40	64.26	13.69	22.05	22.83	22.93	12.81	16.97	-3.27	5.96
K-D	83.80	56.71	11.85	31.44	32.48	23.20	20.09	17.47	-5.62	5.73
Us-R	98.28	71.07	9.25	19.69	20.66	13.16	15.77	15.82	-6.58	-2.66
Us-D	84.11	65.79	11.21	23.00	24.43	17.00	17.21	19.03	-7.82	-2.03
Cs-P	93.85	64.66	9.11	26.24	25.81	17.17	18.17	16.49	-7.38	0.69
Cs-S	94.16	67.07	10.68	22.26	22.54	15.75	17.18	16.07	-5.40	-0.32
Cs-Y	4.65	51.07	9.77	39.15	39.59	17.59	31.33	15.49	-5.72	2.10
Mean	78.96	61.64	10.51	27.85	28.85	18.71	19.65	16.86	-6.35	1.85
SD	31.88	7.33	3.32	9.50	9.83	3.47	8.44	2.12	1.95	2.70

Table 3: Summary of CHNSO elements and inorganic analysis of sludge.

Sample Label	CHNSO of Sludge, Weight% in db					Weight% in Dry Sludge Basis						
						CHNSO of Sludge			Halogens Contents	Inorganic Matters (IM)	Total Inorganic Contents (TI)	Inorganic Elements
						Organics	Inorganics	Total				
U-R	43.56	5.64	5.81	5.47	30.87	89.29	2.06	91.35	0.30	8.35	10.71	7.84
U-D	39.88	6.20	6.04	5.62	27.29	82.17	2.86	85.03	0.20	14.78	17.83	14.54
C-P	37.92	5.89	7.55	4.57	25.33	79.98	1.29	81.26	0.38	18.36	20.02	14.94
C-S	43.98	6.48	3.87	5.30	30.11	87.99	1.75	89.75	0.38	9.88	12.01	9.35
C-Y	31.71	4.88	5.03	4.81	23.41	66.93	2.91	69.84	0.45	29.72	33.07	20.36
J-R	37.16	5.94	4.33	5.37	23.39	72.86	3.33	76.19	0.70	23.11	27.14	20.10
J-D	27.44	4.07	3.21	5.43	20.85	55.91	5.11	61.02	0.60	38.38	44.09	28.01
K-R	43.79	6.56	5.63	5.44	25.42	85.00	1.83	86.83	0.36	12.81	15.00	12.10
K-D	36.51	5.98	6.64	5.38	25.04	77.26	2.30	79.55	0.36	20.09	22.74	17.52
Us-R	42.68	6.28	4.96	4.26	25.91	82.20	1.89	84.09	0.14	15.77	17.80	10.73
Us-D	39.50	5.85	5.91	4.59	26.78	80.21	2.41	82.62	0.16	17.21	19.79	12.69
Cs-P	38.36	5.76	6.80	5.48	25.18	80.07	1.50	81.57	0.25	18.17	19.92	13.92
Cs-S	40.24	5.89	3.46	5.43	27.55	80.60	1.97	82.57	0.26	17.18	19.40	12.01
Cs-Y	30.42	4.56	4.83	5.20	23.45	65.65	2.81	68.46	0.21	31.33	34.35	20.52
Mean	38.08	5.71	5.29	5.17	25.76	77.58	2.43	80.01	0.34	19.65	22.42	15.33
SD	5.15	0.72	1.29	0.43	2.68	9.28	0.97	8.51	0.16	8.44	9.28	5.44

Table 4: Molecular formula and oxygen contents analysis of sludge.

Sample Label	Molecular Formula of Sludge					H/O Ratio	H/N Ratio	Oxygen Contents, Weight%		O _{deviation}	O _{difference} / O _{Total}
	C	H	N	S	O			O _{Total}	O _{difference}		
U-R	1.00	1.55	0.11	0.05	0.53	2.92	13.58	30.87	25.45	5.42	0.82
U-D	1.00	1.87	0.13	0.05	0.51	3.64	14.39	27.29	15.92	11.37	0.58
C-P	1.00	1.86	0.17	0.05	0.50	3.72	10.91	25.33	15.41	9.92	0.61
C-S	1.00	1.77	0.08	0.05	0.51	3.44	23.44	30.11	22.74	7.37	0.76
C-Y	1.00	1.85	0.14	0.06	0.55	3.33	13.57	23.41	14.56	8.85	0.62
J-R	1.00	1.92	0.10	0.05	0.47	4.07	19.22	23.39	12.37	11.02	0.53
J-D	1.00	1.78	0.10	0.07	0.57	3.13	17.75	20.85	11.22	9.63	0.54
K-R	1.00	1.80	0.11	0.05	0.44	4.13	16.31	25.42	16.19	9.23	0.64
K-D	1.00	1.97	0.16	0.06	0.51	3.82	12.61	25.04	13.68	11.35	0.55
Us-R	1.00	1.77	0.10	0.04	0.46	3.88	17.73	25.91	21.99	3.92	0.85
Us-D	1.00	1.78	0.13	0.04	0.51	3.50	13.87	26.78	20.99	5.79	0.78
Cs-P	1.00	1.80	0.15	0.05	0.49	3.66	11.86	25.18	17.12	8.06	0.68
Cs-S	1.00	1.76	0.07	0.05	0.51	3.42	23.84	27.55	22.47	5.09	0.82
Cs-Y	1.00	1.80	0.14	0.06	0.58	3.11	13.20	23.45	15.63	7.82	0.67
Mean	1.00	1.80	0.12	0.05	0.51	3.55	15.88	25.76	17.55	8.20	0.68
SD	0.00	0.10	0.03	0.01	0.04	0.36	4.06	2.68	4.38	2.43	0.11

Table 5: Summary of inorganic elements in sludge for Batch 1 samples.

Sample Label	Major Ash Forming Elements, Weight% in db									Minor Elements, mg/kg in db							
	Si	Al	Ti	Fe	Ca	Mg	Na	K	P	Cu	Zn	Ba	Cr	Mn	Ni	Sn	Sr
U-R	2.52	0.91	0.01	1.33	1.57	0.21	0.09	0.15	0.82	803	778	250	33	81	56	51	48
U-D	5.42	1.86	0.02	2.43	2.33	0.39	0.09	0.28	1.39	1338	1126	408	49	159	86	77	82
C-P	5.04	1.68	0.01	1.33	1.50	0.78	0.15	0.82	3.41	493	1041	224	129	91	51	28	64
C-S	4.23	1.31	0.01	0.88	1.69	0.13	0.09	0.12	0.70	373	1092	167	108	67	52	8	36
C-Y	9.71	2.83	0.02	1.92	2.70	0.55	0.07	0.31	1.97	565	1494	277	167	120	73	27	75
J-R	9.79	2.11	0.04	2.74	2.86	0.35	0.16	0.34	0.00	3497	9543	380	1480	234	1155	193	228
J-D	13.51	3.08	0.06	3.74	4.01	0.50	0.21	0.44	0.27	3890	12683	541	1766	379	1638	310	273
K-R	5.77	1.01	0.01	1.30	1.92	0.29	0.08	0.23	1.03	651	3287	181	81	69	162	77	26
K-D	8.02	0.88	0.01	2.54	1.95	0.64	0.07	0.18	2.13	995	9210	249	101	110	166	72	43
Mean	7.11	1.74	0.02	2.02	2.28	0.43	0.11	0.32	1.30	1401	4473	297	435	146	382	94	97
SD	3.43	0.81	0.02	0.91	0.81	0.21	0.05	0.21	1.06	1335	4662	122	679	102	589	97	89
Sample Label	Trace Elements, mg/kg in db								Weight % in db			Relative Composition %			Weight % in db		
	Pb	Sb	Ag	As	Cd	Co	Mo	V	Major	Minor	Trace	Major	Minor	Trace	Fluoride	Chloride	Bromide
U-R	24	0	9	7	0	0	11	8	7.62	0.21	0.01	97.25	2.68	0.08	0.04	0.21	0.05
U-D	34	0	14	13	0	4	15	18	14.20	0.33	0.01	97.65	2.29	0.07	0.03	0.13	0.04
C-P	13	0	0	6	0	4	7	10	14.72	0.21	0.00	98.55	1.42	0.03	0.25	0.12	0.01
C-S	20	4	6	8	3	4	12	9	9.15	0.19	0.01	97.89	2.04	0.07	0.27	0.10	0.01
C-Y	23	0	3	11	0	5	10	19	20.08	0.28	0.01	98.59	1.37	0.03	0.38	0.06	0.01
J-R	127	41	37	0	29	58	25	86	18.39	1.67	0.04	91.49	8.31	0.20	0.55	0.14	0.01
J-D	204	50	45	5	38	105	37	133	25.80	2.15	0.06	92.11	7.67	0.22	0.49	0.10	0.01
K-R	35	5	0	10	0	3	10	10	11.64	0.45	0.01	96.19	3.75	0.06	0.26	0.08	0.01
K-D	41	0	0	9	0	4	13	6	16.42	1.09	0.01	93.71	6.25	0.04	0.27	0.07	0.02
Mean	58	11	13	8	8	21	16	33	15.34	0.73	0.02	95.94	3.98	0.09	0.28	0.11	0.02
SD	65	20	17	4	15	36	10	45	5.65	0.73	0.02	2.78	2.72	0.07	0.18	0.05	0.02

Figure 1: Simulations of apparent-to-intrinsic distribution ratio R^*/R at three different conditions of (a) apparent degree of oxidation $O_D = 45\%$, (b) $IM = 20\text{wt}\%$ and (c) $R = 3.50$.

Figure 2: FTIR spectra of (a) sludge samples collected from WRPs in Singapore (b) ash residues produced from combustion of sludge at 550°C .

Figure 3: Correlations of apparent degree of oxidation, O_D in % with relative weight% of inorganic elements present in inorganic matters of sludge.